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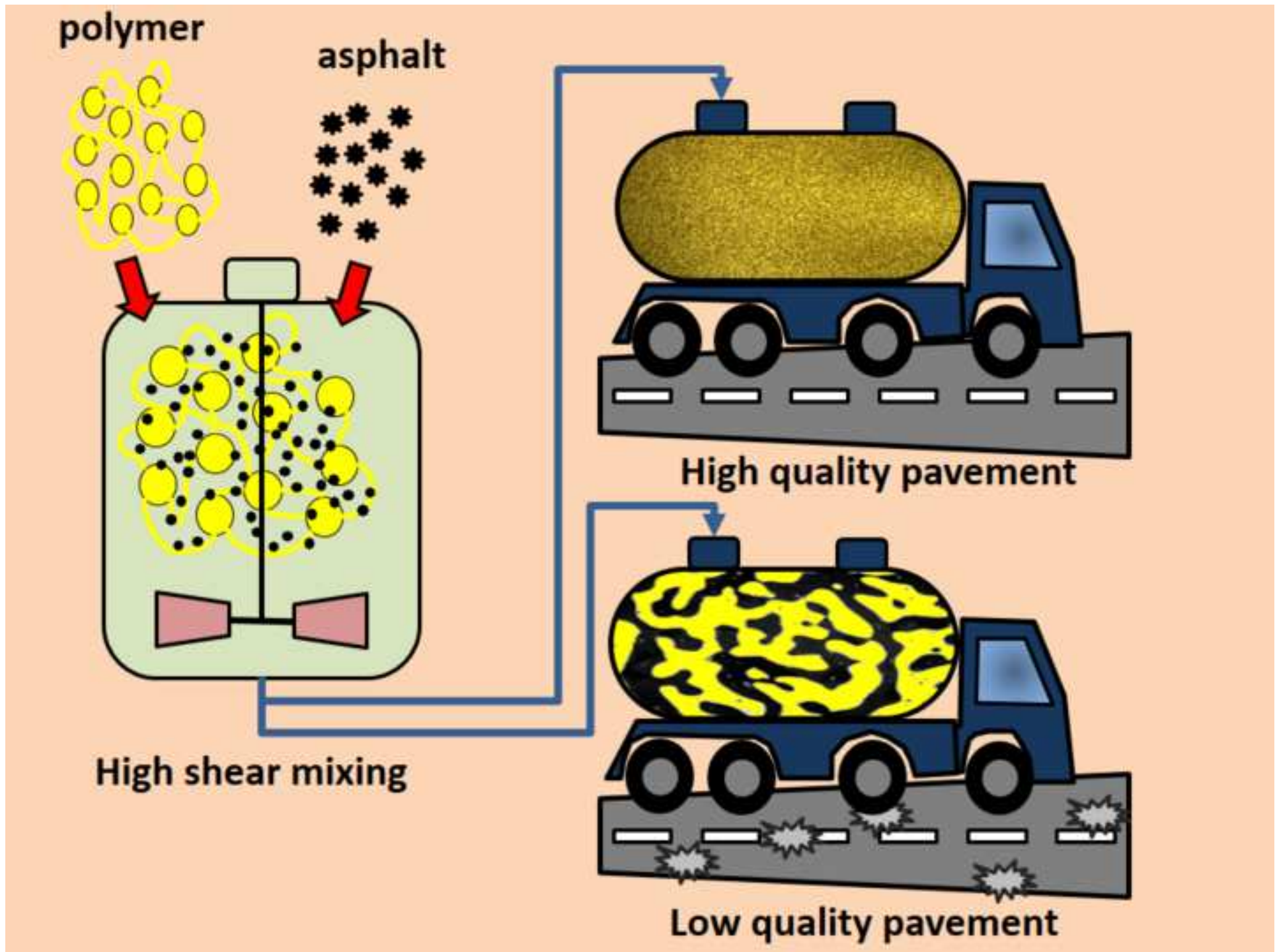
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*Highlights (for review)

- Modification with polymers strongly improves the performances of asphalt binders.
- PMAs are biphasic and often unstable during hot storage under static conditions.
- There is a correlation between interface characteristics and storage stability.
- The polymer/asphalt interface structure and compatibilization strategies are reviewed.
- An emerging solution is the joining of PMA and polymer nanocomposites technologies.

A review of the fundamentals of polymer-modified asphalts: Asphalt/polymer interactions and principles of compatibility

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Abstract

During the last decades, the number of vehicles per citizen as well as the traffic speed and load has dramatically increased. This sudden and somehow unplanned overloading has strongly shortened the life of pavements and increased its cost of maintenance and risks to users. In order to limit the deterioration of road networks, it is necessary to improve the quality and performance of pavements, which was achieved through the addition of a polymer to the bituminous binder. Since their introduction, polymer-modified asphalts have gained in importance during the second half of the twentieth century, and they now play a fundamental role in the field of road paving. With high-temperature and high-shear mixing with asphalt, the polymer incorporates asphalt molecules, thereby forming a swallowed network that involves the entire binder and results in a significant improvement of the viscoelastic properties in comparison with those of the unmodified binder. Such a process encounters the well-known difficulties related to the poor solubility of polymers, which limits the number of macromolecules able to not only form such a structure but also maintain it during high-temperature storage in static conditions, which may be necessary before laying the binder. Therefore, polymer-modified asphalts have been the subject of numerous studies aimed to understand and optimize their structure and storage stability, which gradually attracted polymer scientists into this field that was initially explored by civil engineers. The analytical techniques of polymer science have been applied to polymer-modified asphalts, which resulted in a good understanding of their internal structure. Nevertheless, the complexity and variability of asphalt composition rendered it nearly impossible to generalize the results and univocally predict the properties of a given polymer/asphalt pair.

The aim of this paper is to review these aspects of polymer-modified asphalts. Together with a brief description of the specification and techniques proposed to quantify the storage stability, state-of-the-art knowledge about the internal structure and morphology of polymer-modified asphalts is presented. Moreover, the chemical, physical, and processing solutions suggested in the scientific and patent literature to improve storage stability are extensively discussed, with particular attention to an emerging class of asphalt binders in which the technologies of polymer-modified asphalts and polymer nanocomposites are combined. These polymer-modified asphalt nanocomposites have been introduced less than ten years ago and still do not meet the requirements of industrial practice, but they may constitute a solution for both the performance and storage requirements.

Keywords

Polymer-modified asphalts, storage stability, internal structure, phase morphology, nanocomposite-modified asphalts.

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1. Introduction

Polymer-modified asphalts (PMA) derive their technological and conceptual origin from the need for enhancing the performance and durability of asphaltic materials as well as their adhesion to mineral aggregates. PMAs are produced by mixing asphalt and polymer (usually 3–7% by weight); they were developed because conventional flexible pavements had become inadequate in the last few decades because of a dramatic increase in traffic intensity and load, which shortened their in-service life, thereby increasing the frequency of road maintenance and re-paving required.

Modification is normally achieved through simple mechanical dispersion of the polymer in molten asphalt under high shear. Approximately 75% of all modifiers are elastomeric, 15% are plastomeric, and the remaining 10% are either rubber or miscellaneous under these three categories [1]. The longer life and better quality of PMA-based pavements usually lead to both economical and safety requirements that overcome the initial investment, which is higher with respect to the use of conventional unmodified binders.

Since the introduction of PMA in the paving industry, researchers have attempted to use almost all available polymers as asphalt modifiers, including thermoplastics and thermosetting resins (the latter category represents a particular case of polymer modification and will not be discussed here in detail). However, the produced PMAs should satisfy a long list of requirements including appropriate mechanical properties, storage stability, high-temperature viscosity compatible with the traditional road-building processes and apparatus, and reasonable cost, which remains of primary importance. Given all these limitations, in contrast to the huge availability of different types of polymers, only a very small number of polymers are currently used in industrial applications. The preferred polymers have a common characteristic: ability to form a physical network, which usually originates from the simultaneous presence of both rigid (below glass transition temperature (T_g) or crystalline) and flexible segments in their backbone. If the network is swelled by the asphalt molecules during the mixing phase without losing its main structure, it will become a determining factor for the binder properties. The polymers used in asphalt technology may be listed according to their importance in three main categories: i) thermoplastic elastomers (TPE), ii) plastomers, and iii) reactive polymers.

2. The asphalt-polymer system

2.1. The internal structure of asphalt: a synthetic overview

2.1.1. Asphalt chemistry

Asphaltic materials include a wide variety of complex organic components of different origins, compositions, and industrial uses. Asphalts can be subdivided into natural and industrial types. The former can be found near subterranean crude-oil deposits, while the latter is a product of the fractional distillation of crude oil at 300–350°C and constitutes a specific class of construction materials with their own specific properties and fields of application.

It is important to stress that the term “asphalt” does not unequivocally define a class of materials. The term “bitumen” is often used to indicate both the natural and manufactured forms of asphaltic materials interchangeably.

Moreover, it must be pointed out that the use of the term “asphalt” or “bitumen” depends also on the geographical region; bitumen is the European synonym for asphalt in North America.

Owing to their rheological properties as well as the water-proofing and adhesive characteristics, asphalts are currently recognized as among the most eligible materials in highway paving technologies and roofing-membrane industries; other applications are also known.

The elemental analysis of asphalts has revealed that sulfur, nitrogen, and oxygen constitute between 0% and 10% of asphalts by weight, while the remaining part is predominantly composed of carbon and hydrogen [2]. The association of those elements at a molecular scale depicts a complex picture,

and different authors claim that the chemical composition of asphalt is mostly unknown at present. Textbooks and reviews of asphalt chemistry usually identify asphaltic materials as generic complex mixtures of aliphatic, aromatic, and naphthenic hydrocarbons that also include small quantities of nonhydrocarbon molecules such as organic acids, bases, and metallic or nonmetallic heterocyclic components [3]. Some steps towards a better identification of asphalt molecules may involve fundamental characteristics of organic compounds such as the molecular weight (MW) and polarity. Indeed, a definition provided by the Strategic Highway Research Program (SHRP) claims that “asphalt is a relatively homogeneous and randomly distributed collection of molecules differing in polarity and molecular size” [4]. In the light of the MW distribution, the asphaltic molecules form an extremely wide spectrum starting with low-MW oils (MW: 240-800) followed by higher-MW materials with polycyclic and polyaromatic structures. This category of compounds is often divided, in the order of their MWs, into cyclano-aromatics, polar aromatics (MW: 800-2400), and highly condensed and aromatic asphaltenes, which also contain a considerable amount of heteroatoms (S, O, N) and heavy metals (V, Ni, Fe).

A similar extension of the spectrum can be found with regard to polarity: asphalts are often described as systems in which the components strongly differ in polarity, from slightly polar oils (mainly consisting of alkanocyclanes) through cyclanoaromatic and polyaromatic intermediate compounds to highly polar polyaromatics contained in asphaltenes.

The extreme variability in the quality and relative amount of molecules in asphalts depends on three main factors: 1) the source of the crude oil (virgin composition); 2) the refining process (vacuum distillation, oxidative ageing, etc.); and 3) the in-service life (complexity of molecules increases with ageing even by generating new functional groups) [2]. The variability in crude-oil origin and composition (there are four different macro-regions of crude-oil production in the world), as well as the wide variability in the refining plants and processes, render the asphalt composition intrinsically unpredictable. Therefore, one popular way to analyze and identify asphalt composition is the so-called SARA method. The conceptual origin of the SARA method is the identification of a limited number of fractions into which a large number of asphalt molecules can be separated according to the affinity in their chemical composition.

An early historical investigation on asphalt separation dates back to 1837, which is currently known as the experience of Boussingault [5] (this is probably the first analytical method expressly dedicated to asphalt chemistry). In his “*Memoire sur la composition des bitumes*,” Boussingault stated that asphalts “*may be considered as mixtures, probably in all proportions, of two principles, each of which has a definite composition. One of these principles (asphaltene) fixed and solid, approaches asphalt in its nature. The other (petrolene) liquid, oily and volatile, resembles in some of its properties, certain varieties of petroleum. It may, then, be conceived that whilst the consistency of bitumen varies, it may be said to infinity; it suffices that one or the other of the two principles dominates the mixture, thereby giving such or such a degree of fluidity.*” Nowadays, asphalt molecules are still grouped into two macro-categories: the first category consists of asphaltenes, and the second category consists of maltenes. Maltenes are further subdivided in saturates, aromatics, and resins. Therefore, the four SARA fractions can be defined as saturates (S), aromatics (A), resins (R), and asphaltenes (A) with the MW, aromaticity, polarity, and heteroatomic content increasing in the order $S < A < R < A$.

SARA grouping for technological and scientific purposes was obtained with Thin Layer Chromatography with Flame Ionization Detection (TLC-FID) conventionally performed using an Iatroscan device [6 Ecker]. The SARA method is of vital importance because asphalt scientists and technologists usually specify the asphalt composition simply in terms of the relative content of these fractions. In addition, the SARA fractions constituted the basis for all early theories on asphalt/polymer interactions and are still used to formulate modern interpretations of the asphalt modification mechanisms.

The most critical fraction is that of asphaltenes, identified as the part of asphalt insoluble in n-heptane but soluble in toluene [7-9]; however, several other procedural definitions based on

different solvents may be found in the literature [2 Lesueur]. Asphaltene molecules have a complex and variable molecular architecture, and their chemical form is a topic of debate for petroleum scientists as well as asphalt technologists. The primary aspects that characterize the asphaltene molecule include the contemporary presence of polycyclic aromatics, polar groups, and metal complexes. Asphaltenes have H/C ratios between 0.98 and 1.56 and represent the fraction of asphalt with higher MW, aromatic character, and polarity. This information somehow clarifies some basic aspects related to the nature of asphaltene. Several observations are worth of mentioning. The first one concerns the MW. Asphaltene molecules are indeed considered ones with very high MW. However, the MW of asphaltenes depends strongly on the method of determination and nominally extends over a wide range. Some authors claim that the MW of asphaltenic molecules ranges from 2000 to several hundreds of thousands. Redelius critically reviewed classical items concerning the nature of asphaltene and concluded that the MW of asphalt molecules insoluble in n-heptane ranges from 300 to more than 1000, thereby identifying a quite different interval of variability [10, 11]. Polarity is another critical point. Asphaltenes are traditionally considered as a group of molecules having a highly polar character. This is believed because they are not soluble in nonpolar solvents such as n-heptane; in addition, they are traditionally considered able to aggregate in asphalt and must therefore develop polar attractions among themselves. However, no direct proof of asphaltene polarity is available. It was recognized that asphaltene carries permanent electrical charge but no real evidence of polarity has been collected thus far.

With regard to this particular aspect, Redelius concluded that the only atoms that may induce polarity in asphaltene are nitrogen and oxygen, but the quantities of these atoms are too low in asphaltene molecules to make them polar in a chemical sense. Hence, asphaltenes are probably slightly more polar than other asphalt aromatic molecules. Therefore, the problem of asphaltene's polarity can be outlined by the assumption that they contain some polarizable functional groups that show polar properties when in contact with polar molecules [10, 11].

If MW and polarity are not univocally understood, a more lively debate on the structure of asphaltenes is possible. It was demonstrated that asphaltene molecules are of such complicated isomeric structures that specific associations to form well-ordered crystalline structures are not possible [Sirota 12]. Their structural characterization is still controversial. Although they have been subjected to modern analytical methods, including mass spectrometry and Nuclear Magnetic Resonance, several different chemical structures were identified in the class of asphaltene molecules. In the current literature, it is frequently found that asphaltenes are structurally different from other asphalt molecules because of the higher contents of condensed aromatics rings, polar groups, and heteroatoms (mainly consisting of sulfur, vanadium, and nickel). Lesueur [2] also reported that the fundamental specific characteristic responsible for the structural differentiation of asphaltenes is the presence of fused aromatic structures. Accordingly, in most recent theories, asphaltenes are considered agglomerates of smaller molecules, and they are described as flat planar sheets of condensed aromatic systems with 4–10 fused rings and pending aliphatic side chains of various lengths, associated or dimerized by π - π interactions or other intermolecular forces to form graphite-like stacks [2], [13]. This aspect is closely related to the asphalt structure and therefore will be more appropriately discussed in the next paragraph.

Resins (or polar aromatics) still form a complex structure but have decreased MW and polarity, thus representing a sort of transition between the asphaltenes and conventional aromatic molecules. The boundary between asphaltenes and resins is not well defined. Resins structurally resemble asphaltenes and may be defined as the part of asphaltenes soluble in n-heptane. With regard to their basic characteristics, a few differences can be outlined. Many documents indicate that the average MW of resin molecules is not larger than 1100 g/mol and its H/C ratio is higher than that of asphaltene, oscillating between 1.38 and 1.69. The common point of various authors is that the structure of resins closely resembles those of asphaltenes but with less condensed aromatic rings. It is however curious to notice that some authors have detected and reported the presence of fused aromatic structures even inside the resin molecules, while other researchers firmly state that the

presence of fused structures is a characteristic of asphaltenes. Therefore, the difference between asphaltenes and resins lies in the operational or procedural definition, and with a circumspect gait, we can assume that fused and condensed aromatics are preponderant in asphaltenes, while they are limited to 2–4 units in resins. Given all these limitations, from a structural point of view, no other differences between resins and asphaltenes can be outlined.

Decreasing in molecular complexity, one enters into the domain of aromatics. This third asphalt fraction has been recently indicated as the fraction of naphthene aromatics because it covers a range of asphalt molecules with more regular aliphatic-like structure and shape, where condensed rings are sporadic or even totally absent. This fraction shows decreased MW, which likely oscillates around 800 g/mol.

The last fraction is that of saturates. This fraction constitutes the simplest molecules among the asphalt components. Nevertheless, asphalt saturate molecules are among the major exponents of surprising and somewhat mysterious phenomena inside the asphalt structure. Effectively, they crystallize upon cooling, thereby provoking a series of strange effects that are still not understood. Asphalt saturates are chemically ascribable to the class of aliphatic and alicyclic (naphthenic) hydrocarbons with low MW (about 600 g/mol) and H/C ratios close to 2. With only some ephemeral exceptions, they have a nonpolar character and do not contain heteroatoms. Linear n-alkanes, branched iso-alkanes, and cyclo-alkanes are common examples of asphaltic saturate molecules.

All the above considerations were aimed at determining which chemical species are involved in the composition of asphaltic materials. The next point is how these species interact with each other to generate the asphalt structure.

2.1.2. A few steps into the SARA wonderland

Before introducing the fundamentals of polymer-modified asphalts, it is worthwhile to briefly discuss the internal arrangement of asphaltic materials and to present the basic models used to describe the structure of asphalts. This aspect is not the main object of this review, but it is obvious that both the asphalt composition and structure are important because they strongly affect the interactions with a macromolecular material and thereby the overall properties of PMA.

The internal structure of asphalt has been studied for a long time, but it continuously generates new scientific challenges because a well-established and widely accepted representation was never attained. Opinions about the “real” structure of asphalt have alternated over the years because its complex and quite variable chemical composition makes the internal environment not so easy to understand. In this regard, it is interesting to report the words of Goodrich and co-workers, who in 1986 declared “*Some believe that today’s sophisticated analytical tools, computer-controlled instruments that work with milligrams of asphalt, should make the connection between asphalt composition and performance properties. Yet the complex chemical mix of even a single asphalt may never be adequately described*” [14]. After almost 30 years, there has been some progress from an analytical point of view, but the point remains the same. Consequently, for the asphalt structure as well, there still is no univocal description, and two main philosophies in this regard may be identified. The first one, which is also the most accredited and widely accepted, originates from the science of colloids and essentially states that asphalt has a colloidal nature. In contrast, the second one depicts asphalt as a homogenous fluid with no colloidal characteristics.

The first to recognize the colloidal nature of asphalt was probably Rosinger [15], whose general hypotheses constitute the fundamentals of the early model of asphalt structure. These general hypotheses were refined several times during the first few decades of the twentieth century [16, 17] and led to the definition of the basic colloidal picture, in which the primary idea was that the complexes of molecules residing in the asphaltene fraction can aggregate and arrange themselves in various super-molecular associations. In light of this theory, the asphaltic materials are composed of two basic elements: i) the solid asphaltenic micelles and ii) the surrounding liquid-like environment.

More precisely, the solid-like micelles are built by the aggregation of large and complex hydrocarbon molecules, typically referred to as asphaltenes, and are stabilized by the polar resins, which exert a flocculating/peptizing action. Hence, the resins form a sort of interphase and are interposed between the asphaltenes and the surrounding oily maltenic medium. Finally, the maltenic medium represents the continuous liquid-like phase and is mainly composed of lighter asphaltic components, such as the low-MW aromatics and saturates.

The first analytical description of such a structure dates back to the 1940s and led to the definition of the so-called “sol” and “gel” asphalts by Pfeiffer and Saal [18]. This approach is probably the most popular colloidal picture of asphalt, and it states that sol asphalt is derived from a high content of maltenes, which indicates a high solvating ability and consequent enhanced mobility of asphaltene micelles. Hence, in sol asphalt, the asphaltene micelles are fully dispersed and noninteracting. It is possible to assign a surfactant character to maltenic oil, the abundance of which generates a predominant liquid dispersing phase. In contrast, in gel asphalts, a low maltene content and solvating ability result in micelle aggregation until a continuous solid network is formed. In summary, according to the colloidal theory, asphalt is a multidisperse micellar system with an internal structure that depends on the relative amounts of SARA fractions. In his review dedicated to the asphalt structure and rheology, Lesueur [2] highlighted well how the availability of the modern inspection techniques may help visualize the asphaltenic micelles and micelle aggregates. Whether the colloidal model is correct or not is still highly debated. Although the colloidal theory is, without doubt, the major extant theory, there is an alternative point of view claiming that asphalt is not a colloid but rather a simple homogeneous fluid (sometimes called “dispersed polar fluid”). Instead of considering asphalt as a colloidal dispersion, this theory suggests that asphalt is more like a mutual solution of different molecules. Redelius is probably the first author who questioned the existence of a colloidal structure in asphaltic materials [10, 11]. As a first argument, he claimed that because asphaltenes are mainly soluble in maltenes, no colloidal dispersion can exist, and he suggested that all molecules are kept in solution because of their mutual solubility. He also stated that the main reason the colloidal model is widely accepted is that it is so widespread in textbooks and papers that a person who makes a literature study on asphalt chemistry will easily be convinced of this model. This somehow agrees with the idea that it is not appropriate to talk about different phases in asphalt since this requires a fraction that is insoluble in the rest, which is not the case in asphalt [4]. Accordingly, SHRP Report 686 [19] states “*asphalt is a single phase mixture of many different polar and non-polar molecules, all of which interact with one another.*” Nonetheless, traces and evidences of phase separation in asphalt seem to be the main outcome of advanced studies recently performed using Atomic Force Microscopy (AFM) (see section 4.1.2.). Readers interested in this matter are referred to the review by Lesueur [2] for a detailed discussion.

2.2. Mixing asphalt and polymer: the principles of compatibility

2.2.1. The biphasic nature of the blend

As stated above, the success of PMA originates from the ability of certain polymers to strongly influence and improve the rheological properties of asphalts even if added in relatively small quantities. Nevertheless, this essential and primary feature is not immediately obtained when a polymer is mixed with asphalt. The expected strong enhancement in asphalt quality is uniquely possible when the so-called “phase inversion” (PI) and an appropriate morphology of the blend are obtained. This is the main point in asphalt modification and needs to be better understood. Even though almost all thermoplastic polymers have been tested as asphalt modifiers, the most interesting ones are those with the structure of a physical network. Then, the ideal modification is obtained when the polymer conserves its internal structure after mixing with asphalt, the molecules of which determine only a macroscopic swelling of the network. If the network becomes a continuum that involves the entire material, the overall mechanical properties of the PMA markedly reflect those of the polymer. Whether this can be realized or not depends on the interactions among the asphalt

components and the polymer. Such interactions obviously depend on the chemical affinity, and thus, for a given polymer, they are different for the four SARA categories of asphalt molecules, which are characterized by different polarities. Therefore, the four groups of molecules interact differently with the polymer, which usually is selectively swelled by the most affine asphalt molecules and exerts a sort of internal distillation, driving the formation of a polymeric phase and a residual asphalt phase of different compositions. The systems thus evolve toward the formation of a biphasic morphology characterized by the presence of a polymer-rich phase (PRP) and an asphaltene-rich phase (ARP), the asphaltenes usually being more reluctant to polymer swelling. Depending on the swelling ability and operating conditions (duration, temperature, shear stress, and so on) several different morphologies may be obtained. Such morphologies may be directly observed in several ways, for example using fluorescence microscopy (FM), and may give an immediate idea of the PMA quality. When the polymer is swollen by a small quantity of asphalt molecules, the PRP is dispersed in the continuous ARP, and the overall properties do not differ significantly from those of the unmodified asphalt. In contrast, with a sufficient degree of swelling, PRP may become the continuous phase, and this corresponds to the above-mentioned PI and to a strong influence of the polymer on the binder properties. In the case of complete swelling, the ARP may disappear. This is the ideal situation for PMA if the swelling is not accompanied by a destruction of the polymeric network. To better understand this point, let us consider the limiting case of a polymer completely soluble in the asphalt: its macromolecules would be simply dispersed in the asphalt, as they would be in a low-MW solvent. Similarly to what happens in polymer solutions, the main observable effect would be a modest increase in viscosity, but none of the macroscopic properties of the polymer would be transferred to the blend because its original structure is lost during dissolution [3]. This is an undesirable condition to be avoided during mixing. In other words, a certain degree of relative solubility and swelling is required, but a limited solubility is simultaneously necessary. From a performance point of view, the minimum requested degree of swelling is the one that guarantees PI. At this minimum degree of swelling, the polymer's original structure is conserved, and most of the overall properties will resemble those of the virgin (unswollen) polymer. On the other hand, a modest degree of swelling is reached if only the most compatible asphalt components migrate into PRP. Such intra-distillation determines a considerable difference in the compositions of PRP and ARP, and this markedly biphasic morphology corresponds to a thermodynamically unstable condition: PRP and ARP will have a strong tendency for macroscopic segregation driven by a difference in density. Whether they separate or not is a mere kinetic condition that has critical importance during prolonged storage at high temperatures and absence of stirring. This storage period may be simply limited to the transportation of the binder to the application site, but it may be prolonged because of bad weather or other causes of delay. If the two phases macroscopically separate in the storage tank or in the tank truck, there is a complete loss of homogeneity within the material, which becomes useless; moreover, the PRP part could be too viscous for the usual pumping apparatus. Therefore, the selectivity in the swelling and migration of asphalt molecules into PRP should be sufficiently low to limit the difference in composition between PRP and ARP to a level that sufficiently slows down the kinetics of phase separation to ensure storage stability. Thus, after mixing, there should be a micro-scale metastable equilibrium with a highly swelled PRP, with the thermodynamic instability balanced by a kinetic inertia that inhibits the separation during high-temperature storage. It is also necessary to underline that PI by itself guarantees neither storage stability nor compatibility: any polymer may ideally reach PI if loaded in sufficient quantity.

From a purely qualitative point of view, the above considerations are illustrated in Figure 1, in which the “effect of modification” for a fixed polymer content is shown as a function of the degree of swelling. The abscissa may be seen as blending time (or blending temperature) by assuming that prolonged mixing (at a sufficiently high temperature) may lead to a complete dissolution of the polymer in the asphalt.

At a low degree of swelling (short time of mixing), the PRP is dispersed in ARP and the polymer does not significantly influence the behavior of the binder (which resembles that of the pure asphalt). Then, in correspondence with PI, there is an abrupt change in the binder properties, but the system is likely not stable to storage. Further increases in the degree of swelling result in a modest reduction in the performance, which remain far higher than that of the base asphalt until the mixture enters the region of complete solubility (indicated as CS in Figure 1), where the system becomes a homogeneous blend and the polymer effect are again negligible. From a stability point of view, we can vertically “divide” the graph into two zones: the left one corresponds to storage instability, while the right one corresponds to storage stability. If the abscissa of such a partition is lower than that of the CS line, we have a region where both storage stability and high modification can be achieved. The goal of mixing is to stop at this “ideal” zone, which possibly far enough from the boundaries of both zones corresponding to instability and complete solubility. The squares in the upper part of the image are a simplified representation of the morphology of the mixes, where the black part is ARP while the white one is PRP. Moving from the left to the right, there is a gradual increase in the level of ARP/PRP interface, since the homogeneous (gray) condition corresponding to complete solubility is reached. This aspect will be explained in detail in section 2.3.1. It must again be stressed that in most cases, a complete dissolution may not be obtained even with a very long mixing time (or high temperature). This depends on several factors, such as the asphalt composition, type and quantity of polymer, and operating conditions during mixing. Moreover, it is important to remember that the mixing time must be as low as possible not only for economic reasons, but also because the high-temperature/high-shear mixing process induces ageing and degradative phenomena in both the asphalt and polymer. Therefore, the longer and more aggressive the mixing procedure is, the more the polymer swelling process is influenced by changes in the chemistry and MW of the asphalt and polymer. As an example, Figure 2 reports the viscosities of 4 different PMAs as a function of mixing time [20]. The curves show a maximum, which has been attributed to the incoming degradation and reduction of the average MW of the polymer. Therefore, to optimize the properties of the final product, the manufacturing conditions must take into account not only the kinetics and thermodynamics of the swelling process but also the physico-chemical stress induced during mixing. This is also underlined by Mancini and Italia [21], who suggested to limit the use of high temperature and high shear as much as possible by subdividing the process into two consecutive steps: 1) a high-shear mixing at high temperature for a limited period of time to obtain a homogeneous distribution of the polymer in the asphaltic phase and 2) a low-shear mixing, possibly in an inert atmosphere, until the desired properties are obtained. This or similar mixing procedures based on a first aggressive mixing followed by a “digestion” at low shear rates are used by many manufacturers, and they also have the advantage of limiting the time spent in the production apparatus. The mixing process is completed in separate storage tanks equipped with a low-shear/low-speed mixing apparatus.

2.2.2. The exodus of maltenes or the dynamics of the swelling phenomena

As a general rule, we know that compounds with similar polarity are miscible and that the higher the MW is, the higher the required similarity to obtain a successful mixture (this is the reason why it is rarely possible to obtain a homogeneous polymer–polymer blend). This qualitative rule may be quantified by means of the solubility parameter, which was first introduced by Hildebrand and Scott in 1950 [22] and defined as the square root of the cohesive energy density. The parameter was later split by Hansen into three parameters describing atomic nonpolar interaction, molecular dipolar interactions, and molecular hydrogen-bonding interactions, see, e.g., [23]. The Hildebrand solubility parameter (HSP) of a compound may be calculated either experimentally or theoretically from the molecular formula. Of course, a single HSP value may not be assigned a priori to asphalts, because their composition strongly depends on the source, and a single value (or a range of values) would not be useful considering their extremely complex composition. In the case of homogeneous mixtures, the HSP value can be obtained by averaging the HSP of the individual components

weighed by volume. Again, this is not applicable to asphalts of inhomogeneous structure derived from the coexistence of incompatible molecules. The simplest and most common approach is to assign separate HSPs to the asphalt components divided into groups, in which the discrimination of the groups is based on their solubility. As an example, the ASTM D4124-09 (standard test method for separation of asphalt into four fractions) defines four fractions (saturates, naphthene aromatics, polar aromatics, and iso-octane insoluble asphaltenes) that can be separated from each other through a selective-solvent procedure. Analogously, thin-layer chromatography/flame ionization detection (TLC/FID) allows for the fractionation of asphalt into four fractions of different polarity, namely saturates, aromatics, resins A, and resins B (SARAB). In both cases, the four fractions have different polarities and thus HSP values. Saturates are the less polar and asphaltenes are the most polar components [24, 25]. This separation into groups of different polarities operated by selective solvents is not much different from the above-mentioned distillation operated “in situ” by the polymer during modification. The polymeric network is preferentially swollen only by the compounds with a favorable HSP, which determines the formation of PRP and ARP.

2.2.3. The favorable polymer architecture

TPE constitutes certainly the most important group of polymers for the modification of asphalt. These are block copolymers obtained by joining soft and hard segments, usually in a three-block sequence: hard-soft-hard. Since both segments are in the amorphous state, the words hard and soft simply mean that at the operative temperatures, the segments are, respectively, below and above their glass transition points. Quantitatively, the soft segments are predominant, and the scarce or totally absent compatibility between the hard and soft sequences leads to a biphasic structure constituted by small domains of the hard phase dispersed in the continuous soft matrix. The soft domains are linked on both sides to the hard domains, generating a physical network responsible for the elastomeric behavior. Being completely amorphous and thus with macromolecules in random-coil conformation, block copolymers show fluid-like disorder on the molecular scale. However, the hard domains may assume specific shapes and arrange themselves in a regular manner so that ordering at higher lengths (nanometer scale) may exist. The statistical theory of copolymers allows good predictions of domain shapes and order symmetry for block copolymers [26]. The hard glassy segments play the role of sulfur bridges in vulcanized rubbers, but the absence of covalent links among the macromolecules enables the melting (or softening) of the polymer once the temperature is higher than the T_g of the hard segment. The ideal condition associated with asphalt modification is that asphalt molecules swell mainly the soft matrix and only slightly the glassy domains. In this manner, the structure of the polymeric network is maintained after modification, and thus, its elastomeric character is maintained as well. If a high degree of swelling is reached, the entire material acquires elastomeric properties, thereby enhancing its elastic recovery capacity and resistance to permanent deformations. The swelling is schematized in Figure 3.

In contrast, if the asphalt molecules disaggregate the glassy domains, the nodes of the network are lost and the modification enters the CS zone of Figure 1. However, the image describes only the final morphology because, during modification, the temperature is well above the T_g of the hard segments and the network is probably destroyed. Therefore, such a morphology is not derived from a simple swelling of the soft phase, with the hard one untouched and unswollen during the modification process. It is also likely that the hard domains are swollen or melted during mixing and reconstituted when the blend is cooled below their T_g . Since the hard domains constitute an independent phase, the most appropriate representation is that of a three-phase system, in which PRP is subdivided in two sub-phases constituted by swollen soft segments and partly swollen hard segments.

TPEs applied in the paving industry usually differ in nature and relative amounts of the soft and hard segments. The hard segments are always constituted by polystyrene, the T_g of which is approximately 100°C. Poly(styrene-*b*-butadiene-*b*-styrene) block copolymer (SBS) is by far the preferred thermoplastic elastomer for asphalt modification, but poly(styrene-*b*-isoprene-*b*-styrene)

(SIS) and poly(styrene-*b*-ethylene-butene-*b*-styrene) (SEBS), obtained through the hydrogenation of SBS, are also used.

The most popular thermoplastic polymer is poly(ethylene-*r*-vinyl acetate) (EVA), which has a molecular structure completely different from that of TPE: the ethylene and vinyl-acetate repeating units are randomly distributed along the backbone of the macromolecule. Nevertheless, the repulsion between the two monomers and the presence of homo-sequences of ethylene units lead to a structure similar to the one reported in Figure 3, in which the hard domains are formed by crystalline or semi-crystalline poly(ethylene)-rich zones. Therefore, considerations similar to those of TPE can be done regarding the mechanism of swelling and the presence of a polymeric network. Finally, in the case of reactive polymers, the formation of a polymeric network still exists, but in this case, there are chemical bridges (based on covalent bonds), instead of physical bridges, between macromolecules.

2.3. Compatibility vs. Morphology

2.3.1. Optical microscopy

In the previous section, the term “compatibility” was introduced to describe the “level of interactions” between the asphalt and polymer. This term has an intuitive significance but remains an evanescent property that is rather difficult to be directly measured. Several methods were therefore developed over the years to indirectly estimate compatibility in asphalt/polymer blends. From this perspective, the investigation of the blend morphology is probably the most direct method and optical microscopy is the most popular method because it allows a rapid and economical observation of the sample. A picture obtained using optical microscopy allows for a meaningful representation of compatibility and can be successfully used to predict the macroscopic stability of the blend.

A synthetic overview of the relations between morphology and compatibility may be defined as follows: the morphological arrangement of ARP and PRP within the blend strongly depends on the specific asphalt/polymer compatibility. Therefore, the morphology of the system will assume a well-defined overall arrangement when the polymer and asphalt are compatible, while a completely different morphology will indeed appear in immiscible systems.

Optical observations of PMA are typically carried out through FM, which allows a direct observation of the relative amount and morphologies of both ARP and PRP because they have different UV-excitation responses. For readers not familiar with this technique, it is useful to remember that the aromatic phase of asphalt is usually the most fluorescent one, while the asphaltenic one is not fluorescent. Asphalt observed with a fluorescence microscope appears as a homogeneous material with a yellowish appearance, where the color gradation depends on the aromatic content. The fluorescence of polymers obviously depends on their composition; however, irrespective of the composition, the main point is that polymers are usually swelled by the maltenes and concentrate the fluorescent molecules in PRP. Therefore, in a typical fluorescence image of a biphasic PMA, the PRP appears yellow, while the ARP, depleted of aromatic molecules if compared to base asphalt, appears dark, almost black, depending on how asphaltenic it is. Therefore, a homogeneous sample, with or without polymer, has a yellowish appearance, while in the presence of well-separated PRP and ARP, the former is bright yellow and the latter is almost black (of course, for figures in gray scale, the PRP phase is the brighter one).

If, on one hand, FM is only a qualitative analysis, on the other hand, it provides an immediate and readable picture of the blend. prEN 13632: “*Bitumen and bituminous binders - Visualization of polymer dispersion in polymer modified bitumen*” is the European specification that underlines with a particular emphasis the importance of sample preparation. The procedure suggested by the specification is as follows: after heating and homogenization through gentle hand stirring, the material is transferred to an aluminum basin placed in a sand bath preheated to the same temperature as the sample during homogenization. The sand bath is an evaporating basin containing sand, which guarantees a slow cooling of the sample to room temperature. During this cooling from

the liquid state to the solid state, the sand bath gives a standardized thermal history, which is of fundamental importance because it can strongly affect the morphology. Once room temperature is reached, the sample must be further cooled until it becomes brittle so that small pieces can be prepared through fragile fracturing. Finally, the freshly broken surface is inspected through FM. With regard to the final report, the first point is whether PRP or ARP constitutes the continuous phase, but it is, of course, also possible that the two phases are co-continuous and comparable from a volumetric point of view. The distribution of the dispersed phase is described by using a code of characterization letters: H or I for homogeneous or inhomogeneous; S (small, $<10\mu\text{m}$), M (medium, between 10 and $100\mu\text{m}$), or L (large, $>100\mu\text{m}$) for the size and r (roundish), s (stripes), or o (other) for the shape.

While the reader is referred to the specification with respect to the definition of homogeneity, dimension, and shape of the domains, a few examples may be of help to familiarize one with some of the morphologies that may be encountered. In Figure 4, a few typical morphologies are shown, starting from the most compatible blends towards higher degrees of incompatibility. In this picture, it is supposed that all blends have the same content of polymer, and the differences are determined by the different degree of swelling and relative interactions between the asphalt and polymer molecules. In Figure 4a, a completely homogeneous asphalt/polymer blend is shown. This is the limiting case in which the image shows a single phase, no pattern at all, and a degree of fluorescence depending on the asphalt composition and polymer content. Such a situation corresponds to a complete dissolution of the polymer in the asphalt and, as already stated, it is not desired in practice because an excessively high solubility parallels with a limited effect of the polymer on the binder properties. A desirable and ideal homogeneity is shown in Figure 4b, in which the so-called “orange skin” morphology indicates an intimate mixing, with almost indistinguishable PRP and ARP. Nevertheless, the presence of a well visible pattern testifies that the material is somehow “structured” and the polymeric network positively affects the binder properties. Simultaneously, a morphology such as this almost warrants high-temperature storage stability. A slightly worse compatibility between the polymer and asphalt leads to the image shown in Figure 4c, in which PI has occurred but a few irregularly shaped small ARP islands are clearly visible, indicating the existence of a few asphalt components unable to swell the polymer. In this case, the effect of the polymer on binder properties may be even stronger than in the previous case and the limited extent of the separated ARP gives good chances of storage stability. A progressive decrease of compatibility determines an increase in the ARP dimension and bigger, round black islands dispersed in the yellow phase may appear (Figure 4d) until a co-continuous morphology where neither PRP nor ARP are the dispersed phase is reached (Figure 4e). In this case, the two phases usually form irregularly shaped domains with well-defined interfaces and are destined to separate during the tube test (see section 2.4.2. for the description of the tube test). A further decrease in the interactions and swelling leads to a PRP-dispersed phase (Figure 4f), the shape of which changes progressively to spherical, corresponding to the minimum surface/volume ratio, or, in other words, to the minimum ARP–PRP interfacial area (Figure 4g). Of course, the reported examples are not exhaustive, and many other complex morphologies may be found. The last image (Figure 4h) is dedicated to a quite common error in sample preparation: if the specimen is not fragile during preparation, then shear-oriented stripes may be generated by the blade during cutting. These images help understand how morphology can be an excellent indicator of the blend quality and separation tendency of PRP and ARP. Moreover, a comparison of top and bottom morphologies after the tube test may highlight differences not detectable using other techniques. Operators and researchers familiar with this technique will know how useful it may be and can give an immediate insight of the blend quality.

The main drawback in the use of FM to study the morphology of PMA is the extreme importance of the sampling procedure. Therefore, each time pictures are taken without exactly following a standard, the procedure should be clearly described when presenting morphological images. It is of fundamental importance to know if the PRP and ARP had time to separate from each other or if a

quench-frozen pseudo-homogeneous morphology resulted from a high shear during mixing. It is evident that the more unstable the system is, the higher the differences between these two cases. A systematic analysis of the effect of the procedure was performed by Soenen et al. [27], who compared samples prepared with different methods and subjected to different thermal histories. The high number of reported pictures describes also the changes in morphology occurring during isothermal storage and shows that the bulk morphology may be very different from that on the surface, which has been in contact with air or with a solid surface (like e.g. a silicone mold). As an example, the paper shows images of drops of the same binder taken from samples prepared using the same procedure and then sheared for 10 min at a modest shear rate and at different temperatures. As the temperature decreases, the morphology changes from uniform to coarse, with dispersed spherical domains of PRP. This also suggests the existence of an upper critical solution temperature (UCST) (see section 3.2.3). Moreover, samples taken at lower temperatures show orientation due to the drop flow on the glass plate. With regard to the cooling rate, the morphologies of a freeze-fractured surface obtained with the apparatus described in EN 13632 either after quickly cooling the sample (within 5 min) to room temperature or after slowly cooling the sample (2°C/min) are compared: the first one is homogeneous, while the latter is markedly biphasic. It is also interesting to observe that at high temperature, the sample flows and may form a very thin film. In this case, it is also possible to use transmitted (visible) light so that morphologies may be observed with polarized optical microscopy (POM). A comparison of morphologies obtained using POM and FM is reported by Rossi et al. [28]. Of course, the images of the thin film differ from those taken after freeze fracturing in the bulk because of sample squeezing in a two-dimensional frame.

Another comparison between two different preparation procedures, defined as “freeze” and “drop,” was recently performed by Oliver et al. [29]. In the freeze method, the sample was dropped onto a rubber mold, then immediately immersed in water at 0°C, and subsequently cooled to -20°C. In the drop method, a sample was dropped directly onto a glass cover for direct observation. The paper reports images of samples obtained with the two procedures after a particular storage procedure, which is performed as follows: the binder was maintained at 200°C for 1 h, then samples were taken, and subsequently the binder was returned to the oven at 180°C for 1 h; this cycle was repeated until 100°C was reached. This procedure was developed in order to simulate the slow cooling rate of the binder during transport to the application site. It is particularly interesting that the sampling procedure influences the results even after storage, which means after a long period without stirring. It could have been expected that this effect is important only immediately after the high-shear stirring, which may compensate the tendency for phase separation of a highly unstable mix.

In order to bypass the qualitative nature of microscopy, Sengoz and Isikyakar [30] suggested image processing to quantify the polymer distribution area throughout the PMA samples. The images were transformed to grey scale and then to binary black (ARP) or white (PRP) phases. In this manner, the swelling ability was somehow quantified, so that the relative proportion of the polymer phase was correlated with the polymer content. Image processing was recently used by Aguirre et al. [31]. Unfortunately, such a procedure applied to white grey images is based on the introduction of a black/white threshold that may work appropriately only when a clear and sharp distinction between PRP and ARP exists.

Another possible method to analyze the morphology of the blends is confocal laser scanning microscopy (CLSM). Samples squeezed between glass plates are observed in transmission mode by using a He-Ne or Ar laser scan microscope. A few images of PMAs obtained by using different types of polymer modifiers have been reported by Champion et al. [32] and appear very similar to those obtained using FM.

2.4. Compatibility vs. Stability

2.4.1. Problem statement and description

The problem of phase separation dates back to the earliest descriptions of PMA. In 1980, Kraus and Rollman described the biphasic nature of asphalt/SBS blends and were probably the first to introduce the idea of ARP and PRP [33, 34]. Of course, the tendency of these two phases to macroscopically separate during hot storage is also known since the first studies on PMA; however, it was interpreted in terms of the action of gravity only quite recently [35]. Storage stability can be somehow defined as the compatibility at a macroscopic scale, and it is certainly the first and most important requirement in PMA technology. The differences between PRP and ARP drive toward possible tests to verify and quantify such phenomena. The common points of all the proposed techniques are a first step to simulate hot storage and a second step to verify if and how much a separation took place.

A further consideration may be necessary to point out that the term “stability” is, here and in what follows, intended as the macroscopic separation of PRP and ARP during storage under quiescence and does not include other changes of properties often interpreted as “instability,” such as ageing or further swelling, which may also lead to important changes in binder performance during storage. As an example, Sun and Lu [36] showed that a binder may be storage stable even if its softening point undergoes a drop of 12–13°C after the tube test.

The next subsection is dedicated to standard and experimental techniques useful for evaluating phase separation in PMAs.

2.4.2 Standard methods and experimental devices

In 1995, Isacsson and Lu [37] reviewed the “*testing and appraisal of polymer modified bitumens*” and described three methods for compatibility and storage-stability testing, none of which had been standardized. The first one was the so-called “tube test,” which has survived till the present and is now included in the specification of several countries. The simple idea of the tube test is to place a sample of modified asphalt in a vertical vessel (tube) at high temperature for a certain period of time. This simulates high-temperature storage in the absence of stirring and shearing, during which the PRP and ARP may separate. The lighter PRP phase will migrate to the top part of the tube, while ARP will settle at the bottom. The tube is then removed from the oven and cooled to room temperature, while kept in the same vertical position. Finally, the sample is cut horizontally into three equal sections. The middle section is discharged, while the properties of the top and bottom part are tested and compared. Of course, the least the differences between the top and bottom properties are, the higher the storage stability would be. Over the past few years, several variants of the tube test were suggested, with different duration and temperature for storage as well as different testing procedures on the final sample. Coming back to the review of Isacsson and Lu, they chose two procedures as most significant. In the first one, an aluminum foil tube is filled with PMA and placed vertically in an oven at 180°C for 14 days. The recovered sample is then placed horizontally on a glass plate and subsequently transferred into an oven at 50°C. The sample is then visually inspected for any non-uniform slump or flow from end to end over a 24-h period. If segregation has taken place, then there would be viscosity differences over the length of the tube, and this determines visually detectable differences in the flow of the material. In contrast, if the polymer is uniformly distributed along the sample, its deformation will also be uniform. In the second procedure, the tube is stored vertically at 180°C for 3 days and then cooled to at least below 30°C. The compatibility/storage stability is then evaluated by comparing the softening point and/or penetration of the top and bottom sections. This second version was subsequently adopted in the European standard specification EN 13399 “*Bitumen and bituminous binders - Determination of storage stability of modified bitumen*” introduced in 2003 and then changed in 2010 (the corresponding American specification is ASTM D7173-11 “*Standard Practice for Determining the Separation Tendency of Polymer from Polymer Modified Asphalt*”). EN 13399 suggests the use of an aluminum “toothpaste tube” of minimum height 160 mm and diameter between 25 and 40 mm. The tube is poured with the sample of PMA to a height of 100 mm to 120 mm with due precaution

to avoid the incorporation of air bubbles, squeezed and closed (to avoid any action of air during high-temperature storage), and then placed in an oven at $180 \pm 5^\circ\text{C}$ in the vertical position for 72 ± 1 h. The tube is then removed from the oven and cooled to room temperature while maintained in the same vertical position. After peeling the aluminum, the recovered cylindrical sample is placed horizontally and cut into three equal parts denoted top, middle, and bottom. The top and bottom parts are then used for further testing, such as for the softening point or needle penetration. Usually, the binder is considered stable if the difference $\Delta S = S_t - S_b$ (where S_t and S_b are the softening points of the top and bottom parts, respectively) is lower than a pre-established value.

As an alternative to the softening point and penetration, it is an increasingly common practice to evaluate the two fractions in terms of their rheological properties. The SHRP specification introduces the following “separation index” I_s :

$$I_s = \log \left(\frac{|G|_b^*}{|G|_t^*} \right) \quad (1)$$

where $|G|_b^*$ and $|G|_t^*$ are the complex moduli at 25°C and frequency of 10 rad/s of the bottom and top phases, respectively. Analogously, the viscosity or the ratio $|G^*|/\sin\delta$ (where $|G^*|$ is the complex modulus and δ is the phase angle), also taken from the SHRP specifications, can be used. For example, the latter is used in a recent paper by Kim and Lee [38], which defines the “percentage of separation” as the ratio

$$\frac{(|G^*|/\sin\delta)_{\max} - (|G^*|/\sin\delta)_{\text{avg}}}{(|G^*|/\sin\delta)_{\text{avg}}} \quad (2)$$

where $(|G^*|/\sin\delta)_{\max}$ represents the higher value of either the top or bottom section of the tube and $(|G^*|/\sin\delta)_{\text{avg}}$ is the average value of both sections. To give an idea of the variability in tube-test operating conditions, the same paper lists eleven storage-stability conditions selected from twelve different papers.

The second test described by Isacson and Lu [37] uses UV fluorescence microscopy to investigate the morphology of the blends. Of course, a marked heterogeneity of the samples indicates weak compatibility, which is expected to be accompanied by phase separation during the tube test. Further, in this case, normative specifications were introduced a few years later that describe how to prepare samples as well as observe and define the PMA morphologies (see section 2.3.1.).

The last method described by Isacson and Lu [37], which did not survive to the present day, is the “crushing test.” In this case, a PMA disk (20.5 mm in diameter and 2 mm thick) is placed between sheets of absorbent filter paper and placed under a weight of 100 g in an oven at 135°C for 15 h. The deformation of the pellet is recorded and the stability of the mix evaluated by observing the oil migration.

In summary, it is universally recognized that the tube test is a simple and reliable method to simulate high-temperature storage. Apart from the specification and among the long list of proposed procedures, the longer and hotter the storage is, the higher the probability of phase separation will be. When the instability is high and the separation is completed during storage, usually the differences between the top and bottom parts are macroscopically evident, and the operator may foresee the final result through a simple organoleptic observation of the two fractions. In contrast, when the sample is at the boundary between stability and instability or even stable but showing some differences between the two fractions, then an accurate characterization technique can be useful to quantify the risk connected to a limited inhomogeneity. Thus, irrespective of the definition of stability, as assumed by a specification, the differences between the top and bottom parts can be quantitatively and/or qualitatively evaluated using other methods, for example through the rheological characterization of the viscoelastic properties. This is an important point because a

result of “stable” or “not stable” in the tube test can be incomplete information: in certain cases, a ΔS value slightly below the allowed limit may significantly affect other properties. Moreover, PMAs with a very low polymer content (which may be the case of a small loading intended to fill the gap to the immediately higher performance grade (PG) of SHRP specifications) may remain below the stability limits even after a considerable separation. Therefore, it is always necessary to perform the test by taking into account the specific case under evaluation and not limiting the analysis to the simple normative specification. This directly leads to another consideration for the tube test: this well-known and established procedure was developed specifically for PMAs. This fact must be taken into account when using the tube test to evaluate the stability of asphaltic mixes other than PMAs, such as crumb-rubber-modified asphalts or in the presence of mineral fillers. Of course, exceeding the limit of PMAs is not forbidden, but it should be clear that all the parameters must be at least re-calibrated. As an example, mineral fillers will migrate toward the bottom part of the sample, rendering S_b higher than S_t ; moreover, the value of ΔS would not be comparable with those measured with a PMA.

Another interesting specification is the Australian one, which involves both segregation [39] and ease of remixing [40] tests [41]. The segregation test is conceptually similar to the tube test and involves storing samples in 375-mL metal cans for 48 h at 180°C and then allowing them to cool. After cooling, the degree of separation is evaluated by measuring the softening points of the top and bottom halves of the cans (in the European tube test, PMAs are stored for a longer period, and samples are cut into thirds rather than halves; the softening-point differences are expected to be larger than in the Australian test). The ease of remixing test is aimed at evaluating whether a segregated PMA can be returned to a homogeneous state using mixing protocols conventionally used by manufacturers and users of PMAs. If this is possible, then polymer segregation occurring during storage and transport is not expected to cause significant issues; therefore, the Australian specification [42] allows PMAs that fail segregation test requirements if they meet the requirements of the ease of remixing test. The ease of remixing test follows the same procedure as the segregation test, with the exception of the cooling step. In the ease of remixing test, after storage, the metal can is transferred to a hot plate, and the binder is stirred at a rate of 100 movements per minute for 10 min using a flat-bladed spatula, which simulates conventional mixing protocols used with PMAs in the field.

Segregation and ease of remixing test results are calculated from the softening points of the top and bottom halves of the metal cans using the following formula:

$$S \text{ or } E = \frac{200 (S_t - S_b)}{S_t + S_b} \quad (3)$$

where S and E indicate the segregation and ease of remixing results, respectively.

In a recent report [43], the results of the European storage-stability test and Australian segregation test are compared for a relatively high number of samples with different degrees of asphalt/polymer compatibility. The results show that the two tests are nearly equivalent for highly unstable samples ($\Delta S = 40\text{-}70^\circ\text{C}$), while in intermediate cases ($\Delta S = 5\text{-}35^\circ\text{C}$), the segregation test indicated an almost null percentage difference in the softening points of the top and bottom halves of the sample. Of course, the two test are again equivalent for perfectly stable samples.

An alternative to the tube test was developed by Bahia and Zhai [44] as part of the NCHRP 9-10 project (National Cooperative Highway Research Program for the Characterization of Modified Asphalt Binders in Superpave Mix Design) and named the laboratory asphalt stability test (LAST). At the starting point, the tube test does not properly simulate the real storage conditions, resulting in an unrealistic description of the performances after storage; moreover, it does not help finding the appropriate storage conditions for a given asphalt sample. A simple scaling down of a commonly used vertical storage tank should allow for maintaining the key engineering aspects of the storage. A more realistic simulation of the field storage conditions and the possibility of sampling during the

test allow for evaluating the effects of adjustable parameters such as temperature, time of storage, and level of agitation. In this manner, instead of using a single procedure, the most appropriate storage conditions can be determined and applied to each specific modified binder. Instead of classifying a binder as stable or unstable, the LAST procedure is used to determine the stability/instability conditions for each PMA. This should allow for the optimization of the temperature and level of agitation or the identification of the maximum storage period for a given storage condition. The test system is designed to handle a sample of 400–450 ml and features internal and external heating, variable level of agitation (including of course static storage), sampling from various locations, and temperature control.

The testing procedure includes two main steps: 1) external heat without agitation (static storage) and 2) external heat with high mechanical agitation. These two steps simulate the extreme conditioning steps. A third optional step that simulates slow thermal agitation may also be added. Then, according to the Superpave specifications, the following separation ratios (top/bottom) for $|G^*|/\sin\delta$ and $|G^*| \sin\delta$ are calculated at different sampling intervals over a period of 48 h:

$$R_{sHT} = \frac{(|G^*|/\sin\delta)_t}{(|G^*|/\sin\delta)_b} \quad (4a)$$

$$R_{sIT} = \frac{(|G^*|\sin\delta)_t}{(|G^*|\sin\delta)_b} \quad (4b)$$

where the t and b subscripts indicate the top and bottom of the LAST, respectively, while HT and IT indicate the high-grade and intermediate-grade temperatures, respectively.

The same data are also used for the degradation analysis by calculating the following degradation ratios (R_d):

$$R_{dIT} = 0.5 \frac{(|G^*|/\sin\delta)_t + (|G^*|/\sin\delta)_b}{(|G^*|/\sin\delta)_{in}} \quad (5a)$$

$$R_{dHT} = 0.5 \frac{(|G^*|\sin\delta)_t + (|G^*|\sin\delta)_b}{(|G^*|\sin\delta)_{in}} \quad (5b)$$

where the “*in*” subscript stands for the *initial* state (time = 0).

Usually, the degree of separation after storage is indirectly evaluated. A property depending on the polymer content is measured, and then the difference between top and bottom fractions somehow quantifies the degree of separation.

The latter procedure has the inconvenience that the numerical value depends on the specific asphalt/polymer couple and does not give an absolute degree of separation. Therefore, a direct determination of the polymer content is an interesting alternative. An example is the use of IR spectroscopy. This technique was used by Masson et al. [45] to detect the content of styrene (S)-butadiene (B) type copolymers in asphalts. The average IR molar absorptivity for polystyrene and polybutadiene blocks was obtained for different SBS and SB copolymers, including linear, branched, and star copolymers as well as their blends with asphalt. As the average absorptivity was not significantly affected by the S/B ratio or the copolymer architecture and obeyed the Beer’s law in the presence of asphalt, it allowed for calculating the concentration of SB-type copolymers in blends with asphalt with an accuracy of at least 10%. The starting point of this technique (see also Mouillet et al. [46]) is the comparison of the polymer spectrum with that of asphalt to select the specific, noninterfering IR bands. Then, polymer infrared indexes can be defined as the ratio of the specific polymer absorption band to the specific asphalt absorption band, and a calibration curve is constructed by analyzing PMA with known percentages of polymer. The following bands and ratios were proposed for SBS and EVA [46]:

- out of plane bending vibration γCH_3 of trans-butadiene at 965 cm^{-1} for SBS to the in-plane bending vibration δCH_3 at 1376 cm^{-1} for asphalt;
- stretching vibrations $\nu\text{C-O}$ of vinyl acetate at 1240 cm^{-1} for EVA copolymer to the stretching vibrations $\nu\text{C}=\text{C}$ at 1600 cm^{-1} for asphalt.

In a previous paper by Lu et al. [35], the same technique was applied to binder solutions prepared in carbon disulfide, and the suggested peaks of IR absorbance to identify SBS are at 965 and 700 cm^{-1} . Among other possibilities such as the quantification of polymer content in commercial products or polymer aging in in-service binders or sealants, a simple application of the method is the monitoring of the storage stability. A freshly prepared asphalt/SBS blend was stored at 165°C , and then the changes in concentration of S and B at the surface of the blend were monitored in the following 2 days. An enrichment of S and B blocks on the upper surface of the blend allowed for verifying and quantifying the degree of separation as well as the kinetics of the separation. In this case, the monitoring does not require the use of a tube; the blend is stored and maintained in a conventional can, and the test is performed on samples taken from the upper free surface.

3. Primary mechanisms of asphalt/polymer interaction

3.1. Selective migration and other processes of interaction in asphalt/SBS blends

3.1.1 Asphalt composition and its effect on compatibility

As already mentioned, SBS is the most widely used polymer in the paving industry. Consequently, it is also the most studied polymer in the related scientific literature. Several researchers attempted to understand the effect of polymer characteristics on its blending with asphalt. However, it must be anticipated that owing to the high variability of asphalt composition and the very high number of variables (such as polymer characteristics, polymer content as well as mixing apparatus, and operating conditions) influencing the asphalt/polymer interactions, it is nearly impossible to obtain “universal” rules. Thus, it is not uncommon to find contradictory results from different research groups.

Before proceeding to a detailed description of PMA based on these polymers, it is necessary to review briefly the basic processes that regulate the compatibility within asphalt/SBS blends. The basic question may be formulated as follows: how does the asphalt composition control the polymer/asphalt compatibility?

One of the first papers that address this question is by Lu and Isacson [47], who analyzed several aspects such as asphalt composition, polymer structure, and polymer content. The study was performed using five different crude oils of SARA fractions determined using TLC-FID and two SBSs: Kraton D1101 (linear) and Kraton D1184 (branched), which are still produced and widely used in asphalt modification. PMA from all the crude oils were prepared using a single blending procedure (2 h at 180°C and a low-shear mixer set at a speed of 125 rpm). All base asphalts had a limited compatibility with both SBSs; consequently, a modest swelling degree was obtained, and PI was possible only at high polymer content. This low compatibility was also confirmed by the tube test (see section 2.4.2.), which revealed that all blends were unstable. Nevertheless, the interactions between asphalt and polymer showed strong dependence on the chemical composition of the asphalt: a high aromaticity and low asphaltene content favors the compatibility. Thus, the authors conclude that *“to produce a polymer modified binder with good compatibility, the content of aromatics of the base bitumen should be sufficiently high for the polymer to compete with asphaltenes. Therefore, it is reasonable to expect that the compatibility of SBS modified binders may be improved by the addition of aromatic oil or deasphaltenation of bitumens.”* In other words, the composition of the asphalt should be able to survive the alteration of its colloidal state induced by the polymer. As SBS prevalently absorbs maltenes, there is a reduction in the peptizing molecules still available to cover the asphaltenic micelles. This determines an association of the

latter and favors phase segregation under the influence of a gravitational field. If the base asphalt has a low asphaltene content and high aromatic content, then after polymer swelling, the resin may be still able to peptize the asphaltenes, thereby reducing their tendency to separate or even driving them into the polymeric network. This suggests that the polymer/asphalt compatibility may be evaluated with parameters expressing the asphalt composition, such as the asphaltene and aromatic content or the instability colloidal index (I_c) (also called Gaestel Index [48]) defined as

$$I_c = \frac{\text{Asphaltenes+Saturates}}{\text{Aromatics+Resins}} \quad (6)$$

and expressed as weight percentage.

This seems to be confirmed by the graphs shown in Figure 5, in which I_s is shown to be well correlated with such quantities.

The authors chose to use this separation index because ΔS may not be appropriate to quantify the separation. A high value of ΔS is, of course, related to a high degree of separation; however, the numerical value may not be adequate, because the determination of the softening point can be doubtful for highly elastic modified binders. Indeed, in another paper, the same authors stated that no significant relationship was found between I_s and ΔS [33].

In any case, the existence of some relationships between the asphalt composition and blend stability was clearly found; in addition, I_c seems to accomplish its natural task: the prediction of asphalt/polymer compatibility.

3.1.2. Mechanism of SBS swelling and morphological evidences of maltene migration

An important contribution to the clarification of the mechanisms of polymer swelling in asphalt/SBS blends came from the work by Masson et al. [49], who used modulated differential scanning calorimetry (MDSC) to measure the T_g of asphalt and SBS in their blended and unblended states. The all asphalt/polymer blends showed the T_g of asphalt and polymer alone, in addition to a new one arising from a phase of mixed components containing PB segments and approximately 30% of maltenes, namely alkanes and cyclo-alkanes. The PB not included in the mixed phase was found in a PB-rich phase swollen by the lighter alkanes, and the shifting of the other T_g in the blends indicates that the PB block has good interactions with asphalt, in contrast to PS. Hence, the SBS/asphalt miscibility seems to be controlled significantly by the PB block in SBS as well as by the lighter maltenes in asphalt.

Indeed, the use of MDSC instead of DSC helps to better recognize the T_g , the shift of which is a good indicator of the interactions in multicomponent systems. In this respect, the calorimetric studies by Masson et al. [50, 51] and Kriz et al. [52, 53] are extremely interesting.

Rheology may also be a valid approach to evaluate the effect of mixing on T_g . This approach was followed, for example, by Wloczyński et al. [54], who used dynamic mechanical thermal analysis (DMA). The effect of swelling on T_g can be observed using DMA through both a shift in the T_g value as well as a broadening of the T_g peak. DMA curves of asphalt/SBS blends were obtained in temperature sweep from -70 to 120°C and showed three transitions that were associated with each of the three phases constituting the blend: the first one was below 0°C and attributed to the swollen PB phase, the second one was near 40°C and attributed to ARP, and the third one was near 100°C and attributed to the swollen PS. In order to understand the implications of such transitions better, model systems obtained by substituting the asphalt either with deasphalted or aromatic oil were studied, and T_g was determined using DSC. The behavior of the PB- and PS-rich phases with respect to the oils were very different: the T_g of swollen PB is located between those of pure PB and oil, while the PS phase, when swollen with the deasphalted oil, shows an important antiplastification effect. This is attributed to the presence of high polar compounds, which interact with PS and induce an increase in T_g . Moreover, this effect was observed to be much more

important with branched SBS than with the linear one, and these specific aspects related to polymer architecture will be discussed later (see section 3.3.1.).

A similar approach that provided further confirmation of the above conclusions was followed by Kamiya et al. [55], who used DSC to evaluate the shift in T_g of PB and PS blocks resulting from mixing: SBS with asphalt, PS homopolymer with asphalt, and SBS and maltenes or asphaltene separately (obtained through extraction with n-heptane).

Another interesting study aimed at directly verifying the compatibility among SBS and the asphalt components was based on a pre-separation of saturates, aromatics, and resins by solvent-recycled absorption chromatography separation and subsequent mixing with SBS [56]. The modification of the single fractions by SBS was evaluated using FM, which indicated that aromatics were the most compatible ones, followed by resins and saturates. Asphaltenes were not even taken into consideration, given their solid nature.

3.2. The prediction of compatibility and other open questions

3.2.1. Searching for a general rule (the use of compositional parameters)

Even if the use of I_c is plausible and consistent with the proposed description of the asphalt modification mechanism, it does not overcome the above-mentioned limitations related to the complexity and interconnection of many factors affecting storage stability. Therefore, I_c must be seen as a useful indicator, but not as a general rule. This was well highlighted by Masson and coworkers [32], who performed a similar study a few years after Lu and Isacson [47]. In this case, two base asphalts and four SBS copolymers were used to investigate the effects of polymer concentration, MW, S/B ratio, branching, and asphalt composition. With regard to asphalt composition, the two asphalts, denoted as ABA and PC, had the following aromatic and asphaltene percentage content: ABA 16, 16 ($I_c=0.37$); PC 27, 20 ($I_c=0.41$). These values showed that a result compatible with all three parameters (aromatic content, asphaltene content, and I_c) would not be possible, with PC of both higher aromatic content and higher I_c . The authors concluded that these parameters cannot be considered absolute, because they can be inaccurate and inconsistent among themselves.

If on one hand there is the need for a simple and reliable parameter, on the other hand, it is necessary to take into account the high number of involved variables. I_c may be inappropriate as saturates and aromatics act against each other in this value, but saturates may help establish the blend stability [32].

Another recent paper confirmed the above-mentioned difficulties in finding a general parameter for compatibility and storage stability [57]. Blends made in a twin-screw extruder by using six different base asphalts and an SBS were analyzed, and the intrinsic viscosity was used to determine the compatibility between asphalt and polymer. For all asphalts, the SARA fractions were determined, and the authors attempted to correlate the compatibility results with the following parameters: I_c , light components (saturates + aromatics), and ratio of saturates to aromatics. Moreover, oils rich in aromatics and saturates were added to some of the base asphalt to adjust and modulate the compositional parameters and evaluate their relation with storage stability. Again, even if all investigated parameters showed to be correlated with the asphalt/polymer compatibility, none of them were identified as sufficient to determine and predict the compatibility. As a general indication, the authors suggested that an optimum distribution of components to obtain a high degree of asphalt/SBS compatibility should be with an I_c of approximately 0.3, light-component content above 55%, and saturate/aromatics ratio of approximately 0.55.

3.2.2. Hildebrand solubility parameters

Another method to search for some possible relationships between asphalt composition and the prediction of compatibility may be outlined by the use of the HSP. Various authors made some attempts within this context, but no unambiguous conclusion was found even in this case. As it was

for the above-described parameters, the HSP reported for asphalt components in [58] also give indications that are in discordance with experimental findings: the polystyrenic blocks should be highly compatible with both saturates and naphthene aromatics, while the butadienic block should only be partially compatible with saturates (Figure 6). However, it has been observed that polystyrene is not swollen by asphalts or asphalt components [32].

In another paper, Fawcett and McNally [59] reported solubility-parameter values of approximately 14.3, 17.8, 19.7, and 23 $(\text{J}/\text{cm}^3)^{0.5}$, respectively, for the SARA components, and observed that the polymers have values close to aromatics and resin: PS had a value of $18.7 \pm 0.5 (\text{J}/\text{cm}^3)^{0.5}$ and PB had a value of $17.4 \pm 0.5 (\text{J}/\text{cm}^3)^{0.5}$. Of course, it must be pointed out that a single solubility parameter may be inadequate for the asphalt fractions because, in addition to composition, polarity and hydrogen bonding as well as the amphiphilic nature of the resins and asphaltenes should be considered [60, 61]. Nevertheless, Peng et al. suggested the use of a single solubility parameter representative of the entire asphalt [62] and attempted to relate the theory of solubility parameters with the aging resistance of paving asphalts [63, 64].

A couple of interesting papers were reported by Redelius. In the first one, the solubility parameters are used to develop an asphalt model based on the mathematical description of the stability of asphalt in terms of three-dimensional solubility parameters [61]. In the second one, the parameters are estimated for a Venezuelan asphalt by using solubility data in a set of 48 conventional solvents, and results are plotted as spheres in the three-dimensional Hansen solubility parameters space [65]. Finally, an experimental procedure based on microcalorimetry and ultraviolet-visible spectroscopy to determine the solubility parameters of crude oil and asphaltenes was recently described by Aguiar et al. [66].

By summarizing the literature review reported in these sections, we can say that the use of “compositional” parameters cannot lead to an unambiguous prediction of compatibility and stability in PMA. The next section reviews some papers that attempt to overcome this problem by following a different approach.

3.2.3. *The thermodynamic approach and the construction of phase diagrams*

In previous sections, it has been stated and somehow clarified that a simple relation between the asphalt composition and blend stability does not exist. Masson and coworkers suggested a possible interpretation based on thermodynamic considerations for the case of SBS [32]. Based on a thermodynamic approach, for the blend to be stable, the following condition must be satisfied upon mixing:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0 \quad (7)$$

where ΔG_{mix} , ΔH_{mix} , and ΔS_{mix} are the changes in the Gibbs free energy, enthalpy, and entropy, respectively, that occur upon mixing at temperature T. Of course, during mixing, $\Delta S_{mix} > 0$, while ΔH_{mix} is negative if the blend components have attractive interactions. In this case, both terms may positively contribute to ΔG_{mix} , but depending on the circumstances, their relative weights may significantly vary. For example, the blending of low-MW compounds gives an entropic contribution much higher than that of high-MW compounds. Possibly, the above-mentioned parameters fail because of their inability to account for the combined contributions to ΔH_{mix} and ΔS_{mix} . The instability colloidal index and aromatic content are mainly based on the favorable interactions between asphalt and polymer (which is the enthalpic contribution to the Gibbs energy). In contrast, the minimum asphaltene content corresponds to a minimum content of the highest-MW asphalt components (which is the entropic contribution to ΔG_{mix}). Therefore, I_c and aromatic contents may work well in situations where the enthalpic contribution prevails in ΔG_{mix} . However, given the low polarity of SBS, it appears reasonable that it establishes only weak interactions with asphalt, and for

this polymer, it is the entropic term that prevails in ΔG_{mix} (therefore, for SBS, it may be preferable to consider the asphaltenic component).

Another attempt related to the thermodynamic aspects concerns the construction of a phase diagram for the asphalt/polymer blend. However, even in this case, we found some inconsistencies. Indeed, it is curious that the only two papers that attempted to develop a thermodynamic phase diagram for an asphalt/SBS blend were published almost simultaneously and report contrasting conclusions [32, 67].

In both cases, there is an assumption that the asphalt/SBS system can be considered a pseudo-binary one. This represents a strong simplification, which may be arguable but probably unavoidable. The miscibility diagrams are evaluated by considering the behavior of PRP and ARP, but the two approaches differ in many points. Varma et al. [67] used a single SBS (Kraton 1101) that was blended with asphalt in various proportions through co-dissolution in tetrahydrofuran. The solutions were solvent cast at ambient temperature onto an optical microscope glass, kept in a vacuum oven for 24 h at 65°C, heated to 180°C for 10 min, and cooled down to room temperature prior to characterization. The phase separation dynamics of blends of various compositions were studied using optical microscopy at different temperatures. A digital camera allowed the simultaneous measurement of scattered intensity versus scattering angle. The temporal evolution of the scattering peak maximum was used to calculate the growth of the domain size in the blends. The obtained cloud-point phase diagram shows a UCST with a maximum at approximately 20% copolymer and 200°C. The procedure followed by Masson et al. [32] is completely different; they used 4 different SBS (including Kraton 1101) and prepared the blend through classical high-shear mixing. A simple observation of the behavior during storage at different temperatures (from 100 to 180°C) showed that blends can be stable at low temperatures, but they segregate when the temperature is increased. Moreover, the segregation rate increases with temperature, and the stability time/temperature interval became wider as the polymer content decreased. Hence, in contrast with the observation of Varma et al. (but in accordance with the common experience on blend kinetic separation), the phase diagram has a lower critical solution temperature. Moreover, Masson et al. took into account the non-ideal behavior of asphalt and observed that a tridimensional phase diagram can account for the polymer and asphalt constituents. Figure 7 shows the phase diagrams reported by Varma et al. [67].

3.3. The influence of the polymer structure

3.3.1. Linear and branched copolymers

The same considerations for the use of a compositional parameter to generalize the storage stability apply to the polymer structure. As an example, Lu et al. stated that “*the modified binders with linear SBS display higher storage stability than the modified binders with branched SBS*” [35, 47]. However, Masson et al. [34] underlined that such a conclusion could be generalized only if the two polymers had identical S/B ratios and MWs. Lu et al. used two SBSs with similar S/B ratios, but the branched one had a MW about twice that of the linear polymer, which influences the entropic contribution to blend stability. In other words, the higher stability for the linear SBS observed by Lu et al. [35, 47] could be ascribed to the lower MW of the polymer with respect to the branched SBS, while it is doubtful that a significant difference would have been observed if the linear and branched copolymers had similar MWs. In their study, Masson et al. [34] concluded that MW and the molecular shape determine the rate of segregation, while branching has no effect on stability, which depends mainly on the copolymer composition and MW. A high PB content and low MW favors stability. The first condition results from the fact that the π electrons of the C=C butene double bonds of PB establish a stronger interaction with asphalt than the aromatic electrons of PS segments do (enthalpic contribution); the second one results from its entropic contribution to the free energy. Finally, it must be remembered that the polymer concentration also has a great importance for stability. An increase in the copolymer concentration leads to an effective increase in the MW of ARP and a reduction in ΔS_{mix} .

3.3.2. *The vinyl content in SBS*

The vinyl content of SBS is the last, but probably not the least, aspect concerning the polymer structure that deserves a mention. A few years ago, the Kraton polymers company patented and distributed an SBS named Kraton D-1192 with a high vinyl content in the poly-butadiene mid-block (after a few years, other grades, named Kraton MD 243 and Kraton D-1191, were added). In the classical polymerizations of 1,3-butadiene, butyl lithium (BuLi) is usually used as the initiator, and the resulting structure is mainly (1,4) poly-butadiene with approximately 8-12% of the so-called (1,2) poly-butadiene, which has a vinyl pending group [68] (Figure 8).

Through the use of new initiators and processing conditions, the level of (1,2) poly-butadiene was increased up to 60%–70%, which is the case of the above-mentioned grades, with interesting consequences on the polymer characteristics. First, at comparable MWs, the chain with high vinyl content will be shorter, which implies lower viscosities and better workability. Second, the oxidation of the pending double bond does not involve the backbone but is confined in the vinyl branch; therefore, the polymer characteristics are less sensitive to ageing with respect to (1,4) polymers (see Figure 8). The last but most important point is related to the higher reactivity of the vinyl groups compared to the C=C double bonds on the polymer backbones. If on one hand this higher reactivity exposes the polymer to the risk of deterioration during storage and in service life, on the other hand, it potentially represents a method to obtain a grafting between the polymer and asphalt, which is a sort of stability warranty (see section 5.1.). Thus, the producer claims that given a sufficiently long reaction time, the highly vinyl SBS may be used to modify nearly all types of asphalts. In order to demonstrate the tendency to react with asphalt, the producers published a report [68] in which PMAs prepared with classical and highly vinyl SBS are compared through gel permeation chromatography and show that a higher degree of bonding within asphaltenes and polymers is obtained with the latter. Surprisingly, to our knowledge, a confirmation or contradiction of this theory has not yet been published; however, highly vinyl SBS grades are gaining in interest among PMA manufacturers. The only paper we found that uses a highly vinyl SBS is the one by Luksha et al. [69], which focuses on the mechanical and structural properties of the PMA but unfortunately does not study the storage stability or the existence of chemical bonds within the asphaltenes and polymer.

3.3.3. *The introduction of SEBS in asphalt technology*

In addition to the problem of storage stability and phase separation, other disadvantages related to the use of SBS or SIS are their high cost (the two polymers are produced at low temperatures through anionic polymerization) and their intrinsic chemical instability due to the presence of a high number of unsaturated C=C double bonds. The latter point causes low resistance to heat, oxidizing atmospheres, and UV light, as well as atmospheric agents and thus the insurgence of chain scission and crosslinking reactions. These ageing problems limit the duration and recycling chances of the road pavements and lead to the use of SEBS, which has a nearly identical morphological structure and a very similar chemical composition. The absence of aliphatic unsaturation is the only difference between the PEB block of SEBS and the PB blocks of SBS. As a general observation, the reduced polarity due to the absence of double bonds also determines a reduction in the compatibility between the polymer and maltenes relative to SBS. However, we already underlined that the HSP does not univocally determine the compatibility between asphalt and polymers and, moreover, contradictory results have been reported in the literature. Based on the values reported by Ovejero et al., the middle blocks of SEBS are more compatible with saturates and aromatic compounds than those of SBS are [70], and they may be expected to have better compatibility with asphalt, as observed by Becker et al. [71]. Gonzalez-Aguirre et al. [72] reported that the solubility parameters of the maltenes (17.4–26.6 MPa^{1/2}) are closer to that of PB (16.5–17.6 MPa^{1/2}) than to that of PBEB (15.9–16.5 MPa^{1/2}), thereby suggesting the opposite conclusion.

An interesting approach to the comparison between SBS and SEBS is the partial hydrogenation of SBS, which produces a poly(styrene-*b*[(butadiene)_{1-x}-(ethylene-*co*-butylene)_x]-*b*-styrene) (SBEBS) copolymer that can be obtained with different degrees of partial hydrogenation (x) [73]. The characterization of the polymers showed that hydrogenation conditions were adequate to favor the saturation of the PB block over undesired reactions such as chain scission, crosslinking, or saturation of the PS block; therefore, SBS and SBEBS differed only in the chemical composition of the middle block, and the chain architecture and degree of polymerization were nearly identical. The morphologies of four blends prepared with 8% polymer and increasing degrees of hydrogenation (0, 22, 52, and 77) confirm the great influence of this parameter. On using SBS (x = 0), the blend is highly biphasic and PRP is the dispersed phase, while it became continuous with x = 22 and x = 52, showing a very good degree of dispersion. Finally, for x = 77, the structure is almost reversed as compared to that for x = 0, with ARP dispersed as a big island in PRP. Therefore, it appears that the ideal situation is the intermediate one with partial hydrogenation of the unsaturated aliphatic double bonds. This is due to the presence of two counteracting effects: if on one side the hydrogenation seems to favor the compatibility with asphalt, on the other side, it favors the formation of crystalline regions (in the BE blocks) that reduces the polymer solubility. Indeed, the thermograms displayed a fusion peak, indicating that the saturation of the PB double bonds produced an elastomeric block with a certain degree of crystallinity. The presence of rigid crystalline blocks in the soft matrix of the copolymer certainly limits its swelling and solubility with any type of solvent. Nevertheless, it is interesting to observe that all blends, except the one with SBS, were stable after the tube test, even if differences were found between the morphologies and rheological properties of the top and bottom parts of the stored samples: the separation index was showed to have a minimum in correspondence to x = 52.

The authors also suggest an interpretation of the results in terms of solubility parameters that indicate a better compatibility of maltenes with SEBS than with SBS. Then, in a subsequent paper, the mixtures of two commercial four-branched, star-like SBSs and the corresponding partially hydrogenated SBEBS with maltenes were compared [72]. The maltenes were obtained through n-heptane extraction from a Mexican crude oil, and the blends contained 3% or 10% (w/w) polymer. From FM, it followed that in all cases (irrespective on the polymer type and percentage), the blends were clearly biphasic, and neither the MW nor the composition of the elastomeric middle block of the polymers had a definitive effect on the morphology. In these studies, the storage stability was not evaluated; however, the authors stated that the elastomeric block of the SEBS is more rigid and less compatible with the maltenes than the polybutadiene block of SBS is. This assumption is based on the HSP reported by Ovejero et al. [70]. Recently, the authors studied the morphology and rheological behavior of blends obtained after the modification of an asphalt with the same SBS and SBEBS [29]. Again, a direct measurement of the storage stability was not provided; however, the two polymers led to blends with similar morphologies. In contrast to what was found when using maltenes, the ARP in the blends with SBS here were smaller than in the blends with SBEBS, suggesting a higher degree of polymer swelling (and thus higher compatibility) after partial hydrogenation. It is therefore quite complicated to summarize the results from these three interesting papers, and once again, it is difficult to extrapolate them to a general rule. Nevertheless, we can conclude this section by recalling that in more than one paper, it has been reported that when using SEBS, storage-stable blends can be obtained if the SEBS content is maintained below approximately 4–5 wt% with respect to the total mass [74, 75].

3.4. Asphalt interaction with polyolefins

3.4.1. Asphalt/polyolefins compatibility

The second main category of polymers used for asphalt modification is that of “plastomers.” Of course, this term includes a huge variety of polymers, but in our case, the interest is mainly limited to polyolefinic homopolymers or saturated polyolefin-based copolymers, which should have the

double advantage of being less expensive and more stable than SBS and other unsaturated TPEs. Moreover, owing to their “commodity” origin, olefinic polymers are available with a wide range of characteristics and technical grades. For the same reason, polyethylene (PE) is also abundantly available as waste material, for which asphalt modification may represent an interesting way of recycling. Irrespective of the exact composition, the “plastic” character, instead of the “elastic” character, of this category of polymers make them completely different from the performance point of view; their main expected effects are related to an increase in rigidity and improved resistance to deformations under traffic load.

Obviously, PE and polypropylene (PP) are the two main representatives of the category, but owing to their nonpolar nature and usually high degree of crystallinity (except the case of atactic PP), they are almost completely immiscible with asphalt. For this reason, their main application is in asphaltic roofing membranes, where the high-shear mixing phase is followed by a rapid cooling that freezes the morphology, which remains kinetically stable during room-temperature storage. Nevertheless, extensive literature on olefinic PMAs for paving applications is available (see e.g., [76-93]), but storage stability is not often mentioned.

One of the papers that analyze the storage stability is one by Pérez-Lepe et al. [94] that has the overall objective of studying the separation process during high-temperature storage. Binders containing 1–5% polymer were stored at 180°C in the usual tubes, and after 24 h, a macroscopic phase separation was observed even at low polymer concentration. Then, in order to characterize the separation process better, samples of the modified binder containing 5% of polymer were frozen immediately after preparation, placed on crystal slides, and observed through optical microscopy after heating to different temperatures (above and under 123°C, which is the melting temperature of the used high-density poly(ethylene) (HDPE)). It was found that at 150°C, the modified binders exhibited coalescence-creaming and gross phase separation in less than 15 min, while at 100°C, the binders remained stable, even after long periods of time. In conclusion, even if the degree of inter-diffusion is very limited, at high polymer loadings, the PRP forms a network that may be stable in the presence of a highly liquid asphaltic phase. In contrast, if the temperature is increased beyond the melting temperature of the polymer, the “solid” network collapses, phase separation occurs in a very short time, and the binder would not guarantee the formation of a good paving material even if laid immediately after preparation.

Another interesting study is the one by Fawcett and McNally, who modified an asphalt by using several polyolefins and characterized the blends from the morphological and thermo-mechanical points of view [95, 96]. Even though the blends were prepared with very high polymer loading, which is appropriate for roofing membranes, and the problem of phase stability is not debated, the presented results help in understanding the degree of interactions that occur between asphalt and such polymers. The study encompasses 4 different PEs (including HDPE, linear low-density poly(ethylene) (LLDPE), and low density poly(ethylene) (LDPE)), an isotactic and an atactic PP, an ethylene-propylene copolymer with the propylene blocks grafted onto the main ethylene chain, an EP rubber with monomers in a random distribution along the polymer chain, and a predominately amorphous polyolefin specifically developed for asphalt modification. Thus, almost all possible polyolefins were considered, and they showed a common behavior, where the degree of crystallinity was probably the main parameter that differentiates the various polymers. In all cases, there was an inter-diffusion tendency that led to the formation of PRP and ARP, but both the lower compatibility and, when present, the crystallinity of the polymers strongly reduced the degree of swelling when compared to SB copolymers.

The low degree of interactions is confirmed also by the morphology of the blends, the modest lowering of the melting point of the crystallites, the extent of crystallinity, and the crystallite size. Low polymer loadings increased the temperature at which the blend started its viscous flow, while for sufficiently high polymer fractions, when the crystallites are sufficient to determine PI, the entire blend had a gel character and the flow started only when the crystallites melt. This observation also suggested an attempt to obtain blends with low-temperature flexibility and high-

temperature melting, which would be useful for roofing membranes [97]. The idea was to combine the effect of two polymers: a rubber for the low-temperature flexibility and a polyolefin able to crystallize and create a continuous gel network at high temperatures. Even when several combinations of polymers were tested, it was possible in only three cases to control the T_g with the rubber and high-temperature properties with the polyolefin; it is very difficult to generalize the observed behaviors.

Thus, summarizing the conclusions from these three papers, we can say that polyolefins showed very poor compatibility with asphalt owing to their composition and, in some cases, to their high degree of crystallinity. After hot mixing under a high shear rate, a certain degree of inter-diffusion can be observed, but very high polymer loadings are necessary to achieve PI, and phase separation may occur in a very short time. Therefore, the main application of unmodified polyolefins remains for roofing membranes stored at room temperature. At static hot storage or transportation to the paving site, it is nearly impossible to avoid phase separation. These appear to be general observations valid for almost all polyolefins, as confirmed by Jew et al. [98], who tested several grades of PE and found that despite the rather large differences in composition, MW, and crystallinity of the PE, the differences in viscosity of the mixes were relatively minor. Nevertheless, there are some publications that seem to be in partial disagreement with these conclusions. Punith and Veeraragavan [99] obtained storage-stable mixes by mixing up to 10% by weight of recycled LDPE in a shredded form of approximately 2×2 mm in size from carry bags collected from domestic waste. This surprising result can be related to the recycled nature of the material, where the in-service life and shredding operations are potentially able to alter the chemical composition and introduce functional groups and/or significantly reduce the MW. Unfortunately, those aspects are not considered in the paper, and to our knowledge, a similar degree of compatibility was not confirmed in any other publication available in the scientific literature. Recently, Fang et al. [100] found complete instability with a similar starting material.

3.4.2. The odd case of metallocene catalyzed polyolefins

In a couple of papers, metallocene-catalyzed polyolefins are indicated as particularly interesting. In the first one, blends prepared with metallocene-catalyzed atactic PP (m-aPP) are compared with blends in which conventional aPP is used [101]. The rheological characterization of the blends showed the reduction of the aPP glass transition, in addition to the disappearance of a broad relaxation visible in pure asphalt, indicating that the saturated liquid resins of the asphalt act as a plasticizer on PP. The same phenomena were not observed while using the conventional aPP. In the second paper, a similar comparison was conducted using metallocene-catalyzed LLDPEs (m-LLDPE) and “conventional” HDPEs (supposedly prepared through Ziegler-Natta catalysis) [102]. Table 1 lists some of the properties of the used PE, and it can be seen that appreciable differences between the conventional (HDPE1, HDPE2) and m-PE reside in the average MW, dispersion, and degree of short-chain branching (DSCB). The two conventional HDPEs have much higher average MWs; therefore, a lower compatibility with asphalt should be automatically expected for them. Nevertheless, other considerations can be made about these materials.

The morphology of the blends (Figure 9) immediately revealed a significant difference between the two types of PE; the m-LLDPE was able to give a better dispersion in the asphalt matrix as it consists of smaller droplets (5–10 μm in diameter).

The blends were subjected to the tube test, in which the top and bottom parts were compared using rheological measurement. The HDPE-based blends showed a marked phase separation even after 12 h of storage, while the m-LLDPE was stable after 48 h at 165°C .

As the solubility parameters of the five PE were nearly identical, the authors suggested an explanation for such differences in terms of the lower melt elasticity of m-LLDPEs, which facilitates the drop breakup during mixing. The starting idea comes from the modest tendency of swelling, which makes PE particles remain well separated from the asphaltic matrix and behave as active fillers interacting only with saturate resins that form a layer around them [103]. This allows

us to consider the blend as an “emulsion” (a term used quite often in the case of asphalt/polyolefins blends) with an important viscoelastic role in the breakup and coalescence of polymer drops. In other words, owing to the low compatibility with the asphalt components, the ARP and PRP remain well distinct during the entire mixing process; therefore, in this case, instead of a thermodynamic approach, a more fluid-dynamic approach is useful to explain the behavior and final morphology of the blends. From the parameters indicated by Lin et al. [104], it is concluded that an enhancement of the elasticity of the droplets provokes a decrease in the ratio of the breakup/coalescence, thereby making it more difficult for the droplets to breakup. As the m-LLDPEs were showed to have higher elasticity than HDPEs from the rheological measurement, they can also break. Even though a small PE content (1 %w) and quite drastic operating conditions (mixing at 180°C and 1,800 rpm for 6 h) were necessary, with m-LLDPE, it was possible to obtain droplets below the critical value indicated by Sabbagh and Lesser [105], giving rise to stable dispersions. Since the authors did not observe differences between the three m-LLDPEs, they argued that the average MW did not significantly affect the particle elasticity and thus attributed the higher elasticity to their narrow MW distribution. A couple of considerations are necessary here. The first one is that this paper showed that with the appropriate choice of PE and under certain conditions, stable mixes may be obtained, but at the same time, it confirms the very low compatibility because the stability is obtained only with very low amounts of PE (a phase separation was detected in 3% m-LLDPE blends after a storage time of 24 h at 165°C). Second, the statement that the average MW does not significantly influence the dispersion is quite surprising. This is in contrast with the observations by Yousefi [106], who compared 11 polyethylenes with melt flow indices (MFI) ranging from 0.15 to 20 g/10 min (190°C/2.16 kg) and claimed that a decrease in MFI increased the instability. Nevertheless, in that case as well, none of the tested PEs gave a PMA with good storage stability.

3.4.2. Phase separation in asphalt/polyolefin blends

With regard to the mechanism of phase separation, a specific study by Hesp and Woodhams [107] evaluated the evolution of the particle size distribution as a function of time and position in the tube during the high-temperature storage test. PMAs were prepared, poured into test tubes, and subsequently incubated in an oil bath at 110°C for 15 min, 1 h, 5 h, 24 h, and 48 h. After high-temperature incubation, the tubes were cut at different heights of 2, 6, and 10 cm to recover the asphalt samples, which were dissolved in toluene at room temperature. In this manner, the PE particles remained in a solid state and were recovered by filtering the toluene dispersion. The PE particles were then observed using scanning electron microscopy (SEM). The obtained data were compared with the theoretical behavior expected from the possible breakdown mechanism of emulsions. As an example, Figure 10 shows the evolution of the particle size distribution with time for a specific position in the tube. The shift toward larger particle diameters during the first 24 h of storage suggests the occurrence of coalescence phenomena. During this phase, the polymer particles come into contact via diffusion (either Brownian or a combination of Brownian and gravity-induced). Then, after 24 h, in the final stage of the separation process, the few and large residual polymer particles become susceptible to creaming, where the density difference between the polymer and asphalt drives the polymer particles to the surface. This observation drove the same research group to the development of a “steric stabilizer” [108] to modify the interface between the asphalt matrix and particles and to stabilize the particles against the coalescence induced by the Brownian motion. Thus, the simple idea is the use of a block or graft copolymer, which should be located at the asphalt/polymer interface and provide an energy barrier that increases the stability of the system to an acceptable level. It is worth remembering that this approach cannot be adopted for block PS copolymers, because in that case, no well-defined asphalt/polymer interface exists. In a first attempt, four commercially available copolymers were studied: a di-block SEB copolymer, two chlorinated PE and a poly(ethylene-g-(poly-(hydroxystearic acid))) copolymer. Then, as none of these gave positive results, the research shifted to asphalt-soluble compounds that can be located at the interface between the asphalt and polymer.

However, as conventional high-MW steric stabilizers were not sufficiently soluble to form an effective steric barrier, the so called “in situ” steric stabilization was used. A low-MW precursor was directly bonded with both asphalt and polymer. This was obtained from a low-MW PB. The reaction with asphalt was promoted by the use of sulfur, while the reaction with PE occurred through an amine anhydride condensation reaction with the use of a small fraction of amine terminated butadiene precursor and a small amount of added PE functionalized with succinic anhydride groups.

The procedure was further investigated in [109], in which the same authors suggested the use of devulcanized rubber tire as a replacement for the virgin polybutadiene precursor to reduce the cost of the technology. The whole procedure of steric stabilization is also the subject of an international patent invented by Hesp et al. [110]. One year later, the same approach was used to stabilize the asphalt/PE emulsion and examine the mechanical behavior, morphology, and stability of the emulsions [105]. The unstabilized particles were found to have a different shape (defined as teardrop shape) from that of the stabilized ones, which appeared more spherical. Moreover, in addition to the spherical particles, a fibrous morphology was observed in the stabilized emulsions. For unstabilized PE emulsions, the authors suggested the existence of a critical particle radius (approximately 4 μm at 110°C) at which the dominant mechanism for phase separation shifts from coalescence to creaming. Both coalescence and creaming were observed to be hindered by the stabilizer.

3.5. Asphalt interaction with EVA and other ethylene-based plastomers

A simple way to use plastomers while maintaining the main advantages of olefinic polymers without penalizing the storage stability too much is the use of olefinic copolymers, where the comonomer contains polar functional groups able to improve the interactions with asphalt. This led to the use of the EVA [90, 111-119] copolymer, which is probably the second in order of importance after SBS for asphalt modification. Similarly to EVA, other plastomers derived from copolymerization of a functionalized vinyl monomer with ethylene have been suggested and studied, including the entire class of acrylic polymers such as polyethyl acrylate (PEA), polymethyl acrylate, polybutyl acrylate (PBA), poly(ethylene-co-butyl-acrylate) (EBA), poly(ethylene-co-acrylic acid) (EAA), poly(ethylene-co-methyl acrylate) (EMA), and poly(methyl methacrylate) [25, 30, 91, 114, 120, 121].

EVA has ester functional groups and is available in a huge variety of commercial grades, which allows for choosing among a wide range of acetate contents (and thus degree of polarity and crystallinity) and MW. This important versatility is accompanied by a competitive-cost, which positions EVA between pure polyolefins and SB copolymers.

The polar groups may associate with themselves or with asphaltenes so that the polymers may supplement or compete with the resins as dispersants for the asphaltenes in the aromatic and aliphatic medium or, alternatively, directly bind to the asphaltenes [114].

Another important issue is the presence of crystallites derived from short ethylene sequences in the backbone, which may act as the rigid PS domains in block elastomers and create a gel network within the amorphous aromatic matrix. A DSC characterization performed by Fawcett and McNally [114] for asphalt/EAA blends showed that the interactions involving the polar groups (the amorphous part of the polymer) do not reduce the tendency of the polymer to crystallize, but rather the polymer crystallized more easily with greater dilution in the asphalt matrix. The main effect on the asphalt on crystallization was the formation of smaller crystalline regions of the copolymer (compared to pure copolymer), as testified by a broadening and lowering of the maximum in the DSC peak of the melting transition. This effect is even more marked in blends with 10% of an EVA (9% by weight of VA) for which a greater fraction of the polymer apparently crystallized from the asphalt blends than from the pure polymer itself. Again, the crystalline regions are smaller and the melting peak appears broadened and shifted to lower temperatures with respect to pure polymer. A possible interpretation is that both the olefinic segments of the polymer backbone and the saturated

components of asphalt had to contribute to the observed melting. Going to a higher VA content (29% by weight), the crystalline fraction appeared barely detectable. However, as both EVAs raised the modulus of the blends at high temperatures, this was interpreted as due to the formation of the above-mentioned network (which, of course, failed when the crystallite crosslinks melted) for the 9% VA polymer or due to the polar groups bonding to the asphaltenes for the 29% VA polymer. However, the presence of the ester or similar groups does not solve the compatibility problem by itself, and from this point of view, EVA may be seen as an intermediate between polyolefins and SB copolymers. EVA is a semicrystalline polymer, the structure of which after swelling is reminiscent of swelled SB copolymers; the rigid domains in this case are constituted by small ethylene-rich crystalline domains. The domains are interconnected by ethylene-co-vinyl acetate chains, the polarity of which may allow a reasonable degree of polymer swelling [122], but the degree of polymer/asphalt interaction remains quite limited. This was clearly shown by Airey [123], who made an extensive rheological evaluation of PMA obtained with several different EVAs and concluded that *“filler type modification is evident at low temperatures, temperatures above the melting temperature of the semi-crystalline EVA copolymer and for those modified binders that do not exhibit a dominant polymer network.”* Consequently, the typical morphology of PMAs obtained with EVA is markedly biphasic, as shown by many researchers. As an example, in the already cited work by Mouillet et al. [46], a PMA obtained through modification with 6% EVA is described as biphasic, with bitumen nodules dispersed in the polymeric phase. Moreover, based on FTIR, the heterogeneity was somehow quantified by calculating that the polymer content varied by more than nine times between ARP and PRP, and the procedure of spectral subtraction showed that the chemical species responsible for the EVA swelling are more aromatic and substituted by linear chains in a little more cases than for SBS-modified asphalt.

A quite extensive list of FM images of PMAs prepared using two different base asphalts, two different EVA copolymers (containing 14 and 28 % by weight of VA respectively), and 4% or 6 % by weight of polymer can be found in Giuliani et al. [25]. Depending on the cases, the dispersed phase may be either PRP or ARP, and the dimensions and shapes of the two phases may strongly depend on the considered blend. However, in all cases, the markedly biphasic aspect is clearly visible and far from the homogeneous or orange-skin morphology. This is the prelude to a “not stable” nature of the mixes, and as a general consideration, it may be expected that a high VA content would be beneficial for compatibility as it should have the double advantage of entailing higher polarity and lower crystallinity. However, it has already been underlined that generalizations are not possible owing to the presence of many co-interacting factors. Indeed, diverse and somehow contradictorily results can be found in the literature. As an example, Bulatovic et al. [124] reported that mixtures prepared using a 70/100 penetration grade BA and an EVA with 28 wt% vinyl acetate and a melt index of 6 showed a ΔS increasing with the polymer content and were stable up to 6% by weight polymer, but were unstable for higher polymer contents. The FM image of the 4% blend indicates a homogeneous structure in which PI has already occurred, while, oddly, at 5% EVA content, a biphasic structure appears.

García-Morales et al. [117] used an EVA/LDPE = 2/1 waste-polymer mix with an overall VA content of 5% with respect to the total polymer. This modest content of polar groups led to the production of unstable blends for which the entire phase separation process occurred within the first 24 h of storage at 163°C.

Panda and Mazumdar [125] obtained stable mixtures by using up to 10% of two EVAs containing 18% and 28% by weight of VA. Results presented are consistent with the idea of a high VA content being helpful for asphalt/polymer interactions, but other available data indicate that this is not necessarily the unique and leading parameter to be considered. Giuliani et al. [25] mixed two EVA polymers with 14% and 28% VA contents with two different base asphalts of different SARA compositions and found that for one BA, the most compatible EVA was that with the lower VA content, while for the second BA, the EVA with the higher VA content was most compatible. Moreover, Hussein et al. [126] compared the effects of two LDPEs and two EVAs, the

characteristics of which are listed in Table 2. Basically, the two LDPEs (LDPE1 and LDPE2) had different MWs, while the two EVAs (EVA1 and EVA2) had MWs similar to that of LDPE2 and VAs content of 19 and 27.5 wt%, respectively.

The storage stability was evaluated in terms of percent differences between the top and bottom values of $|G^*|$, and from this point of view, the better polymer was LDPE2 (which has the higher MW and is completely apolar), while the worst one was EVA2 (which has an MW much lower than that of LDPE2 and is the most polar polymer among those tested). A tentative explanation given by the authors for this surprising result correlates the compatibility with the “rigidity” of the backbones, which was much higher for the VA containing arms.

Gonzalez et al. [127] prepared 1% and 3% blends by using fresh and recycled EVA contents of 6% and 5%, respectively. Rheological measurements were performed after storage at 165°C prolonged until a maximum of 4 days, which showed that phase separation occurred in the blends with the higher polymer proportion in less than 24 h, while the 1% blends were stable until the fourth day. The FM images of the top and bottom fractions clearly showed, for the 3% blends, the accumulation of polymer in the top part of the sample. In contrast, for the stable samples, there was no migration of the polymer, and the top and bottom samples are nearly identical. Nevertheless, a comparison of such samples with the freshly prepared mix shows that polymer coalescence occurred (Figure 11); therefore, a sort of horizontal instead of vertical separation occurs.

In conclusion, the use of EVA does not eliminate the problem of storage stability, but rather represents a valid improvement with respect to pure polyolefins. The availability of several commercial grades allowed for good tunability of EVA properties and thus the stability of the modified asphalt. Of course, in the case of EVA, there are some possibilities to increase the compatibility further, such as the use of a commercial MAH grafted EVA, as suggested by Luo and Chen [128].

With regard to acrylates, the paper by Iqbal et al. [121] evaluated the storage stability of PMAs prepared using an EBA containing 27% by weight of butyl acrylate. Samples containing 4% by weight of polymer were tested after zero and 72 h of continuous mixing at 160°C and 500 rpm. The complex moduli at 76°C and 10 rad/s of the top and bottom sections were compared, and the percentage differences were found to be equal to 16.06%, which indicates the presence of phase separation within an “acceptable” limit of 20%.

A final consideration regarding polymers containing the ester group is that such functionality is potentially able to undergo a trans-esterification reaction, which, depending on the operating conditions, may lead to crosslinking and, in the worst case, gelation.

3.6 Asphalt interaction with reactive polymers (RET) and acids

3.6.1. Asphalt modification with RET

From all the above-mentioned studies, it clearly appears that, in the case of polyolefins, the chemical compositions of polymer and asphalt are too complicated for simple mixing, and compatibilization is effective only by creating a covalent linkage. This directly leads to the use of functionalized polyolefins, which can react with asphalt. Good examples of such polymers are the so-called reactive ethylene terpolymers (RET), which are ethylene-based but contain an ester group (usually methyl, ethyl, or butyl acrylate), and glycidylmethacrylate (GMA), which justifies the use of “reactive” in “reactive polymers.”

RETs have been developed as compatibilizers for blends of polyolefin and other polymers containing a functional group able to react with the ossiranic ring. This should obviously include asphalts, which may have, for example, carboxylic, hydroxyl, and amine groups. Thus, compared to PE, RETs have two potential advantages. The first one is an increased polarity due to the acrylic functionalization, while the second one is the reactivity. In contrast, two main disadvantages may also be easily described: 1) the higher cost; 2) the risk of gelation due to the rather high number of GMA groups on a single RET macromolecule, coupled with the presence of poly-functional

asphaltene aggregates or molecules. Therefore, to avoid this risk, the amount of RET that can be used for asphalt modification has a very small upper limit, which is around 2–2.5% but may be even lower than 1% by weight [129].

Recently, Bulatović et al. [130] reported the evaluation of storage stability for two base asphalts modified using two poly(ethylene-butylacrylate-glycidylmethacrylate) substances: Elvaloy® AM (butylacrylate 28 wt%, glycidylmethacrylate 5.3 wt%) and Elvaloy® 4170 (butylacrylate 20 wt%, glycidylmethacrylate 9 wt%). The contents of reactive polymers Elvaloy AM and Elvaloy 4170 were 1.6 and 1.9 wt%, respectively (these were the maximum possible values without inducing gelation phenomena), and all the samples were homogeneous after high-temperature storage, showing no difference in the softening-point value between the top and bottom of the tube. Thus, the use of RET basically guarantees storage stability, even though Pérez-Lepe et al. [131] showed that a certain degree of instability may appear under severe conditions of temperature and time of storage. Nonetheless, the risk of gelation and the resulting use of small polymer quantities implies that RETs are not ideal to be used alone as an asphalt modifier, because the overall effect on the performances can be quite poor [94, 129, 132]. Unfortunately, the efficacy of RET as compatibilizers between asphalt and polyolefins does not seem to have been investigated yet.

The use of glycidyl functionalities may also be obtained after the direct functionalization of the polyolefin, thus having the potential advantage of a lower content of epoxy rings with a reduced risk of gelation. Li et al. [133] compared the use of an LDPE before and after grafting with GMA. Unfortunately, the grafting procedure and final GMA content of the functionalized polymer are not described; however, both the blend morphologies (Figure 12) and the ΔS measured after the storage-stability test (Table 3) indicate a high efficacy of the GMA groups in stabilizing the mixes. Analogously, maleation may improve the compatibility, as shown for PP by Yeh et al. [134], who did not evaluate the storage stability but demonstrated through DSC an improvement in the asphalt/polymer interactions relative to unfunctionalized PP.

In summary, we can state that a limited amount of chemical reactions between the polymer and the asphalt, possibly with asphaltenes, is beneficial because it plays the double role of consolidating the polymeric network and stabilizing the asphalt/polymer blend. Among the proposed methods, the use of sulfur, carboxylic acids, and epoxy functionalities are certainly the most reasonable ones for industrial practice; however, all of them are somehow limited by the increase in costs, risk of gelation, and safety considerations (e.g., the generation of hydrogen sulfide in the case of sulfur [135]).

For the sake of completeness, some other reactions that have been proposed or patented as suitable for PMAs can be mentioned. Kawakami and Ando [136] suggested the use of a polyoxyalkylene polymer having one or more reactive silicon groups capable of crosslinking by forming siloxane bonds through the silanol condensation reaction. Turmel and Dony [137] proposed the use of a modifying polymer (similar to EMA) containing grafted moieties with terminal unsaturation, allowing both classical vulcanization with sulfur and converting part of the ester groups to, for example, acyl chloride groups that then reacted with allylamine.

Even if not directly correlated to the storage stability, in the list of reactive polymers, a rapid mention can be dedicated to epoxy and poly-urethanic asphalts. Epoxy asphalt [138-143] is an asphalt binder (either polymer modified or not) containing the components of a thermoset epoxy resin that do not complete the chemical crosslinking during the phase of mixing. Therefore, the mix can be applied and compacted with conventional equipment and is quickly ready for traffic in its partially cured state. Then, the crosslinking reaction slowly continues at ambient temperature, and the binder develops full strength over two to four weeks. These binders were first developed by Shell Oil Company in the late 1950s as jet-fuel-resistant pavement for airfield applications. In 1967, an epoxy binder was used to pave the San Mateo–Hayward bridge across San Francisco Bay, and it represents an interesting solution for special applications such as flexible decks, extreme climates, and very heavily loaded trucks. Thus, in their cured state, epoxy asphalts are composed of a chemically crosslinked network that entraps the entire binder and guarantees many advantages from

practical and application viewpoints. As the network develops slowly, it does not represent a solution for phase separation, which may occur as in all other binders. However, it is obvious that this type of binders may not be subjected to long-term high-temperature storage; therefore, the phase-separation problem is basically limited to the transportation to the paving site.

A quite similar philosophy that is not yet commercial is the idea of a poly-urethanic network, which was suggested by a research group of the University of Huelva and obtained by modifying the asphalt with low-MW isocyanate-functionalized polymers, with polyethylene glycol and di-isocyanate [144-149], or with thiourea [150]. Again, there is a “short-term” modification, which corresponds to the mixing of asphalt and polymer; the network is not yet formed, and owing to the low MW, the modifier has little influence on the binder properties. Then, the network develops during the “long-term” modification, which is a long period of curing (up to several months) at room temperature. Alternatively, the reaction can be expedited by adding water to the system, which rapidly leads to the formation of a polyurethane/urea network, which, owing to the development of gaseous carbon anhydride, may foam the binder [147].

Similarly, Singh et al. [151] prepared a binder made through the addition of polyethylene glycol to an asphalt previously treated with 4,4-diphenyl methane di-isocyanate and then modified with SBS. The chemical and thus irreversible nature of the network suggests the restricted use of such a procedure to waterproofing/sealing purposes. Finally, Sing et al. suggested peroxidation using H_2O_2 to activate poly(vinyl chloride) particles and promote their adhesion to asphalt [152].

3.6.2. Asphalt modification with polyphosphoric acid (PPA)

Modification with acids consistently alters the physico-mechanical properties of asphalts, and its effects are somehow comparable to those obtained with air-blowing [2]. Since the process is quite complicated, it initially did not garner industrial attention, mainly because of corrosion problems and the generation of dangerous by-products. However, it recently became less expensive and attracted renewed attention. At the moment, PPA is by far the most important acid introduced in asphalt technology. PPA was used in 3.5% to 14% of the asphalt placed in the United States between 2005 and 2010 [153].

PPA is an oligomer of H_3PO_4 , which may have more than 10 repeating units (the length of the chain mainly depends on the production method) [154], and is used to modify asphalt either alone or in combination with a polymer.

Even though it is commonly recognized that PPA reacts with asphalt, the exact nature of the reaction is not completely understood. An NMR study indicated a tendency of PPA to revert to orthophosphoric acid after mixing with asphalt [155]; therefore, the main effect is not dissimilar to that of other acids. It has been suggested that PPA acts through the neutralization of polar interactions between the stacked asphaltene molecules, either through the protonation of basic sites or through esterification. However, many other reactions have been proposed, such as co-polymerization or alkyl aromatization of saturates, crosslinking of neighboring asphalt segments, formation of ionic clusters, cyclisation of alkylaromatics, generic reaction with asphaltenes, phosphorylation, and, of course, any combination of these. A more detailed description of such effects can be found in [2, 154, 156] and in the cited literature thereof.

Irrespective of the mechanism, the overall effect is to alter the solvation of the asphaltenes, thereby increasing the solid fraction and, hence, the viscosity and the gel character of the asphalt. The impact on the thermal and rheological properties of asphalts was described by Thomas and Turner [157], while Orange et al. [158] showed that PPA increases the high-temperature performance grade without significantly affecting the low-temperature performance grade. Moreover, they showed that PPA can be used as a partial substitute of the polymer to obtain the same performance grade at a lower polymer content. The literature describing the effect of PPA modification on asphalt and PMA performances, ageing, etc. is relatively abundant [159-172].

Regardless of the reaction mechanism and the effect on asphalt properties, which are widely described in the scientific literature, our interest in PPA and other acids lies in the fact that they

have been thought to improve the storage stability of PMA. Probably the first group to report this effect was Giavarini et al. [173], who used three ethylene-propylene copolymers of different MWs to modify four different straight-run asphalts and in all cases found a strong reduction in ΔS if at least 3 wt% of PPA was added. The same effect of improvement of storage stability was also the subject of patents. For example, in 1991, Moran [174] observed that the storage stability can be improved by adding the polymer to an asphalt that has previously been reacted with an inorganic acid. Sulfonation of the asphalt-polymer blend [175, 176] and the use of diterpenes containing carboxylic acid groups are the other two examples of suggested solutions [177, 178]. Nevertheless, the scientific literature that directly investigates this aspect of acid modification is scarce and insufficient to clarify the role and efficacy of the acid. As an example, recently, Zhang and Hu [179] found that the addition of 0.5 wt% of PPA to a 3.5 wt% SBS-modified asphalt slightly reduced the ΔS from 60°C to 50°C, remaining at values far away from the storage stability, which was obtained with further addition of sulfur.

4. Inside PMAs

4.1. Morphology and composition of the polymer-rich phase

In previous sections, the primary mechanisms of asphalt/polymer interaction were described separately for the main classes of polymers currently used in asphalt technology. Several basic mechanisms of asphalt modification were presented and discussed in the light of more diffused models and theories. The species mainly involved in asphalt/polymer interaction were identified, and the migration of asphalt molecules and polymer swelling were described based on several experimental findings. Nonetheless, in most cases, the picture emerging from the literature review underlines difficulties that are still present and unfailingly arise when asphalt technologists attempt to predict asphalt/polymer compatibility. This section is mainly dedicated to PRP and how polymer swelling influences the overall morphology.

4.1.1. The honeycomb structures

An interesting confirmation and insight into polymer swelling caused by asphalt components came from the group of J. P. Planche. In an early work, [46] infrared microscopy was used to investigate the aging of PMAs. The technique allowed for the separate characterization of PRP and ARP, which enabled the determination of the polymer content in the two phases as well as the distribution of asphalt components (by subtracting the polymer spectrum from the PMA spectrum) to identify the species involved in the polymer swelling. The investigation was conducted on binders prepared using a linear SBS, an EVA, and two SB copolymers slightly crosslinked by sulfur. As an example, Figure 13 shows the analysis of a $250 \times 300 \mu\text{m}$ surface of a 6% by weight SBS-modified asphalt, in which the infrared spectrum is directly converted into a mapping of the polymer content. Even if not observable with an optical microscope, the polymer content was equal to 0.3% in ARP, which is not a negligible quantity. In contrast, the polymer content was 12.2% in PRP, which is nearly double the value of the nominal polymer content (thus suggesting that PRP and ARP are almost equivalent in terms of volumetric extension inside the blend). A comparison of the original asphalt composition with that of asphalt in PRP and ARP confirmed that the species responsible for SBS swelling appear as aromatic, slightly condensed, and substituted by linear chains. In addition, the rate of highly condensed aromatic molecules was found to be higher in ARP than in PRP, confirming that the asphaltenic fraction is not compatible with the polymer.

In a second paper, the structure of the physically and chemically crosslinked asphalt/SBS blends was observed using high-resolution field emission gun (FEG) scanning electron microscopy instruments, coupled with low-contamination, high-vacuum cryo-preparation equipment, which allowed the extension of FTIR and FM studies to a sub-micrometer scale [180]. This technique overcomes the disadvantages of conventional ambient-temperature scanning electron microscopy,

which causes the volatilization of the lighter asphalt components during the observation of the specimens owing to their exposure to an electron beam under vacuum. Images of 1) a base asphalt, 2) its physical blend with 5% of a styrene-butadiene (SB) di-block copolymer, and 3) a chemical blend consisting of the previous physical blend after reaction with sulfur were presented. While the chemical blend showed a smooth, homogeneous, and featureless fracture surface, the physical blend showed polymer-rich domains with diameters between a few microns and tens of microns and with macrostructures greatly varying with the size. The largest domains had a complex honeycomb structure, which resembles that observed using FM, with walls composed of tiny nanoparticles of polymer only tens of nanometers in diameter. These particles are supposed to be polystyrene domains because of their poorer solubility in asphalt compared to that in polybutadiene. In contrast, the smallest domains had a much more condensed internal structure. In addition, single nanoparticles were dispersed throughout the asphalt matrix.

4.1.2. Surface morphology: AFM (the bees) and SEM

One of the first accurate studies of asphalt and PMA morphology using microscopic techniques is probably the one by Loeber et al. [181], who combined AFM, SEM, and FM. As the authors stated, one of the main advantages of AFM is that samples do not need a “pre-preparation”; therefore, the real morphology is observed directly without risks of alteration due to cooling, heating, stretching, use of solvents, and so on, which inevitably alter the original colloidal structure of asphalt. Moreover, the technique does not rely on optical transparency, as it does for optical microscopy, and the resolution is not limited by the wavelength of light. Indeed, the three techniques required different preparations of the samples. The procedures chosen by Loeber et al. for the three microscopy techniques were as follows. A hot liquid drop was placed on a steel support for AFM observations (at 140°C for pure asphalt and 180°C for PMAs) or on a thin slide for FM, while it was necessary to remove the nonconducting oily maltenic phase before performing SEM analysis. Therefore, in that case, the asphalt was spread in a thin film onto a Whatman filter paper, and then the oil phase was leaked out through solvent extraction in the hope that the paper can act as a support protecting the asphalt structure. This represents the main problem of SEM, which requires the removal of maltenes, thus limiting the observation to asphaltenes, the isolation of which intrinsically alters the original colloidal structure. The importance and criticism of sample preparation for SEM analysis was already known and described in 1977 by Donnet et al. [182], who reported images of a sol and a gel asphalt and compared three different techniques of asphaltene isolation. The first one was a simple recovering of asphaltenes through precipitation in n-heptane from a benzene solution. The second one was a relatively complex procedure called transfer-replica that was ideated to preserve the real morphology (the asphalt sample was spread over a mica plate, then covered with a carbon film of approximately 10-nm thickness, and subsequently dipped in toluene until partial dissolution of the asphalt). The third one was ultramicrotomy, in which sheets are prepared and then treated with heptane.

The evaluation of a suitable sample preparation procedure for SEM observation was also the subject of a more recent paper by Stulirova and Pospisil [183], who compared several techniques of maltene removal in which the dissolution in n-heptane was always the first step of the procedure. An alternative to the prior removal of maltenes is the use of OsO₄ staining and electron-beam etching in environmental scanning electron microscopy (ESEM). These techniques were applied by Shin et al. [184], who showed a “highly entangled three-dimensional network structure” in samples exposed to an electron beam. As this network was observed in both unmodified and SEBS-modified asphalts, the authors exclude a polymeric nature and suppose that the electron beam volatilizes the oils, leaving only asphaltenes. This is consistent with the observations that the structure is stable even during prolonged exposure to the beam, while it disappears after annealing at 50°C (diffusion of oils to the surface) and re-appears under exposure to a new beam. Curiously, under a uniform tensile stress, the “chains” elongated without losing their structure. Staining with OsO₄ was used also by Puente-Lee et al. [185], who compared images of a 12% SBS PMA obtained with FM

(Figure 14a) and SEM (Figure 14b). In this case, there is no trace of the network structure, and the two techniques resulted in very similar images with higher resolution obtained using SEM. For completeness, we mention a recent paper by Wei et al. [186], who used SEM to characterize a rubber asphalt but did not show high-magnification images or describe the preparation of the sample prior to observation. Nevertheless, SEM is not ideal to observe asphalt samples, and in the last few years, there has been a considerable increase in papers that use AFM for both morphological and mechanical characterization. It is well known that with AFM, observations can be made in the height mode (which gives information on the topography of the sample) or in the force mode (which records force variations on the sample surface and may “see” interacting forces between different phases). The two modes were compared, for a base asphalt, in the above-mentioned pioneering work by Loeber et al. [181]. The height mode showed a network structure, almost identical to that obtained using SEM, that is formed by spherical particles with diameters of approximately 100 nm and interpreted as asphaltenes. The force mode showed domains with alternate dark and light lines described as “bees” because they resemble the stripes of a bumble bee and are composed of a series of aligned protrusions (hills) and depressions (valleys). The authors also reported images of a PMA prepared with the same base asphalt through the addition of an unspecified polymer, where the bees are absent. The absence of the bumble-bee structure was interpreted as due to a “rearrangement” of the original colloidal structure. Curiously, after this paper, which was the first to use AFM for asphalt imaging and included PMA, a large number of studies used the same technique, but almost all of them were dedicated to unmodified asphalts. In particular, the bumble-bee structure attracted the attention of many researchers, and their nature has been the subject of an interesting debate, which merits a short mention as it belongs to the never-ending questions on the asphalt structure. Since the bee structures were observed especially in gel-type asphalts, the same authors suggested in a later work that the composition of these structures is directly related to asphaltene colloidal particles and/or the gel nature of the asphalt [187]. The asphaltenic nature of the bee-like structures was also supported by Jäger et al. [188], who observed their disappearance after the precipitation of asphaltenes through the addition of n-heptane; their results are consistent with the images reported by Wu et al. [189], who showed that for a base asphalt, such structures increase in size after artificial ageing. Moreover, in the case of an SBS-modified asphalt, the bee-like micelles became visible only after ageing, and the authors supposed this was due to the disappearance of the network structure that hid the asphaltene micelles (Figure 15).

Probably, the first doubt about the composition of the bee phase came with the work by Masson et al. [190], who analyzed 13 asphalts and described four different phases named as follows: 1) catanaphase (bee-shaped); 2) periphase (around catanaphase); 3) paraphase (solvent regions); 4) salphase (highphase contrast spots). The authors stated that “*no correlation was found between the AFM morphology and the composition based on asphaltenes, polar aromatics, naphthene aromatics and saturates.*” Nevertheless, “*a high correlation was found between the area of the ‘bee-like’ structures and the vanadium and nickel content in asphalt.*” One year later, the same authors described the first use of cryogenic AFM and phase-detection microscopy to characterize asphalt nano- and microstructures and still associate the bee structures with asphaltenes [191]. Then, a few years later, Pauli et al. noticed the disappearance of the bee structures as a consequence of repetitive scanning over the same area, which might have heated and thus softened the sample [192]. This can be due to asphaltene aggregation, which might be involved in the observed structuring, but an alternative interpretation is suggested based on solidification/crystallization phenomena. This possibility was strongly supported by a couple of previously published papers, which showed that the bee structures change in correspondence with the melting temperature of asphalt waxes [193, 194]. In order to elucidate this aspect, Pauli et al. collected a huge number of AFM imaging of asphalt samples, taking into account thermal conditioning, hysteresis effects, and the thickness of the sample and also observing isolated SARA fractions as well as wax-doped asphalts [192]. In this paper, it was shown that the bee structures were present in asphaltene-free fractions. Therefore, they

concluded that i) the interaction between crystallizing paraffin waxes and the remaining nonwax asphalt components is responsible for much of the micro-structuring, including the bumble bee structures; ii) the structuring occurs in the nonpolar oil fraction, which contains most of the wax-type materials; and iii) the surface structuring depends on the wax type, wax concentration, and crystallizing conditions, as well as on the asphalt source. As it was well summarized by Das et al. [195], “*even though different research groups concluded significantly different reasons for the structures to appear and disappear, the extensive AFM studies have proved that asphalt has the tendency to phase separate under certain kinetic conditions and is highly dependent on the temperature history.*” This is why they coupled AFM and DSC studies and observed a direct correlation between the change of microstructures and the DSC results: the bees always appear during wax crystallization and disappear as the wax melt. Moreover, only the asphalt with wax contents sufficiently high to be detected with DSC showed the bees, while the nonwaxy asphalt resulted in a flat AFM image until synthetic waxes were added to it. These evidences have been also confirmed in other papers by Soenen et al. [196] and Fisher et al. [197] as well as in a very recent paper by Allen et al. [198]. In the latter, the SARA fractions were separated and used to produce doped asphalts, and it was observed that only saturates had a consistent impact on the structuring; when saturates were maximized, the bee structuring was high, while low saturate contents corresponded to a low bee structuring. In contrast, almost every combination (high and low percentages) of the nonsaturate fractions resulted in similar bee structuring. Therefore, wax-induced or saturate-induced structure formation is perhaps the best conclusion, even though Das et al. [195] underlined that the percentage of bee phases does not exactly correlate to the wax content of asphalt; therefore, the possibility of a complex structuring involving other asphalt components remains open. We can thus conclude that a cautious approach is necessary to avoid bee stings so that the expression “wax-induced phase separation” remains the most recommended one when referring to such structures.

Coming back to the work by Masson et al. [190], it should be remembered that it followed a paper by Jäger et al. [188], which suggested an alternative identification of four phases observed with AFM, two of which constitute the bees: 1) the hard-bee phase, presumably containing high polar molecules; 2) the soft-bee phase; 3) a hard-matrix phase surrounding the bees and supposed to result from the arrangement of the same molecules constituting the bees; 4) a soft-matrix phase. Finally, it is worth mentioning that AFM has also been used to investigate mechanical properties such as the relaxation modulus [199], local stiffness and elastic recovery [200], adhesion [201], elasticity/Young’s modulus, stickiness/adhesion, hardness and energy loss [202], interfacial interaction between asphaltic binders and mineral surfaces [203], as well as the morphology of wax-modified asphalts [204], aging [205, 206], healing properties [207], structure of thin binder films [208], and asphalts modified with nanoclays [209, 210].

4.1.3. The polymeric network

Two very interesting studies and by far a better demonstration of the network structure formed by the polymer came from the research group headed by Macosko [58, 211]. The interactions of asphalt with SBS and SEBS were studied by monitoring changes in blend microstructures and the morphology observed using transmission electron microscopy (TEM) [211]. In contrast to almost all other papers, which simulate the polymer concentrations usually adopted in the paving industry, the entire compositional range of the binary asphalt/SBS blend was investigated, starting from neat SBS, which is gradually diluted with asphalt, until a maximum of 96% by weight. When the asphalt content was between 10% and 90%, the PRP constituted the continuous matrix and was classified as a macro-network, while at 92%–96% PRP was the dispersed phase. Based on the TEM images, inside PRP, a micro-network of asphalt-swollen PB midblock with PS microdomains acting as physical crosslink was observable. At low asphalt concentration, the shape of the PS microdomains

transformed from short cylinders to lamellae and hexagonally perforated lamellae, indicating that the PS segments were slightly swollen by some asphalt component. At high asphalt concentration (40–94%), the shape of the PS microdomains changed from lamellae to short cylinders and finally to spheres. This indicated stronger swelling of the PB segment by the PB-compatible component(s) of asphalt. This was also confirmed by the shifts of the T_g of PB blocks, which increased with asphalt concentration, while those of the PS blocks remained nearly constant.

In a subsequent paper [58], a similar approach was followed by using SEBS as a block copolymer, while the asphalt was divided into asphaltenes and maltenes by using n-heptane. As expected, asphaltenes were immiscible with both blocks of SEBS, while the maltenic fraction was miscible. The latter gave an interesting sequence of morphological transformations of the domains, which passed from a hexagonal cylinder through perforated layers to lamellae and then back to the original hexagonal cylinder, depending on the maltene content (Figure 16). This sequence reflects a limited solubility for both S and EB domains, and similarly to what was observed for SBS, at low concentrations, maltene is a preferential additive for S domains, while at higher concentrations, it preferentially swells the EB-rich microdomains. Images taken with the use of TEM are reported also in [212].

A different approach was followed by Fawcett and McNally, who produced a series of papers in which the effect of several copolymers was evaluated by gradually increasing their content in the blends or through their partial substitution with similar copolymers or with the related homopolymers [59, 60, 95, 114, 213]. In the paper dedicated to SBS [60], SBS was gradually replaced either with a mixture of PS and PB homopolymers in the same proportion as in the block copolymer or with only one of the homopolymers. In the first case, there is a constant composition of the polymeric phase but a gradual reduction of the proportion of styrene-butadiene block links, which stabilize the interface of styrene-rich micelles and butadiene-rich macrophases. The DMTA curves of the blends containing SBS showed that they are softer than the asphalt at low temperatures and that replacing the SBS causes a slight additional fall in the stiffness. Therefore, the addition of PS and PB without block junctions was more effective to plasticize the asphalt, presumably because they create less microscopic order. Furthermore, from DMTA, it was observed that there was a critical point (between 18%–25% replacement of SBS) for the formation of polystyrene micelles as crosslinking entities. Further replacement generates a progressive decrease in stiffness related to the loss of coherence among the remaining polystyrene-rich micelles. The observation that the stiffness of blends decreases below a plateau at high temperatures only when a critical proportion of the block copolymer was replaced with the two homopolymers supports the idea of an extensive network created by the PS domains that remains effective even above the melting point of such domains. The replacement of SBS with PS alone allowed for the observation of the effects related to an increase in the number and dimension of the polystyrene-rich micelles (and removal of rubber blocks), and it was found that the effectiveness of the SBS polymer in creating PS microphases was preserved until at least 75% of the SBS (at 15% by weight with respect to asphalt) was replaced by PS. Thus, in those blends, there were PS domains larger in size and smaller in number (as demonstrated by FM), but yet the central PB blocks were observed to be able to maintain the network structure. In contrast, when SBS was replaced with PB, in certain cases, a stiffness almost three times that of the blend with SBS alone was observed. This seems to be related to a network-forming effect, which, at a very low concentration of PS domains, probably involves the asphaltenes.

4.1.4. Physical interconnections: A rheological point of view

Another interesting result related to the network structure originates from the shear viscosity functions of SBS-modified asphalts [214]. These functions were studied at different temperatures in steady-state rate sweep tests, which mostly showed the classical Newtonian behavior at low shear rates, followed by two distinct shear-thinning phenomena. Moreover, the first shear thinning was, in some cases, preceded by a weak shear thickening. The behavior is qualitatively shown in Figure 17.

As the second shear thinning was also observed in the unmodified asphalt, it can be attributed to a disruption or alteration of the colloidal network mainly formed by asphaltenic micelles or micelle aggregates. In contrast, the first shear thinning is strictly related to the presence of the polymer. It was already mentioned that styrenic domains of block copolymers can be arranged in a mesophase structure. Complex phase diagrams can be built for such systems, and, as the inter-block repulsion decreases with increasing temperature, it is often possible to identify an order–disorder transition temperature. However, an order–disorder transition can also be induced through an applied stress (and, in this case, a shear thinning is observed) or, in solutions, by varying the solvent concentration [215, 216].

A mechanism similar to the order–disorder transition is also involved in this case, starting with the first shear thinning (occurring at the lower shear rates) associated with a rearrangement of PS domains. This is consistent with the fact that an increase in temperature favors the transitions and shifts the onset of this shear thinning to the left (while it shifts the onset of the second transition to the right). Therefore, at high temperatures, the two shear regions appear more distinct than at low temperatures. This order–disorder transition corresponds to a “rigid” rearrangement of the domain structure, which necessarily involves a temporary detachment of flexible chains that “jump” from one domain to another, thereby determining a temporary nature of the polymeric network. This hypothesis is in agreement with the observed shear thickening. Such a phenomenon was previously described for solutions of the so-called amphiphilic or associating polymers [217-219]. The simplest examples of such polymers are telechelic polymers consisting of water-soluble chains with short associating groups at both chain ends. In aqueous solutions, the hydrophobic segments segregate and form the inner core of micelles, while the longer hydrophilic chain segments assume the so-called “flower” conformation. [220]. At a certain micelle concentration, some chains may bridge from one micelle to another, building a network that can include the entire solution. Owing to its physical nature, the network is not permanent; further, if the association energy is comparable with the thermal energy, the chain ends can jump from one micelle to another. Analogously, the jump can be determined through an applied shear.

5. Improving the storage stability of PMAs

5.1. Conventional solutions in asphalt/polymer compatibilization

Over the years, a large number of solutions have been suggested and patented in order to solve, or at least reduce, the problem of phase separation during storage at high temperatures. Those solutions include the use of additives to achieve physical or chemical compatibilization, as well as the functionalization of the asphalt or polymeric phase and the use of vulcanization agents to introduce a chemically crosslinked network in the PMA structure.

Even if not easily generalizable, the importance of asphalt composition is widely recognized. Therefore, it is obvious that one of the simplest ways to improve compatibility is the modification of asphalt through the addition of light components highly compatible with the polymer. The addition of aromatic oils (easily available from crude oil refineries) is therefore one of the most suitable and adopted solutions in industrial practice. However, in order to achieve good compatibility, it is often necessary to add a considerable amount of oil, which may have other drawbacks, such as the excessive softening of the base asphalt or the risk of dissolution of the polystyrene domains. Nevertheless, this remains as a good solution and any oil highly compatible with SBS can be used for this purpose. As an example, Santos Fernandes et al. [221] suggested the use of oil shale from sedimentary rocks and showed that in blends containing 3.5% by weight of SBS, the addition of 2% to 4% of oil resulted in a reduction in ΔS from 15–26°C to 6–8°C.

5.1.1. Sulfur-based techniques

As is well known, the use of sulfur as a vulcanizing agent of unsaturated rubbers dates back to the end of the nineteenth century. Since its discovery by Charles Goodyear, there has been a large

amount of research in the field of vulcanization processes, and nowadays, tire producers use very complex recipes that include a considerable amount of additives, catalysts, accelerators, and so on, which vary depending on the application and desired performance. Nevertheless, sulfur remains the most widely used vulcanizing agent, and its capability of interaction with C=C double bonds was revealed to be useful in improving the storage stability of natural and/or synthetic rubbers or their latex-modified asphalts in 1958 [222].

However, it must also be pointed out that sulfur itself is able to strongly influence the properties of asphalts. This is why its use in asphalts has been suggested even before the appearance of the first synthetic polymers. Henderson [223] in 1916 patented “*a bituminous binder consisting of 5 to 10% sulfur and from 90 to 95% bituminous residuum of asphaltic base petroleum*” in order to “*to produce a plastic binder of superior ductility.*” This idea was also used in a patent issued in 1978 [224] with the same primary objective of obtaining an asphalt with high ductility, and the procedure uses rather high quantities (3% to 7% by weight) of elemental sulfur and a small amount (0.5% to 1.5% by weight) of a natural or synthetic rubber.

Therefore, the early applications were based on the use of sulfur as an independent asphalt modifier, able to improve the mechanical properties of asphaltic binders without requiring the association with other materials, such as polymers. The modern expression of this technique is a quite large group of commercial products, named as “sulfur extended asphalts”, in which sulfur is added in large quantities and represents the primary modifier (e.g. Shell Thiopave), with the triple role of binder, filler and chemical co-reagent. Among the factors controlling the reaction between sulfur and asphalt, the mixing temperature plays a determinant role. At temperatures below 140 °C sulfur incorporation into the asphalt molecules or dehydrogenation with formation of hydrogen sulfide may occur. At higher temperatures, the formation of C-S bonds promotes a dynamic vulcanization of asphalt, through the formation of bridges within aromatic and naphthenic components, thus deeply altering the chemical composition and colloidal structure of asphalt. Some authors also suggest the idea that sulfur itself “polymerizes” when added to the binder. The interested reader may start from the paper by Syroezhko et al. [225].

Of course, this kind of application does not directly concern with the stabilization of PMAs, where the polymer is the main modifier and sulfur is usually added in very small quantities. Even if we attempt to limit this review to the scientific literature, the use of sulfur to improve the storage stability of PMAs cannot be treated without starting from the patent literature. The first patents appeared in the 1970s. In 1971, Petrossi [226] described a process for preparing a rubber-modified asphalt by blending rubber, either natural or synthetic, at 145–185°C and then slightly reducing the temperature (125–160°C) and adding sulfur such that the weight ratio of sulfur to rubber is between 0.3 and 0.9. A catalytic quantity of a free-radical vulcanization accelerator is also added to aid vulcanization. However, most cited patents are by Maldonado et al. [227, 228] of the Elf Union Company. The authors recommend starting with the preparation of a homogeneous PMA by stirring asphalt and SBS for 2 h and then adding 0.1%–3% by weight of sulfur and stirring for 20–60 min further. During this period, the sulfur is supposed to chemically react, but the exact nature of such a reaction is not “completely clear.” The authors underline that it is very important that sulfur addition follows the obtainment of a homogeneous blend because a premature loading may lead to an “*ultra-rapid*” vulcanization, which freezes the undesired heterogeneity, resulting in a useless material: “*The precise nature of the sulfur's action on the bitumen and the conjugated diene styrene copolymer can still not be completely defined. However, this action is rather similar to that of vulcanization. The action of the sulfur causes a modification in the structure of the mixture which leads to the obtention of bitumen polymers having thermally stable and improved mechanical properties. It is important that the mixture be homogeneous before adding the sulfur since if the sulfur is added prematurely it can cause a setting cross-linking of the copolymers- which is a very fast vulcanization of the components of the mixture, and lead to an unusable heterogeneous bitumen-polymer.*” It is interesting to report these words (taken from the US patent [228] but identical to those reported in the first French version [227]) because we can somehow say that they

contain more or less all the knowledge and skills we have about 40 years later. Basically, it is assumed or supposed that sulfur chemically crosslinks the polymer molecules and chemically couples polymer and asphalt through sulfide and/or polysulfide bonds. Therefore, it is important to obtain an appropriate distribution of the sulfur bridges that must be sufficient to create a network that chemically induces the compatibility; the network should be formed after the polymer has attained good dispersion and swelling because it would otherwise freeze the morphology at an earlier stage. Finally, the crosslinking degree must be sufficiently far from the gel point. Since the publication of the above-mentioned patents, there has been a huge proliferation of patents that essentially follows the same idea. In 1994, Bellomy observed that, in certain cases, the amount of required sulfur can be reduced to 0.015–0.075 wt% based on the amount of asphalt [229]. In a more recent patent, Gros [230] inverted the order of addition of ingredients and started by contacting sulfur with asphalt and then contacting a polymer with the sulfur–asphalt mixture. With regard to the risk of gelation, which can occur if an excessive amount of crosslinking agent is used and/or in the presence of high polymer loading (in the latter case, the risk of gelation is present even without the addition of crosslinking agents), Germanaud et al. [231] suggested the use of an “*antigelling*” adjuvant with the formula R-X, where R is a C₂₋₅₀ monovalent organic radical and X is a carboxylic acid, sulfonic acid, or phosphoric acid group. Another solution to gelation should be represented by the incremental addition of sulfur and/or elastomer to the asphalt [232]. Another possible solution is the one proposed by Chevillard [233], who first prepared a crosslinking elastomer concentrate (by adding the thermoplastic elastomer and a crosslinking agent to a suitable carrier oil) and subsequently added it to the heated asphalt cut in a stirred tank. A further alternative was proposed by Ho et al. [234] and is based on the mixing of a polymer/asphalt master batch with a predetermined amount of an asphalt-crosslinking agent blend.

As already stated, a potential drawback of elemental sulfur is that during the incorporation of the polymer and sulfur into asphalt, it is difficult to distribute the sulfur throughout the mixture, giving rise to the risk of preparing nonhomogeneous PMAs. Moreover, if the polymer and sulfur are added after the preparation of a mother solution, local over-vulcanization of the polymer can occur. A possible solution to this problem is replacing elemental sulfur with a polysulfide, especially dihydrocarbyl polysulfide, which is more easily soluble in asphalt [235].

In summary, after the use of sulfur was revealed to improve the storage stability, there has been a considerable proliferation of patents that progressively expanded the procedures, operating conditions, and compositions for obtaining storage-stable PMAs. It is difficult to produce an exhaustive list of the available patents because of their often cryptic titles, and interested readers are referred to the usual search engines dedicated to patents. Moreover, after the first waves of patents based only on sulfur and rubbers, the use of sulfur has been extended, with the same compatibilizing purpose, to other polymers not necessarily containing unsaturated double bonds and has been coupled or substituted by other compounds such as sulfur donors, vulcanization accelerators, and catalysts. An example of a patent that broadens the list of compounds that can be used to achieve or improve the vulcanization process dates back to 1990 [236]. In this patent, the operating conditions and crosslinking procedure are identical to those described in the previous patent [226], but the word “sulfur” is substituted by a “*coupling agent susceptible of providing sulfur*.” This, of course, includes sulfur, as well as any sulfur-donor or nonsulfur-donor curing accelerator. A long list of potential compounds was reported, including benzothiazole sulfonamides, dithiocarbamates, thiuram sulfates, morpholine sulfates, and caprolactamsulfates. Similarly, in three patents filed by Butler et al., the use of other crosslinking agents are described; these include zinc mercaptobenzothiazole, zinc oxide, and dithiodimorpholine (as a replacement for sulfur); a thiopolymer and elemental sulfur or mercaptobenzothiazole; zinc oxide and elemental sulfur; as well as compositions without elemental sulfur such as mercaptobenzothiazole, zinc oxide, and mixed polythiomorpholine and zinc 2-mercaptobenzothiazole and dithiodimorpholine [237-239]. The interesting point of these three patents is that in some of the proposed recipes, elemental sulfur is not included. As one of the main drawbacks in the use of elemental sulfur is that it may cause the

emission of hydrogen sulfide during preparation of the asphalt/polymer mixes, the use of such crosslinking agents as alternatives to elemental sulfur is supposed to eliminate or at least reduce such emissions. Nevertheless, it seems that in all those patents, the sulfur source releases elemental or radical sulfur during the preparation process, which may favor the undesired formation of hydrogen sulfide. In 1996, in a patent of the Shell Oil Company [240], the use of a disulfide that does not release sulfur (and therefore hydrogen sulfide) during mixing at an elevated temperature was suggested. In this case, the disulfide should act as a direct compatibilizer between the polymer and asphalt and not as a conventional source of free sulfur. The proposed disulfide is preferably a diaryl disulfide in which each aryl group is a phenyl group unsubstituted or substituted by one or more of the same or different substituents selected from methyl groups, t-butyl groups, chlorine atoms, and carboxylic acid groups. A final, foregone conclusion is that all these additives are so expensive that they have not, in general, been used commercially.

Leaving the vast and disordered world of patents, we can return to the scientific literature, which is relatively quite limited for this specific topic. As already mentioned, the common idea is that sulfur crosslinks the polymer chains and couples polymer and asphalt through sulfide and/or polysulfide bonds. However, this supposition primarily originates from the well-known and extensively studied process of vulcanization of unsaturated rubbers, but clear evidence for the occurrence of such chemical reactions in the case of PMAs has not yet been reported. Wen et al. [222, 241] suggests that the reaction of sulfur with the polymer corresponds to the “dynamic vulcanization,” which is usually adopted in rubber/plastic blends to prepare the so-called thermoplastic vulcanizate. During the mixing of a thermoplastic polymer (usually a polyolefin) with a small amount of an immiscible, unsaturated rubber, vulcanizing agents are added, and the rubber undergoes crosslinking while mixing continues. This allows for obtaining a final morphology consisting of small elastomeric droplets finely dispersed in the plastomeric matrix. In order to follow and describe the reactions occurring during this process, Wen et al. prepared an asphalt/SBS/sulfur blend at a temperature (120°C) that is high enough to achieve low viscosity and obtain a macroscopically homogeneous blend but simultaneously low enough to limit the occurrence of reactions between asphalt and sulfur or the vulcanization of SBS. Then, samples were heated to a fixed value in the range of 150–180°C, in which the reactions may start. A simple evidence for the crosslinking reaction originates from the torque necessary to maintain a constant rpm of the high-shear mixer, which remains constant for both binary asphalt/sulfur and asphalt/SBS blends, while it gradually increases for the ternary asphalt/SBS/sulfur blend. The effect of sulfur was monitored by recording the input electric current of the high-shearing mixer (the torque is proportional to the input electric current of the mixer) while adding first the polymer alone and, one hour later, the sulfur. Sulfur addition causes a rapid increase in torque, which reaches a maximum and then diminishes to gradually approach a stationary value slightly higher than that with the polymer alone. The authors hypothesize that the rapid increase is due to the dynamic vulcanization of the C=C double bonds, leading to a crosslinked network, which is then partially destroyed by the high shearing. The formation of sulfur bridges within the aromatic and naphthenic components of asphalt may create structured complexes able to “wrap” the SBS particles through polysulfide or sulfide bonds, which leads to improved compatibility with asphalt. In other words, the sulfur determines the vulcanization of not only the unsaturated rubber but also the functionalized asphalt components and, of course, creates interconnections between the polymer and asphalt. As these connections are made of primary covalent chemical bonds and link the polymer with the otherwise polymer-incompatible asphalt components, storage-stable blends can be obtained. The same evidence for vulcanization was shown by Jin et al. [242], who presented the curing curves obtained in a rheometer at different temperatures and PS contents in asphalt/PS/SBS/sulfur blends as well as the ΔS values demonstrating the beneficial effect of sulfur for storage stability.

Another indirect evidence for vulcanization was reported by Martinez-Estrada et al. [243], who modified asphalts by using either SB or SBS copolymer and performed a detailed rheological characterization of the blends. Among the long list of reported rheological data, the main

observation that supports vulcanization is that the rheological behavior of SBS-modified asphalts (with or without sulfur) is far different from that of SB-modified asphalts without sulfur, while it is fairly well reproduced by the same blends after the addition of relatively small amounts of sulfur. This of course suggests that sulfur promotes the formation of a polymeric network, which allows SB to impart elastomeric properties to the blend. Owing to the di-block nature of SB, this would be impossible without a chemical linkage. For all the sulfur-added blends, improved storage stability and blend morphology has been reported. Similarly, highly improved storage stability was reported by Zhang et al. [244], Sun et al. [245], Chen and Huang [212], Wen et al. [246], and Aguirre et al. [247]. Chen and Huang [212] observed the morphology of blends containing 7% by weight of SBS and variable sulfur content through the use of TEM. In all cases, SBS constituted the continuous phase, and a gradual reduction of the ARP droplets was observed while increasing the sulfur content.

In the paper by Wen et al. [246], classical FM images of modified binders containing 3.5 wt% SBS and sulfur show the development of the morphology during mixing (Figure 18). The first image (Figure 18a) corresponds to 1 h of mixing without sulfur. Then, sulfur is added and the mixing prolonged for another hour, during which the particle size of SBS becomes progressively smaller, reaching a very fine structure at a magnification of 400, as shown in Figure 18d.

As a general consideration, with the use of sulfur, as well as any other crosslinking agents (among which we can also mention radiation-induced crosslinking [248]), it is obvious that the critical point is the appropriate dosage of chemical bridges, which must be below the gel point. It is also quite obvious that from a rheological point of view, the effect of sulfur addition may be easily summarized as a “more elastic” behavior with respect to the PMAs without sulfur [212, 222, 246]. This especially determines an improvement in the high-temperature performance of the binders, as well as a reduction in the temperature susceptibility. To close this section, the paper by Ghaly [249], which shows that SBS and sulfur can be used to improve the storage stability of rubber asphalts (asphalts modified by using ground tire rubber), can be mentioned.

5.1.2. The use of maleic anhydride

Among reactive molecules, one that received great attention in the asphalt literature is maleic anhydride (MAH), which has been widely used as an asphalt modifier or asphalt-polymer compatibilizer. In the first case, the reactions occurring with asphalt are not easily identifiable. A first hypothesis is that the MAH double bonds lead to the formation of a copolymer in which MAH alternates with various asphalt components [250]. However, Diels–Alder reactions between MAH and the complex aromatic ring of coal [251, 252] and mesophase pitches [250] have also been observed. Nevertheless, irrespective of the exact mechanism of interaction, it is well known that MAH induces significant changes in the physical properties of asphalt. Nadkarni et al. [253] modified base asphalt by using 5%, 10%, or 15% by weight of MAH and tested several reaction times and temperatures. The materials were then characterized using dynamic mechanical analysis, melt viscosity, and softening point. On the basis of the collected data, the authors concluded that the chemical modification of asphalt with MAH improves both the low-temperature cracking resistance and high-temperature cohesive strength, and they hypothesized that MAH induces a thermally initiated polymerization of the asphaltenes. Another description of the effect of asphalt maleation was provided by Singh et al. [254], who recorded a stiffening effect that made the asphalt less temperature susceptible. Then, a simple mechanism was proposed, suggesting that the maleated asphalt interacts with the hydroxyl functionalities contained in the recycled LDPE.

In order to improve the elastic recovery of the blends, SBS was also added, and in all cases, ΔS was shown to be far lower than that in the absence of maleation. Moreover, the stability of the blends was further improved when LDPE was pre-milled with MAH. This is not an isolated result, and it is generally recognized that homogeneous and storage-stable mixtures of asphalt and polymer can be conveniently prepared by adding dicarboxylic aliphatic acids or the relative anhydride, with MAH probably being the most effective one. Mancini suggested the addition of MAH in quantities

ranging from 2% to 12% by weight, followed by polymer loading [255]. The obvious drawbacks associated with this process are mainly the costs and MAH handling in a refinery. Ciplijauskas et al. [256] found the use of MAH (as well as sulfonic acid or carboxylic acids) beneficial for the problem of moisture sensitivity, which may determine the loss of adhesion between the asphaltic binder and aggregate and thus the degradation of paving surfaces. The attachment of acidic substituents may be subsequently neutralized by basic metal oxides such as lime or magnesium oxide, leading to the formation of insoluble bituminous salts, which strongly improve the binder resistance to water. Such water-insensitive salts or polar complexes of asphalt have been designated by the authors as “asphalt ionomers” in analogy with ionomers derived from polymeric materials. A further enhancement in understanding the chemical reaction occurring between MAH and asphalts comes from Herrington et al. [250], who compared the effects of MAH and related di-acids and anhydride, such as succinic acid (SAH). The FTIR and gas chromatography-mass spectroscopy indicated for both MAH and SAH a rapid opening of the anhydride ring to give the di-acid, followed by a slower process in which the double bond reacts and the acid functionalities (probably free and hydrogen-bonded acids) remain detectable. The effect on the rheological properties of the asphaltic binder was decreasing in the following order: MAH > SAH ~ dicarboxylic acids > monocarboxylic acid and were interpreted in terms of the formation (or enhancement of existing) transient networks of asphalt species linked by hydrogen bonding and dipole–dipole interactions with the dicarboxylic acids. In other words, the two carboxylic acid groups are able to link two asphalt species, forming a sort of “alternating polymer” built through hydrogen bonding or dipole–dipole interactions. The addition of MAH through the double bond to an asphalt molecule allows an additional linking and explains the larger effect of MAH with respect to SAH. The presence of a single acidic functionality is incompatible with this mechanism and leads the mono-acid to have an effect similar to that of hydrocarbon oils. However, the complexities of asphalt species and structures again make it nearly impossible to obtain convincing evidences for the existence of alternating copolymers or Diels–Alder products. A more recent paper by Kang et al. [257] investigated the reaction of asphalt and MAH using FTIR and chemical titration. In contrast to the results of Herrington et al. [250], FTIR indicated that the cyclic anhydride band in MAH was retained during the reaction, which occurred through both Diels–Alder and π – π charge-transfer mechanism. The latter was possible because of the polynuclear aromatic nature of asphaltenes that behaved as donors in the charge-transfer processes owing to the presence of the substituted alkyl groups.

Even if not completely clear or, as usual, generalizable, the chemical interaction of some asphalt components with MAH is important and may be used to both improve asphalt properties and promote interactions and thus compatibility with polymers. Unfortunately, the high reactivity of MAH also has an important drawback related to its handling and storage. Therefore, instead of introducing such chemical compounds in a refinery or asphalt production plant, it is preferable to introduce a pre-step of polymer–MAH reaction and then modify the asphalt with the MAH-grafted polymer. Of course, this introduces a production step, which should also include an adequate purification to avoid the risk of having unreacted toxic monomer, and it increases the cost of the material.

Zhang et al. [258] prepared a “polymer modifier” composed of HDPE and SBS melt blended in the presence of variable quantities of LLDPE grafted with MAH (LLDPE-*g*-MAH) (Table 4) and compared the performances of the blends with those without the maleated compatibilizer. The tube test showed that the presence of a modest quantity of compatibilizer guaranteed very good storage stability, where the good quality of such blends was confirmed through optical microscopy (Figure 19).

Polymer maleation is a good solution and often simple to realize because it involves a single-step melt processing in a screw extruder. However, the MAH grafting is realized through a radical mechanism, and free radicals may lead to uncontrolled and undesired crosslinking of unsaturated polymers such as SBS and SIS. Therefore, this reaction is more indicated for saturated polymers;

therefore, the best candidate among TPEs is SEBS. Indeed, maleated SEBSs are already commercially available and were used by Becker et al. [71], who compared the storage stability of PMAs prepared using SBS, SEBS, and two commercial SEBS-g-MAH containing 1.0 and 1.7 % by weight of MAH. The latter polymers gave the best results in terms of storage stability, but they did not significantly improve the rheological behavior of the binder. This is probably due to the high MAH content of the two polymers, which leads to excessive compatibilization (it was already underlined that a high compatibility does not necessarily imply an improvement in mechanical properties). A lower and somehow modulated degree of grafting can be easily obtained using a self-made SEBS-g-MAH, as in the work by Vargas et al. [143]. Of course, a similar improvement of the compatibility between asphalt and polymer can be obtained with other functional groups such as GMA having the same, or similar, reactivity with functional groups available in asphaltenes. As there are no commercial SB-type copolymers available in the case of glycidyl groups, the first necessary step is their synthesis. This was performed in the molten state by Canavesi et al. [259], who followed a classical procedure of GMA grafting of SEBS under high shear, and in solution by Rojas et al. [260], who prepared epoxy-functionalized tapered styrene-butadiene copolymers through a two-step process: anionic polymerization of styrene and 1,3-butadiene and subsequent functionalization. Different levels of functionalization, with up to five epoxy groups per polymer chain, were obtained. The formation of a weak network, which became stronger as the degree of epoxy-modification increased, was observed through the rheological characterization of PMA prepared with these materials.

However, as the grafting reaction can be initiated using different techniques (such as X-rays, plasma treatment, ultraviolet rays, and chemical initiators) and operating conditions (such as solution or melt), determining the appropriate conditions for SBS also seems possible. Therefore, in spite of the risk of crosslinking during the grafting reaction, examples of functionalized SBS used for asphalt modification were also reported. Cong et al. [261] performed grafting after dissolving the polymer in toluene to use low temperatures (80°C), limiting the risk of undesired reactions. Of course, even if it allows the grafting of SBS, it is obvious that this technique is time consuming and very expensive; therefore, it is not suitable for industrial applications. Nevertheless, depending on the MAH concentration in the solution, grafting degrees up to 5% by weight were obtained, and PMAs prepared with a high (7% by weight) SBS content showed a tendency to separate that diminished with the MAH content in the polymer.

A similar approach is the one attempted by Engel et al. [262], who combined the use of SBS with the “ionomers” of Ciplljauskas et al. [256]. In this case, both asphalt and SBS were initially grafted separately with MAH, then mixed, and, finally, the acid groups were neutralized by adding zinc acetate di-hydrate to the blends. This leads to the formation of a reversible ionomeric network, the storage stability of which was qualitatively evaluated by monitoring the evolution of the morphology during storage at high temperature. The blends obtained using unmodified components were less stable than those obtained with maleated components, which, in turn, were less stable than those based on ionomeric interactions.

Following the same philosophy of using an acidic vinyl monomer, Fu et al. [263] suggested the use of methacrylic acid, grafted to SBS through a radiation method with ^{60}Co γ -rays and obtained a graft degree of approximately 6% by weight. Again, the morphological analysis confirmed improved storage stability with respect to the blends obtained with the unmodified polymer.

Another possible method to combine the use of SBS and reactive functional groups was suggested by Wang et al. [264], who synthesized SBS with either amino, carboxylic acid, or hydroxyl functionalities as the end-group. TEM images showed that the group at the end of the polystyrene segment made the morphology of the PS domains disordered and incompact. Both amino- and carboxylic-acid-terminated polymers showed improved compatibility and storage stability of the corresponding modified asphalt, while no similar effect was observed for the hydroxyl functionalities.

5.1.3. Compatibilization of asphalt/polyolefin blends

Following the same idea of creating a covalent bond between the asphalt and polymer, all the solutions already described for the SB-type copolymers can be attempted. As already stated, one of the most popular methods to obtain such chemical anchorage/grafting is the use of sulfur. As an example, Zanzotto and Zanzotto [265] patented the use of styrene butadiene block elastomer and sulfur to prepare stabilized PE-modified asphalt binders. A similar solution was also suggested by Prejean and Babcock [266], who extended the idea to ethylene copolymers such as EMA, EAA, and EBA. The use of oxidized polyolefins and sulfur is another possibility [267].

Another classical way to anchor the polymer on asphaltene molecules is the use of the maleic group, which was achieved by preparing a maleated asphalt and then modifying it with LDPE; LDPE and SBS; or, even better, LDPE previously milled with MAH [254]. More precisely, recycled LDPE was used as a partial replacement of virgin SBS and natural rubber. Again, the idea is to obtain the features of both polymers, but a compatibilizer is needed and the MAH group is supposed to work with not only SBS but also the polyolefin owing to hydroxyl functionalities deriving from its recycled nature. Storage stability was then studied through the tube test and evaluated in terms of the softening point, rheological changes, and microstructural features. The maleated blends were found to be subjected to phase separation (creaming process was assumed to be dominant). Nevertheless, they showed a small difference in all parameters (especially in the rheological ones) of the top and bottom portions of the test tube compared to those obtained with the base asphalt.

The effect of MAH grafting was also studied by Li et al. [268], da Silva et al. [269], and Yeh et al. [270], who did not show storage-stability data, and more recently by Vargas et al. [271], who evaluated the thermal stability, morphology, and viscoelastic properties of asphalts modified by an LDPE, an HDPE, and a BHDPE (which is a bimodal high-density PE) and with the corresponding maleic grafted polymers obtained through reactive extrusion. From FM, it can be seen that biphasic materials were obtained in all cases: the LDPE was dispersed in isolated spherical particles, which became smaller after grafting; in the case of HDPE, the polymer swelling was almost absent without grafting, while after the grafting, the PRP covers the entire image, indicating an important effect of the MAH. Finally, the BHDPE is the only one that, after grafting, shows some irregularities in the shapes of the particles with the presence of small and lamellar structures. Thus, the morphology shows that MAH has an important impact on polymer–asphalt interactions, but simultaneously, it reveals that a high degree of incompatibility survives in the mixes. This is confirmed by the storage stability test, which in all cases gave lower ΔS values for the grafted polymers, except for one case (HDPE-g-MA) that gave an acceptable value.

Ouyang et al. [272] used MAH for compatibilizing an LDPE with a waste tire powder (WTP) and then the resulting blend with asphalt. After trials with five different MAH-grafted polyolefins, an octane-ethylene copolymer (POE-g-MA) was selected as the most promising compatibilizer, and blends composed of POE-g-MA/WTP/LDPE = 8/70/30 were added to asphalt in variable amounts. The tube test indicated that in this particular case, the ΔS plotted versus the polymer content has a minimum and only PMAs prepared with 8.5% by weight of the polymeric additive are stable to storage, while even a small variation in polymer content leads to storage instability. This result is confirmed by morphological analysis, which shows a homogeneous dispersion only for that particular polymer content. The existence of this minimum is tentatively explained in terms of Stock's law by supposing that the optimal composition corresponds to ARP and PRP with equal densities.

Analogously to MAH, the GMA functional group also has good potential compatibilizing properties, as previously reported by Li et al. [133].

Recalling that steric stabilization (see section 3.4.2.) works well for asphalt/PE emulsions, other similar solutions may be suggested, starting from the consideration that a copolymer with some affinity with both components should localize at the asphalt/PE interface even without a chemical covalent bond. Ait-Kadi et al. [273] modified asphalt by using a 90/10 PE/EPDM (ethylene

propylene diene monomer) mix prepared in the molten state by using a twin-screw extruder. Storage stability was not evaluated in terms of the tube test, but the morphology of the blends after different times of static storage at 160°C show that compared to PE alone, in the presence of EPDM, the polymer particles were smaller and remained well dispersed after more than 48 h. Nevertheless, phase separation occurred, but it is interesting to observe that the phase separation problems are less pronounced for HDPE samples subjected to artificial ageing than for the unaged ones. The same authors later arrived at the same conclusions of unsuccessful stabilization in mixtures obtained with recycled PE mixed either with EPDM or with an ethylene-butylene copolymer [103]. Even if the softening points were coincident in some cases ($\Delta S = 0^\circ\text{C}$), optical microscopy and rheological tests revealed large differences in the concentration of polymer particles in the top and bottom parts of the test tubes. Later, this recipe was further modified by adding a used-tire-derived pyrolytic oil residue loaded in considerable quantities (about 10 wt%) [274]. Again, a consistent phase separation was observed, even if the micrographs showed an increase in the volume of asphalt entrapped in the polymer particles and SEM showed a reduction in the dimensions of the particles. However, the scarce effect of tall oil pitch as compatibilizers for asphalt/polyolefin blends was already described a few years before by Kellomiiki and Korhonen [275, 276], who observed that it helped in obtaining mixes “*somewhat more homogeneous, but it increases polymer miscibility only slightly and is not able to stabilize mixes.*” Perez-Lepe et al. attempted to use several modifiers, among which an HDPE (previously blended in the molten state with EPDM by using a twin-screw extruder) was shown to have “a low degree of instability” [94, 131]. As an alternative to EPDM, SEBS was shown to have a positive effect on the control of the emulsion stability, particle size, and compatibility of the dispersed PE phase [98]. Finally, the ozonization of PE has also been suggested as a possible method to improve its adhesion with asphalt [277] or the mechanical properties of the blends [278].

6. Nanocomposite-modified asphalts

Polymer/clay nanocomposites or polymer/layered silicate (PLS) nanocomposites have attracted great interest because they may exhibit improved materials properties when compared with the virgin polymer or conventional micro- and macro-composites. Improvements may be observed in mechanical properties, heat resistance, gas permeability, flammability, and biodegradability [279-281]. Of course, the simple mixing of a polymer (usually hydrophobic) and a native hydrophilic layered silicate does not necessarily give rise to the formation of a nanocomposite. On the contrary, the poor physical interaction between the two components usually leads to biphasic systems with hardly improved mechanical and thermal properties. The simplest way to promote the interactions between the polymer and layered silicate is to convert the silicate surface from hydrophilic to organophilic. Since pristine layered silicates usually contain hydrated Na^+ or K^+ ions, this is achieved through ion-exchange reactions with cationic surfactants such as alkylammonium cations. When dispersion is obtained at a nanometer level, the material can be defined as a nanocomposite, and it may exhibit unique properties not shared by its micro counterparts or conventionally filled polymers. Moreover, it is a peculiar characteristic of nanocomposites that such improved properties may be obtained with very small amounts of layered silicate loadings. This is possible owing to the very high aspect ratio, which enables a few weight percent of layered silicates properly dispersed throughout the polymer matrix to create a very high surface area for polymer/filler interaction as compared to conventional composites.

Depending on the obtained dispersion, two main types of PLS nanocomposites are identified: i) intercalated nanocomposites, in which the layered silicate structure still occurs in a crystallographically regular fashion, and ii) exfoliated nanocomposites, in which the individual clay layers are dispersed in a continuous polymer matrix (Figure 20).

The two technologies of PMA and PLS, although known for several decades, were combined only recently. The main and simple idea was to transfer the advantages of the second one into the former. However, even if improvements in the performance have been achieved using ternary asphalt/polymer/clay (APC) systems, the main advantage that was immediately observed concerns increased asphalt/polymer compatibility. Even though somehow unexpected, this is not surprising, because it was already known that clays may be used as compatibilizer agents in polymer blends [282-291]. This is possible because the organoclay, even if preferentially located within the bulk of the most compatible polymer, may also localize at the interfacial region. Consequently, the interfacial tension is reduced, the minor phase-dispersed particles lose the typical rounded shape they possess in the pure polymer blends, the droplets coalescence is inhibited, and a finer dispersion is obtained. It is reasonable to suppose that a similar compatibilizing mechanism may be found in APC, with asphalt playing the role of a low-MW polymer.

6.1. The asphalt–clay binary system

From a chronological point of view, the study of asphalt/clay interactions started well before the introduction of polymeric nanocomposites and probably dates back to the use of the so-called oil-sands, which are naturally composed of both components. In this case, the main goal was somehow opposite because it was necessary to remove the clays from the native oil. In the most common extraction process, the oil-sands are conditioned with hot water, steam, and caustic to release the bitumen from the sand and other solids. Gravimetric separation and air floatation then produce bitumen froths, which contain significant amounts of water and solids that must be removed before bitumen upgrading. Therefore, there are several studies dedicated to i) the interactions between bitumen and clays through zeta potential distribution measurement [292-294], AFM [292], and model systems such as particles coated with asphaltenes [295] or model water-in-hydrocarbon emulsions [296] and ii) the removal of the solids from the bitumen before the upgrading process [297-299].

In asphalt mastics, the aggregates are added in the form of a powder to asphalt and can be somehow considered as “additives” or fillers, paralleling the classical addition of micro-fillers to polymers with the main difference being the high level of loading used in the case of asphalts. Clays used to substitute such conventional fillers may result in asphalt-nanocomposites, which closely resemble polymeric nanocomposites. In the case of asphalts, the interactions with clays are slightly favored by i) the asphaltenes, which guarantee the presence of polar functional groups, and ii) the lower-MW components of maltenes, which may easily intercalate between the clay platelets owing to their small dimensions. However, this is not sufficient to counteract the overall hydrophobic nature of asphalt; further, in this case, the use of organo-modified clays helps the intercalation-exfoliation process. This is confirmed by a few studies in which both modified and unmodified clays were added to asphalt. Yu et al. [300] obtained an intercalated structure when using montmorillonite (MMT) and an exfoliated structure when using organomodified montmorillonite (OMMT) exchanged with octadecylammonium ions. Unfortunately, the authors did not specify if this result was extended to all the investigated clay concentrations (ranging from 0% to 10% by weight). However some indication may be obtained from the plot of viscosity vs. clay content (Figure 21), in which the MMT and OMMT curves appears very different until 5% clay content. Then, the viscosity of the asphalt modified with OMMT shows a sharp reduction in slope. This suggests that 5% may correspond to the maximum clay content able to provide a good degree of exfoliation. Higher clay contents do not lead to further exfoliation, and the properties converge to the MMT values.

In another paper, the same research group [301] reported an intercalated structure using OMMT and a micrometer-scale dispersion with MMT. Again, the better dispersion has a strong influence on the binder properties. As an example, in a frequency sweep test, the storage modulus of the original binder and the MMT-modified binder are very similar and show the classic trend of base asphalts. In contrast, with OMMT, a plateau zone for the phase angle is clearly visible and indicates a

profound variation in rheological properties, which are strictly correlated with the internal structure of the material.

An accurate characterization of the asphaltic nanocomposite was performed by Zare-Shahabadi et al., who compared sodium bentonite (BT) and organically modified sodium bentonite (OBT) as nanoadditives [302]. The XRD analysis revealed that the interlayer spacing of clay increased from 1.48 nm (BT) to 3.16 nm (OBT) owing to the organo-modification of clay. After mixing with asphalt, it became 1.95 nm for BT, indicating the intercalation of asphalt molecules into the clay galleries, while in the case of OBT, the XRD pattern did not show any peak, suggesting an exfoliated structure. Similar observations were reported in other papers (see, e.g., Jahromi et al. [303] and You et al. [304]); however, it was also found that native (unmodified) clays may form intercalated structures in the asphaltic matrix (see, e.g., Zhang et al. [305]).

A recent study performed an interesting characterization using AFM of a binary asphalt/OMMT mix in which XRD analysis had shown the exfoliation of the clay [209]. The topographical and phase images with a dimension of $60 \times 60 \mu\text{m}$ were nearly identical for the control asphalt binder and 4% nanoclay asphalt composite, suggesting a uniform dispersion of the clay within the asphalt binder, while a few differences were appreciable at a smaller scale. The addition of clay does not significantly affect the shape and dimension of the bee-like structures, but it increases the contrast between the dispersed phase and the matrix. This is interpreted as a “higher degree of molecular coordination between the exfoliated layers of the nanoclay material and the dispersed domains in comparison with the flat asphalt matrix.” In other words, the bee-like structures should interact better with the nanoclay layers than with the asphalt matrix, where they are dispersed. In apparent contrast with this interpretation is the one reported by Zhang et al., who compared images of a base asphalt and its mixtures either with a sodium MMT or with the corresponding OMMT [210]. After MMT modification, the contrast between the matrix and the dispersed bee structures is inverted with respect to base asphalt, but this inversion is prevented with the introduction of OMMT “due to the good compatibility between the OMMT and the asphalt.” Similar considerations are then repeated for a ternary asphalt/polymer/clay system (see the next section/paragraph) [306].

It is worth noting that in a few papers, the storage stability of the binary asphalt/clay systems was evaluated. In the above-mentioned paper by Yu et al., this was achieved through the tube test (163°C , 48 h) [300 Yu]. Of course, the method is not designed for an asphalt/clay system, and the difference between the top and bottom softening points does not readily translate to a direct conclusion on the degree of clay migration. Nevertheless, the reported values help to parallel mixtures prepared with different clays and indicated a slightly better stability with the use of OMMT compared to the use of MMT. More recently, Cong et al. [307] used the same procedure to evaluate the stability of mixtures of asphalt and diatomite. The differences between the softening points of the top and the bottom sections were found to increase from 0.3°C at 5% by weight of clay content up to 1.4°C at 20% clay. These values were interpreted by the authors as proof of very high storage stability. However, it is again necessary to recall that the test was developed for PMA. Thus, a result of stable or unstable in this test has a different numerical meaning. If, for example, a 5 % SBS content may easily enhance the softening point by $40\text{--}50^\circ\text{C}$, then it is obvious that a ΔS value of a few degrees centigrade corresponds to a very small difference in the polymer contents of the top and bottom sections. The situation changes completely when using fillers that, even if added in high quantities, scarcely affect the softening point. In this case, it is obvious that the acceptable ΔS should be lowered accordingly. Unfortunately, the authors report only the ΔS and did not provide absolute values for the softening point; therefore, it is not possible to extrapolate the degree of diatomite separation during storage. Nevertheless, based on our personal experience, when nanoclay is dispersed and asphalt starts to intercalate the clay platelets, the increase in viscosity makes it absolutely impossible to manage such a high clay loading. Thus, the reported values seem to indicate dispersion at the micrometer scale. Another recent paper that evaluates conventional and rheological properties (and aging resistance) of OMMT-modified asphalts is the one by Mahdi et al. [308].

6.2. The asphalt–polymer–clay ternary system

Before considering the APC ternary system, it is useful to remember that there are three main techniques to prepare PLS. 1) From solution: the silicate is first swollen in a solvent of the polymer, and then the polymer is added so that its chains may intercalate and displace the solvent within the interlayers. During the last step of solvent removal, the polymeric chains maintain their position in the silicate interlayers, forming the nanocomposite. 2) Through melt compounding: this is an annealing process, static or under shear, of the polymer (above its melting temperature) and the silicate. 3) In situ polymerization: the layered silicate is swollen within the liquid monomer or a monomer solution, and the polymer forms directly between the clay platelets.

Among the three methods, the third one is certainly not of our interest, while the other two deserve a few comments from the point of view of asphalt modification. First, it is quite obvious that melt compounding is the only method that can be easily applied in the field of asphalts because it is compatible with current industrial process and suitable for all types of thermoplastic polymers. Asphalt, polymer, and clay may be added and mixed in a single step. Otherwise, it is possible to divide the process into two consecutive steps: the first step is to prepare a classical nano-composite to be subsequently used as an asphalt modifier in the second step. In the latter case, the three methods of nanocomposite preparation can be potentially used during step 1. The differences between these two mixing procedures are very important and will be discussed in detail; however, it is obvious that from a practical point of view, the use of a solvent is not possible in the paving industry. Therefore, in both cases (direct mixing of the three components and pre-mixing of polymer and silicate to prepare the nanocomposite), melt compounding remains the only suitable method of preparation. Nevertheless, the mechanism involving the use of a solvent is not completely extraneous to APC: thus far, we depicted asphalt as a low-MW polymer, but we can also reverse our point of view and describe it as a high-MW solvent. Its smaller-MW molecules can intercalate the silicate layers more easily than the macromolecules of a polymer. In this sense, the contemporary mixing of asphalt, polymer, and clay can be considered as an intermediate method between melt compounding and solution intercalation. It is a method of melt compounding by definition, but the asphalt components of lower MW may play the same role of the solvent as in solution intercalation. They can both swell the polymer and delaminate the clay, favoring polymer intercalation. The main difference is that in the case of nanocomposites, the solvent is removed from the system at the end of the procedure, while in APC, the asphalt remains as a blend component.

The first research group that reported the production of APC used (i) SBS and kaolinite [309], (ii) SBS and organobentonite (a silane coupling agent was also added to the blend) [310], (iii) poly(styrene-*b*-ethylene-*b*-butene-*b*-styrene) (SEBS) and kaolinite [311], and (iv) LDPE or EPDM and silica [312]. In all cases, the polymer and clay were premixed to form a nanocomposite subsequently used for asphalt modification. Several polymer/clay ratios were tested and the storage stability, blend morphology, mechanical and rheological properties of the APCs were characterized, while the intercalated or exfoliated nature of the mixes was not investigated. In all cases, a positive impact of clay on storage stability was observed and mainly attributed to a reduction in the density gap between PRP and ARP. As already mentioned, the migration of PRP toward the top of the tube is due to its lower density relative to ARP. If we suppose that clay (which has a density more than double compared to those of both polymer and asphalt) preferentially locates in PRP, then its presence will reduce the density gap between the two phases. This is the simplest explanation and may be formulated irrespective of any other consideration of the role of clay in the overall structural arrangement of the blend. Unfortunately, there are no direct experimental evidences supporting the hypothesized prevalence of clay in PRP. Nevertheless, the recorded values of ring and ball are certainly consistent with this interpretation. As an example, Table 5 lists the softening point of the top and bottom sections for the asphalt/SEBS/kaolinite mixes. For a given SEBS content, the higher the clay content, the lower the ΔS . Moreover, at high clay loadings, this difference can even become

negative, indicating that PRP migrates toward the bottom of the tube. As an example, we can consider the mixes with 4% SEBS, in which ΔS decreases with increasing clay content until it reaches negative values. At high clay loads, the polymeric phases become the heaviest and storage stability is obtained at clay amounts that balance the PRP and ARP densities. A similar effect of the inorganic content on ΔS was reported in [312] for LDPE-modified asphalts.

However, from the reported studies, it appears that the storage stability is not simply due to a missing migration of two well-distinct phases: there are clear evidences of an improved compatibility between asphalt and polymer. First, the shape and dimension of the dispersed phase strongly change in the presence of clay. Moreover, the clay influences the physico-mechanical properties of the mixes in a manner that suggests a complete rearrangement of the internal structure [313]. Therefore, the improved storage stability is certainly related to the clay density, which implies that the clay resides prevalently in the PRP, but it is more likely due to a real asphalt/polymer compatibilizing effect.

Another interesting aspect is the importance of the preparation procedure. As anticipated at the beginning of this section, APC may be prepared in two different ways. The first one may be named “physical mixing” (PM), and it consists of the addition of clay and polymer to asphalt as separate entities. The second one is a “master batch” (MB) procedure that involves the addition of a PLS to asphalt (the two procedures are schematized in Figure 22).

All the mixes reported in Table 5, except for one, were obtained using MB. The only mix prepared using PM was shown to be unstable during high-temperature storage. Thus, storage stabilization is achieved only with premixed polymer and clay, which is consistent with the idea of clay residing preferentially in the PRP. In the absence of polymer/clay premixing, clay would preferentially interact with asphalt for two reasons: 1) the asphaltene composition, which is rich in polar groups, and 2) the statistical probability due to the strong prevalence of asphalt in the mix. In contrast, in the case of MB, the two components interact and bond with each other before coming into contact with asphalt molecules. This suggests that the already established interactions may at least partially survive the subsequent asphalt modification. This leads to completely different arrangements in the microscopic structures of APC prepared using MB or PM and, consequently to different effects on properties and storage stability. The same research group lately confirmed this point and found similar results using a styrene-butadiene rubber (SBR) and both a palygorskite and an organo-modified palygorskite clays [314].

This first interesting series of paper thus introduced the APCs, and firstly observed the effects on storage stability and the importance of the preparation procedure. However, the internal structure and nanocomposite nature of the blends were not directly investigated, and this aspect was first explored by Polacco et al. In the first paper, a base asphalt was modified with SBS and an OMMT (Cloisite 20A, prepared from sodium MMT through treatment with dimethyl-dihydrogenated-tallow ammonium chloride and subsequently referred to as 20A) through melt mixing [315]. First, binary asphalt/clay and polymer/clay blends were prepared, and subsequently, the ternary blends were prepared using both PM and MB. Thus, four sets of blends were available: (1) SBS/20A, (2) BA/20A, (3) BA/SBS/20A PM, and (4) BA/SBS/20A MB. All the ingredients and blends were characterized using XRD in order to determine if and what types of nanocomposites were formed (Figure 23). Starting from the binary BA/20A blend, it was found that irrespective of the clay load, the interlayer spacing of the clay nearly doubled (compared to 20A alone) owing to asphalt intercalation. Moreover, the XRD spectra indicated a partial exfoliation of the stacks, and the storage tests showed the absence of phase separation. All these data clearly indicate a high degree of interaction between BA and 20A. Furthermore, the SBS/20A binary blends were prepared with different clay loads, and in all cases, intercalated nanocomposites were obtained. Again, the interlayer spacing was found to be independent of the clay load and it was lower than that of BA/20A blends, suggesting that the clay had higher compatibility with the asphalt than with the polymer. Finally, the XRD patterns of the ternary blends showed that both PM and MB mixes resulted in intercalation with interlayer spacing equal to that obtained by mixing asphalt and clay

without the polymer. This indicates that the swelling ability of asphalt molecules to enter the clay stacks is not affected by the mixing sequence. This was somehow predictable because the polymer chains are present in a very small amount with respect to asphalt molecules and they interact with a limited amount of clay functionalities. Therefore, polymer chains, even if already intercalated between some of the clay platelets, are not expected to inhibit the interactions between clay and the small and abundant asphalt molecules. Thus, the degree of intercalation is fully determined by the asphalt molecules and is independent of the mixing sequence. In contrast, the mixing sequence is expected to strongly influence the ability of the polymer to intercalate the clay stacks at least for two reasons: 1) during melt blending with asphalt, the shear rate is lower than in a polymer/clay blending, and 2) polymer chains may not compete with asphalt molecules to swell the clay stacks, but their high inertia in the swelling parallels a high inertia also in leaving the stacks. Thus, once the clay-polymer interactions are established, asphalt molecules are not necessarily expected to substitute the polymer chains in clay interlayers. In other words, the similarity in the XRD spectra does not necessarily correspond to a similarity in the internal structure of PM and MB mixes. Effectively, the two types of blends showed different storage stabilities, morphologies, and rheological properties.

Starting from the morphology (Figure 24), the binary BA/SBS blend has a typical biphasic morphology, which results in high-temperature storage instability and indicates a swelling of the polymer limited to the lighter asphalt fractions. In the PM ternary blend, the situation is significantly different. The pattern is still biphasic, and the shape of the microdomains is somehow similar to the previous one, but the dimensions are smaller, indicating an improved compatibility and stability of the system. A further improvement of the morphology is observed for the MB blends, which had the canonical aspect of a perfectly compatible PMA with an “orange skin” pattern, where the PRP and ARP phases are almost indistinguishable.

The simplest explanation of these differences follows directly from the combination of morphological and XRD analyses. We already noticed that asphalt molecules tend to intercalate quite easily into clay platelets. Moreover, owing to their polar functionalities, it is expected that asphaltenic molecules are also involved in this intercalation, even if they are not favored by their dimensions in comparison with the maltenic molecules. Once the clay interlayers are swollen by the asphalt molecules, the polymer intercalation follows the mechanism of the solution intercalation, where, as already stated, the solvent molecules are the asphalt molecules, which are destined to remain in the system. The role of asphalt is that of the solvent in solvent intercalation. However, by switching the point of view from that of nanocomposites to that of PMAs, we also observe an important role of the clay, which favors the contact between the polymer chains and those asphalt molecules that would otherwise be confined in the ARP. In this sense, the clay action resembles the already mentioned compatibilizing effect exerted at a polymer/polymer interface. In this case, the clay acts as the substrate where polymer and asphaltene molecules may come into contact, reducing the differences in composition between the PRP and ARP phases. Of course, the polymer being the one that is more difficult to move among the clay interlayers, the MB procedure had a favorable starting condition, in which half of the procedure is already completed and only the “ease to move” asphalt molecules remain to intercalate the clay.

A second analogous study was performed by using EVA as a polymeric modifier and by comparing the effect of two different organoclays [316, 317]: 20A and Dellite 43B (subsequently referred to as 43B), an OMMT modified using dimethyl dibenzyl hydrogenated tallow-ammonium. The results paralleled those just described for SBS: the binary blend was markedly biphasic, the two clays worked as compatibilizers, and the MB procedure gave better results than the PM procedure in both cases. The morphological analysis gives a clear picture and shows that clay 43B has a compatibilizing effect less pronounced than 20A has (Figure 25).

It is interesting to observe that this result could have been predicted from the XRD spectra of the two binary EVA/20A and EVA/43B master batches. The first one, in accordance with other spectra reported in the literature [318, 319], corresponds to intercalated/exfoliated nanocomposites, in

which all the tactoids were intercalated by EVA chains. In contrast, in the EVA/43B pattern, the original peak of 43B is still present and a new peak trace at a lower angle indicates a partially intercalated hybrid structure. Moreover, the basal peak of the clay in the hybrid had a shoulder at higher angles, indicating that a part of the original tactoids collapsed, perhaps due to degradation of the organo-modifier [320]. Therefore, this observation seems to suggest that better compatibilizing effect should be expected from the clay that interacts better with the polymer. This is not unexpected, because the polymer is the limiting factor in the formation of APC nanocomposites and the MB procedure based on the establishment of pre-interactions between polymer and clay. Of course, the differences observed among the blends prepared using PM or MB are reflected in the macroscopic behavior. Rheological properties studied in small-amplitude oscillations, start-up of shear flow, and repeated creep and recovery tests showed improved thermo-mechanical properties of the ternary blend prepared using MB [317].

It is therefore ascertained that the MB procedure is preferable to the PM procedure because it guarantees better homogeneity, stability, and mixture performance. However, the PM procedure has at least the advantage of being simpler from an applicative point of view because it involves a single step using classical paving equipment. Therefore, PM deserves further attention, and it must be pointed out that, in the above mentioned studies, physical mixing was performed by simultaneously adding polymer and clay to the melted asphalt. However, based on the idea that pre-established interactions may at least partially survive in the subsequent mixing phases, it could be expected that a sequential addition of polymer and clay may result in an internal structure different from the one obtainable with simultaneous mixing. This interesting aspect was found in recent papers by Galooyak et al. [321, 322], who prepared a mix using PM and APC based on SBS and OMMT and claimed that the order of mixing does not significantly affect the characteristics of the final samples. Therefore, the chosen procedure was to add OMMT into an SBS-modified asphalt and XRD analysis was performed only in this case. Even if the authors claim that an exfoliated structure was obtained, the reported spectrum does not clearly confirm this claim. The same mixing procedure was used by Tang et al. [323], who added an MMT to SBS-modified asphalt.

Unfortunately, the XRD spectra do not seem to reveal the internal structure in this case as well. The same authors then evaluated the properties of paving mixes prepared with this binder [324].

Zhang et al. prepared an APC with an intercalated structure by first adding SBS to melted asphalt and then, after approximately 30 min of shearing, an OMMT [306]. AFM images of BA, SBS-modified asphalt, and OMMT/SBS-modified asphalt confirms the dramatic effect of clay on the blend morphology (Figure 26). The unmodified base asphalt showed domains with the previously described bee-like structure in the presence of SBS, the polymer-rich domains were visible, and the phase contrasts in Figure 26a and Figure 26b are inverted compared with BA. This is due to a change in the tip-sample interactions, which is affected by the sample stiffness. Finally, after OMMT addition, the contrast between the dispersed domains and the matrix decreases, and the overall aspect resembles that of BA, demonstrating that the material has a quite homogeneous structure.

Recently, the same research group published a similar study with the same mixing sequence performed with SBS and expanded vermiculite, both organomodified and not [325]. The XRD patterns of the modified asphalts showed that the unmodified clays maintain their interlayer spacing after blending, while the two modified vermiculites seem to be completely exfoliated. The two different structures are also characterized with slightly different storage stability, which is better for the blends with organomodified clays. However, the unmodified clay also results in a stable blend, but unfortunately, the stability or instability of the asphalt/SBS binary blend is not reported; therefore, the real contribution of the clay may not be evaluated. Nevertheless, from these studies, we can conclude that, depending on the cases, the PM procedure may be sufficient. Unfortunately, a comparison with an alternative mixing sequence is not available, and the order of addition of ingredients in the PM procedure deserves further investigation for a complete understanding: 1) its

influence on the APC structure and properties and 2) an appropriate choice of the sequence and mixing times may at least partially fill the gap between PM and MB procedures.

A further few recent studies are worth of mentioning. Jasso et al. modified conventional asphalt by using linear SBS and OMMT [326] and stated that MB is more time consuming and expensive with respect to PM, which was used for this reason, by adding all the ingredients at simultaneously. This paper does not compare different mixing procedures and does not investigate either the APC structure or its storage stability; it is mainly devoted to the evaluation of effect of clay on the rheological properties. Nevertheless, it is somehow related to our topic because the mixes are prepared by adding a fourth component, which is specified as a “sulfur-based compound.” The clay and sulfur-containing compound probably cooperate for the improvement of both asphalt/polymer compatibility and binder properties.

Fang et al. used an OMMT and a PE packaging waste (from fresh milk bags) to modify an asphalt using both PM [327] and MB [328]. The XRD analysis indicates the presence of an exfoliated structure in the ternary blends, and FM showed that the OMMT addition improves the polymer dispersion in the asphalt. The spherical shape of the PRP domains show that, even in the presence of clay, PE remains sufficiently far from storage stability.

The effects of nanomaterials on the binder performances have not been considered here, because the review was mainly dedicated to the storage stability. However, interested readers may find this aspect in many of the above-cited papers as well as in a very recent review by Fang et al. [329].

7. Conclusions

PMAAs are continuously gaining importance in the paving practice, and nowadays, almost all highways and main routes are prepared by using such binders, which have many advantages. In addition to a prolonged resistance to the usual failures related to traffic load and atmospheric conditions, the presence of the polymer allows for the production of soundproof open-graded pavements with anti-skid properties for rainy days. All these advantages, plus the reduction of maintenance operation easily counterbalance the initial investment, estimated at about one and half that of unmodified asphalts.

The main difficulty in the PMA industry is related to the poor compatibility between asphalt and polymer, which is manifested by the tendency to separate during high-temperature static storage or during transportation to the paving site. In the worst case, this phenomenon causes a macroscopic segregation of asphalt-rich and polymer-rich phases, the latter being highly viscous and difficult to handle. Thus, paving must be performed before the thermodynamically unstable asphalt/polymer blends prepared with a high-temperature/high-shear process can separate. Almost all PMAAs are subjected to this risk and whether they will separate or not is basically a kinetic problem. Therefore, since the first application of PMA, a high number of researchers focused their attention to this problem, which may be approached in several ways and represent the subject of this review.

First, it is useful to determine if a given PMA is storage stable or not, and several specifications to determine this were developed in different countries. In all cases, the test consists of a small-scale simulation of the storage, during which the two incompatible phases may separate and vertically segregate; therefore, a comparison of the top and bottom properties allows for quantifying the stability. Since most asphalt specifications have been developed in the first decades of the twentieth century, such a comparison is often based on indirect measurements of classical quantities such as the ring and ball or penetration tests, which are still currently used but do not provide a direct quantification of the polymer segregation inside the sample. More recently, the Superpave specification introduced the use of more accurate rheological measurements; however, in all cases, there is an arbitrary threshold in the difference between top and bottom properties. Such an approach is useful from the specification point of view, but it is unsatisfactory to describe and understand the separation process. Therefore, many other techniques have been introduced. The modern approach is mainly dedicated to the study of the structure and morphology of PMA. Optical

and electronic, as well as AFM, X-ray, thermal, and rheological analyses have been extensively used, which resulted in a big improvement in the understanding of PMA, which is constituted by a polymeric network swollen by the asphalt molecules. However, given the high complexity and variability of asphalt composition, a generalization of the parameters that influence the storage stability of PMA is nearly impossible. The interactions between asphalt molecules and polymer depend on their polarity and reciprocal affinity, which may also depend on other parameters related to, for example, the polymer architecture and MW. Nevertheless, the most important characteristics of both asphalt and polymer leading to an improvement of the storage stability have been established, and only a few polymers proved to be suitable for asphalt modification, even if none of them guarantee storage stability. It is always necessary to verify the stability, which depends on the asphalt, polymer and modification process (mixing apparatus, operating conditions, and so on). As is the case for polymer blends, an important part of the research has been dedicated to the development of compatibilizing agents. However, in the case of PMAs, the physical compatibilization based on the reduction of the surface tension between the two ingredients has limited effect, and the most effective method is chemical compatibilization. As the most widely used polymer contains unsaturated double bonds, a mild vulcanization process, which creates chemical bonds among polymer chains or among polymer chains and asphalt molecules, has always proved to be the most effective one. Unfortunately, the use of sulfur or other crosslinking agents also has many drawbacks that limit the diffusion of such techniques, and the “magic” universal compatibilizer remains elusive. In this context, the recently introduced asphalt/polymer/nanoclay ternary systems are very interesting. In addition to the potential advantages in the performance of the asphaltic binder, the APC systems showed that the clay may act as a compatibilizer and strongly enhance the morphological properties and storage stability of the asphalt/polymer blends. When comparing the APC systems with the classical polymeric nanocomposites, double paralleling is possible. On one hand, the asphalt may be seen as a low-MW polymer: during the mixing with a high-MW polymer, the clay partially localizes at the interfacial region, acting as a compatibilizer between the two polymeric phases. On the other hand, asphalt may be seen as a high-MW solvent, which swells both polymer and clay, aiding polymer/clay interactions. Owing to its lower MW and higher polarity, asphalt is usually more compatible with organo-modified clays than with the polymer. Moreover, asphalt constitutes the major part of the mixture; therefore, its interaction with clay is also favored from a statistical point of view. This explains the observed differences between the physical-mixing and master-batch preparation procedures. In the first procedure, only a minor part of the clay acts as a surfactant and enhances the asphalt/polymer interactions, while in the second procedure, the polymer/clay pre-mixing enables interactions between the clay and polymer that survive the subsequent phase of mixing with asphalt. One of the main drawbacks of APC can be related to the increase in binder viscosity due to the presence of clay. Consequently, higher temperatures may be required during paving, which is in contrast with the recent tendency to warm mix asphalts introduced to reduce temperatures traditionally required for production, laying, and compaction. Therefore, a desirable future perspective is the joining of APC and warm-mix asphalt to keep the advantages of both technologies.

8. References

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9. Acknowledgements

Filippo Merusi wants to address a special thanks to Roberto De Renzi for his permanent, continuous and essential support.

10. Appendix A – List of abbreviations

G*	magnitude of the complex modulus
AFM	atomic force microscopy
APC	asphalt/polymer/clay system
ARP	asphaltene rich phase
B	butadiene
BHDPE	bimodal high density PE
BT	sodium bentonite
CLSM	confocal laser scanning microscopy
CS	complete solubility
DMA	dynamic mechanical thermal analyses
DSCB	degree of short chain branching
EAA	poly(ethylene-co-acrylic acid)
EBA	poly(ethylene-co-butyl-acrylate)
EMA	poly(ethylene-co-methyl acrylate)
EPDM	ethylene-propylene diene monomer
ESEM	environmental scanning electron microscopy
EVA	poly(ethylene- <i>r</i> -vinyl acetate)
FM	fluorescence microscopy
FTIR	Fourier transfer infrared spectroscopy
GMA	glycidylmethacrylate
HDPE	high density poly(ethylene)
HSP	Hildebrand solubility parameter
I_c	instability colloidal index, or Gaestel index
I_s	separation index
LAST	laboratory asphalt stability test
LDPE	low density poly(ethylene)
LLDPE	linear low density poly(ethylene)
MAH	maleic anhydride
MB	master batch
MDSC	modulated differential scanning calorimetry
MFI	melt flow index
MMT	montmorillonite
M_n	number average molecular weight
MW	molecular weight
M_w	weight average molecular weight
OBT	organomodified sodium bentonite
OMMT	organomodified montmorillonite
PBA	polybutyl acrylate
PEA	polyethyl acrylate
PI	phase inversion
PLS	polymer/layered silicate
PM	physical mix
PMA	polymer modified asphalt

POE	octane-ethylene copolymer
POM	polarized optical microscopy
PP	polypropylene
PPA	polyphosphoric acid
PRP	polymer rich phase
RET	reactive ethylene terpolymers
S	styrene
SAH	succinic acid
SARA	saturates, aromatics, resins, asphaltenes
SBS	poly(styrene- <i>b</i> -butadiene- <i>b</i> -styrene) block copolymer
SEBS	poly(styrene- <i>b</i> -ethylene-butene- <i>b</i> -styrene)
SEM	scanning electron microscopy
SHRP	Strategic Highway Research Program
SIS	poly(styrene- <i>b</i> -isoprene- <i>b</i> -styrene)
TEM	Transmission Electron Microscopy
T _g	glass transition temperature
TLC-FID	thin layer chromatography with flame ionization detection
TPE	thermoplastic elastomers
UCST	upper critical solution temperature
WTP	waste tire powder
$\Delta S = S_t - S_b$	difference between the softening points of top (S_t) and bottom (S_b) sections of the tube test

Greek symbols

δ phase angle

11 Tables

Table 1. Physico-chemical characteristics of the polyethylenes (Table 1 of [102]). M_n = number-average molecular weight, and M_w = weight-average molecular weight.

PE	M_w	M_w/M_n	DSCB (CH ₃ /1000C)
HDPE1	247,500	18.5	-
HDPE2	171,000	7.7	0.77
m-LLDPE1	142,000	1.7	10.8
m-LLDPE2	115,000	1.7	10.5
m-LLDPE3	96,500	2.5	12.8

Table 2. Polymer characteristics (adapted from Table 1 of [126]).

Polymer	M_n (g/mole)	M_w (g/mole)	M_w/M_n	VA content (w%)	Storage stability (%)
LDPE1	7,400	72,000	9.7	-	9
LDPE2	8,300	103,000	12.4	-	3
EVA1	7,600	36,000	4.7	19.0	5
EVA2	5,800	30,000	5.2	27.5	18

Table 3. Composition and storage stability of the blends (adapted from Table 2 of [133]).

Polymer	Polymer content (%)	ΔS (°C)
LDPE	3	Polymer separation and agglomeration
	4	
	5	
	6	
GMA-g-LDPE	3	0.8
	4	1.1
	5	1.5
	6	2.5

Table 4. Blend compositions and tube-test results (from Tables 3 and 5 of [258]).

Sample ID	HDPE/SBS/LLDPE-g-MAH	ΔS (°C)
a	4/1.3/0.13	15
b	4/1.3/0.27	2.75
c	4/1.3/0.4	0.15
d	4/1.3/0.0	25.5

Table 5. Effect of Kaolinite (KC) content on the high-temperature storage stabilities of SEBS/KC-modified asphalts (from Table 4 of [311]).

Formulation		S (°C)		
SEBS % (w/w)	SEBS/KC (w/w)	Top (S _t)	Bottom (S _b)	ΔS
3	100/0	53.0	50.0	3.0
3	100/50	52.5	52.8	-0.3
4	100/0	57.0	53.8	3.2
4	100/10	56.5	50.8	5.7
4	100/30	55.0	52.0	3.0
4	100/50	55.5	55.8	-0.3
4	100/50 ^a	59.0	52.0	7.0
4	100/70	52	52.5	-0.5
5	100/0	70.5	58.0	12.5
5	100/50	57.0	58.0	-1.0
6	100/0	85.0	67.5	17.5
6	100/50	59	60.5	-0.5

^a mix prepared using PM.

12. Figure captions

- Figure 1 Qualitative behavior of a generic property “P” as a function of polymer swelling.
- Figure 2 Viscosity as a function of time while mixing SBS with two different base asphalts (B and M) at two different shear rates (Figure 1 of [20]).
- Figure 3 a) Virgin block copolymer and b) swollen copolymer. The gray dots represent the asphalt molecules, which are mainly located in the soft matrix.
- Figure 4 Schematic representation of typical morphologies observable using FM.
- Figure 5 Relationship between I_s and asphalt composition and between I_s and I_c (Figures 4 and 5 of [47]).
- Figure 6 HSP for the PS and PB blocks and asphalt fraction (adapted from Table 1 of [58]).
- Figure 7 Phase diagram reported by Varma et al. [67] (Figure 4 of [67]).
- Figure 8 1,4 and 1,2 addition in butadiene polymerization.
- Figure 9 Morphology of PE-modified asphalts: a) 1% HDPE1 and b) mLLDPE2 (Figure 1 of [102]).
- Figure 10 Particle size distribution for a PMA prepared with 1% LDPE (Figure 5 of [107]).
- Figure 11 Morphology of binders containing 1% recycled EVA: (a) before storage, (b) top after storage, and (c) bottom after storage (Figure 11 of [127]).
- Figure 12 Morphology of the LDPE and GMA-g-LDPE binders (Figure 5 of [133]).
- Figure 13 Polymer mapping in SBS-modified asphalt (Figure 4 from [46]).
- Figure 14 (a) FM and (b) SEM images of a 12 % SBS-modified asphalt (Figures 1 and 2 of [185]).
- Figure 15 AFM images of (a) base asphalt, (b) aged asphalt, (c) SBS-modified asphalt, and (d) aged SBS-modified asphalt (Figure 3 of [189]).
- Figure 16 Microstructures of melt-processed maltene/SEBS blends with maltene content (by weight) of: a) 10%, b) 20%, c) 30%, d) 40%, e) 50%, and f) 80. (derived from Figure 4 of [58])
- Figure 17 Qualitative behavior of a viscosity function with shear thickening and two shear thinning phenomena.
- Figure 18 Morphology development with the mixing time of SBS-modified asphalt with sulfur. (Figure 8 of [246]).
- Figure 19 Optical microscopy of the four blends of Table 4 (Figure 2 of [258]).
- Figure 20 Schematic illustration of three different types of PLS nanocomposites (Figure 4 of [279]).
- Figure 21 Viscosities of MMT- and OMMT-modified asphalts as a function of clay content. (Figure 3 of [300]).
- Figure 22 Schematic representation of physical-mix and master-batch procedures (A = asphalt, P = polymer, C = clay).
- Figure 23 XRD patterns of BA, 20A, SBS/20A = 95/5, BA/20A = 95/5, BA/SBS/20A = 93.3/4/2.7 PM, and BA/SBS/20A = 93.3/4/2.7 MB. All ratios are in w/w (Figure 1 of [315]).
- Figure 24 FM of (a) BA/SBS (b) BA/SBS/20A PM, and (c) BA/SBS/20A MB.

Figure 25 FM of (a) BA/EVA, (b) BA/EVA/20A PM, (c) BA/EVA/20A MB, (d) BA/EVA/43B PM, and (e) BA/EVA/43B MB (from Figure 1 of [316]).

Figure 26 AFM images of (a) BA, (b) BA/SBS, and (c) BA/SBS/OMMT on a scale of 15 $\mu\text{m} \times 15 \mu\text{m}$ (Figure 4 of [306]).

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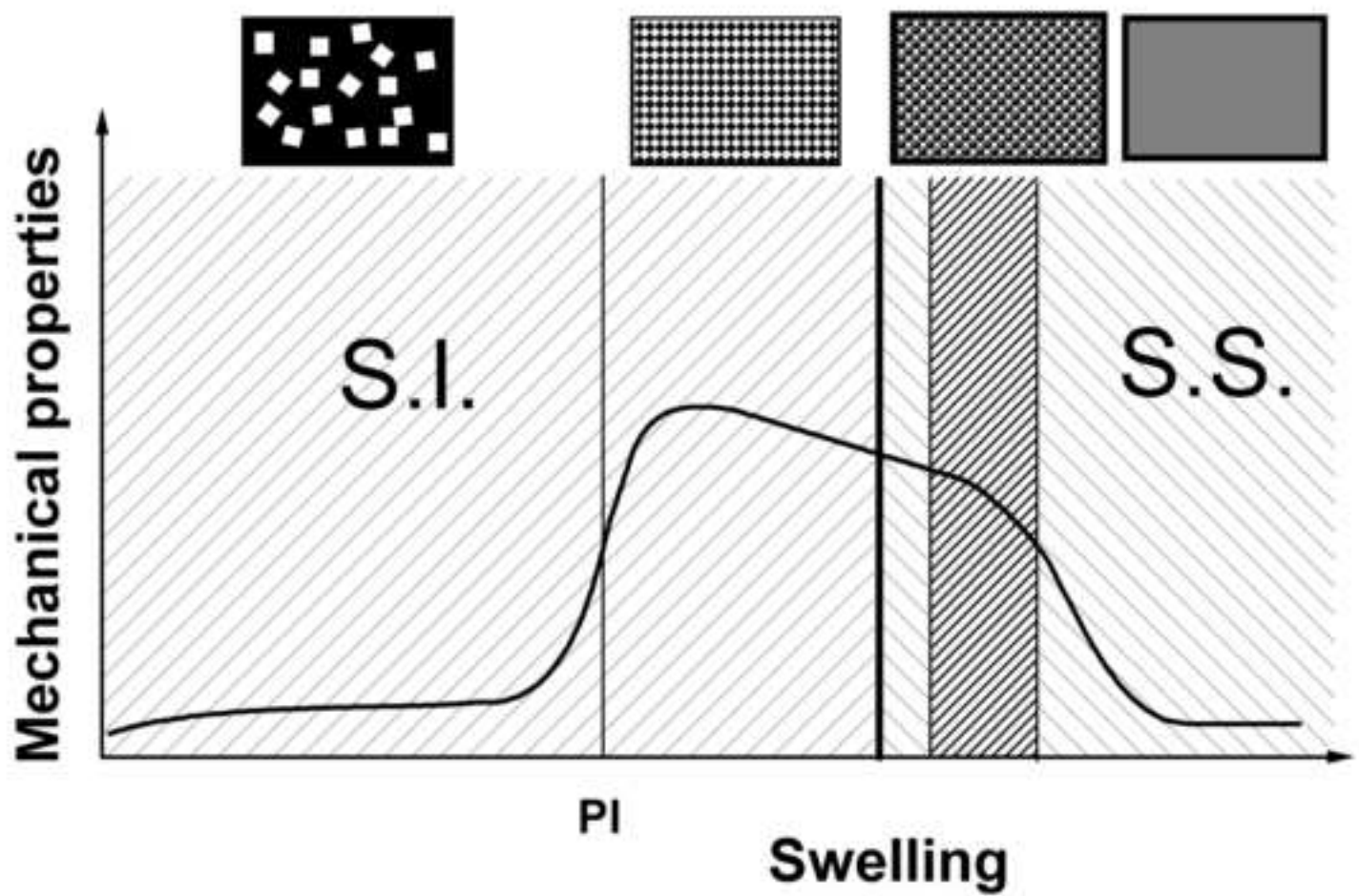


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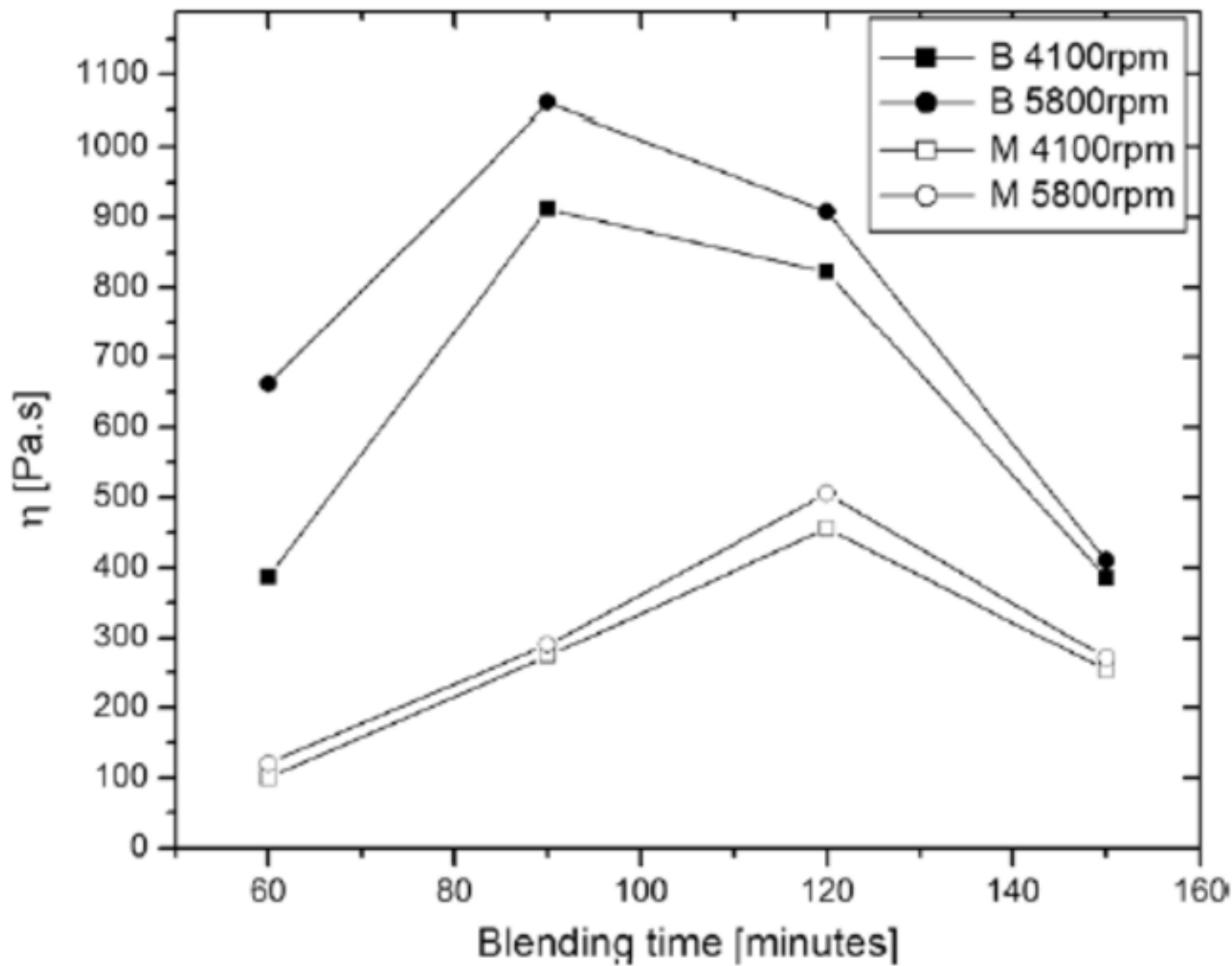


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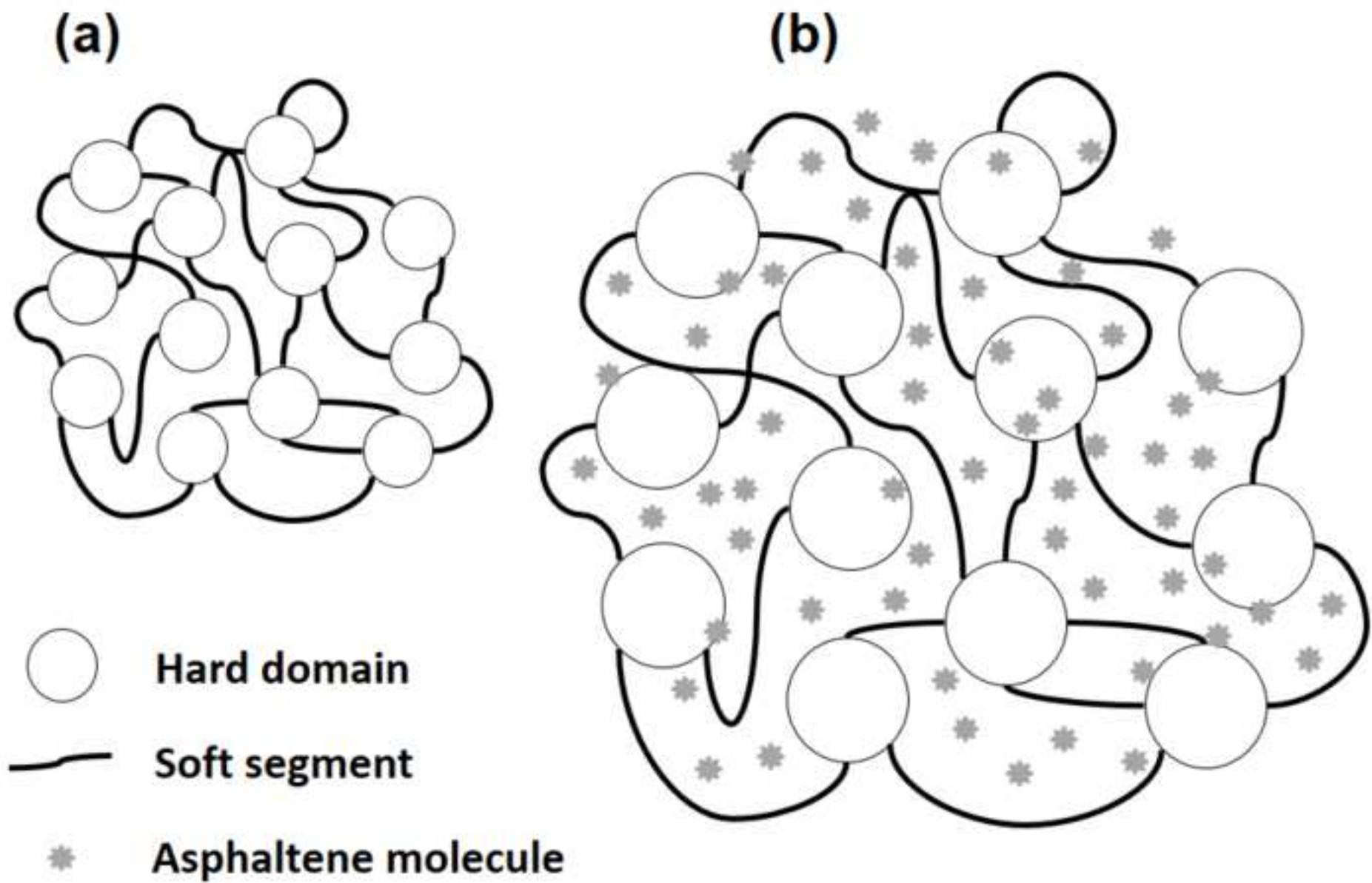


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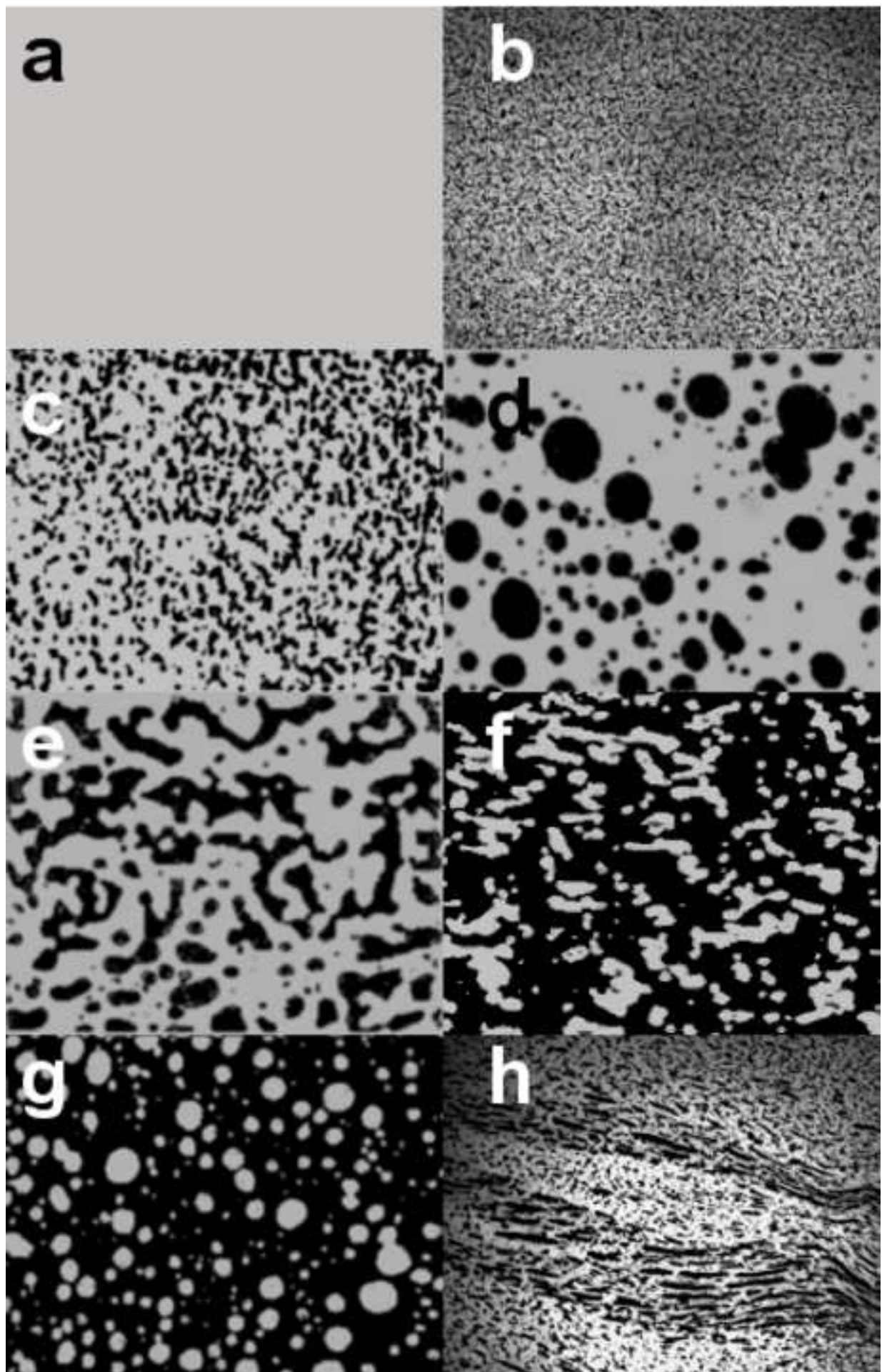


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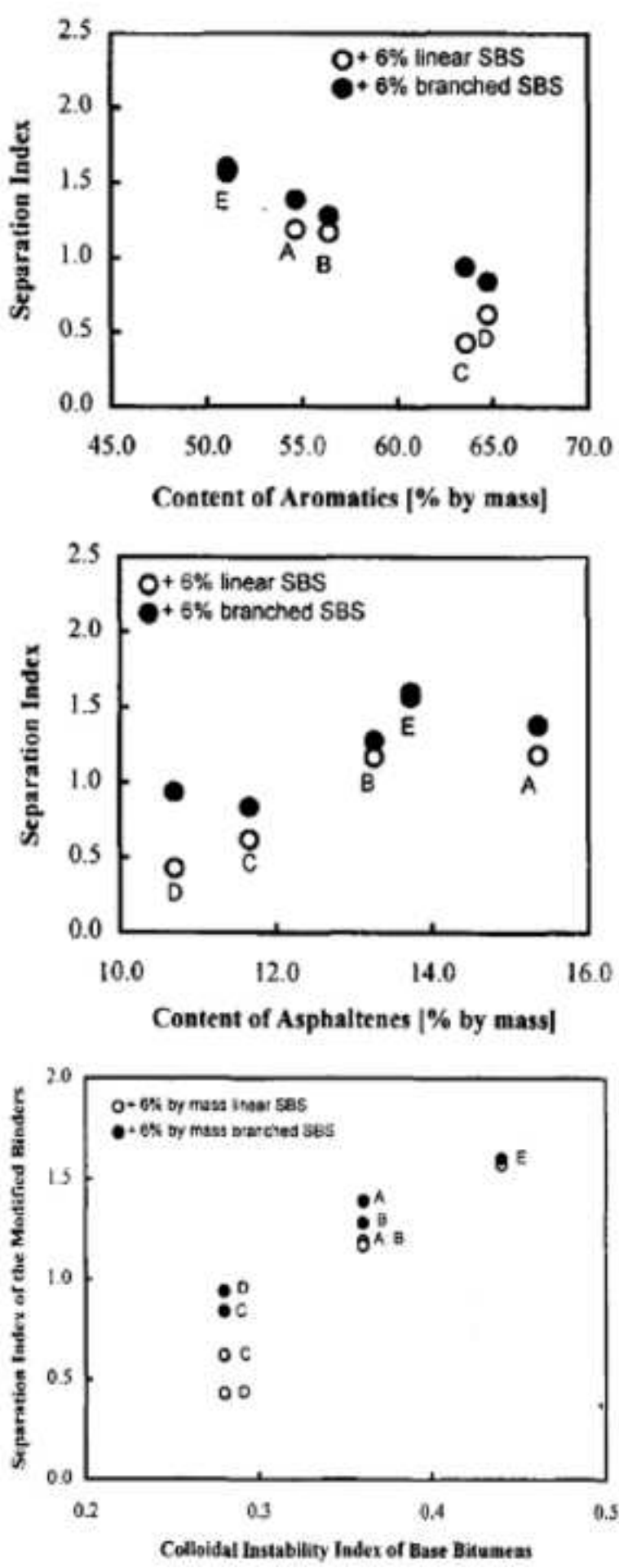


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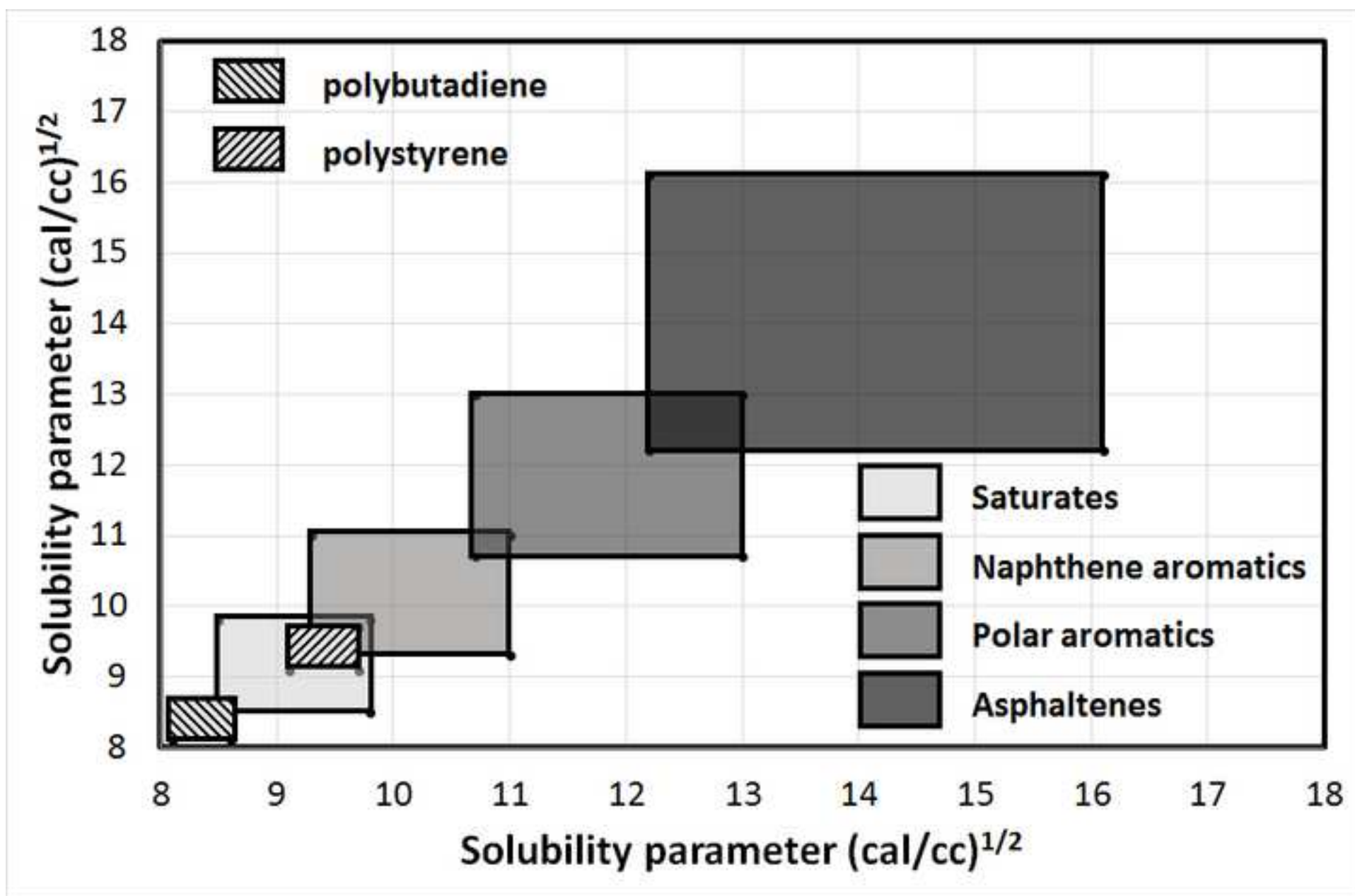
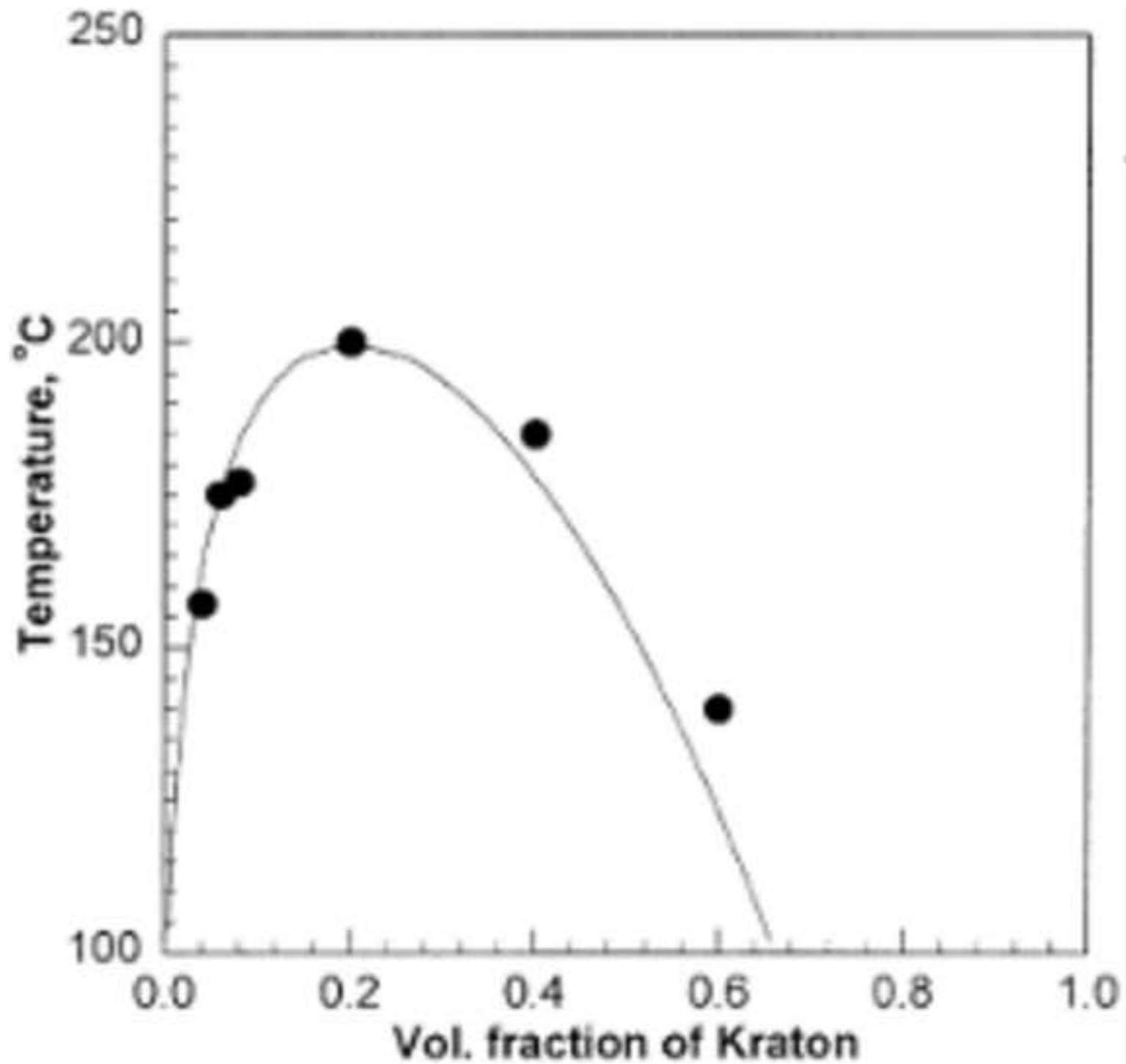


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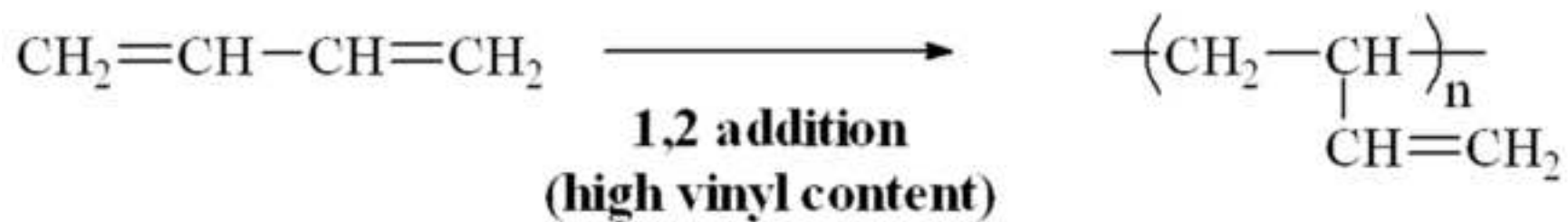


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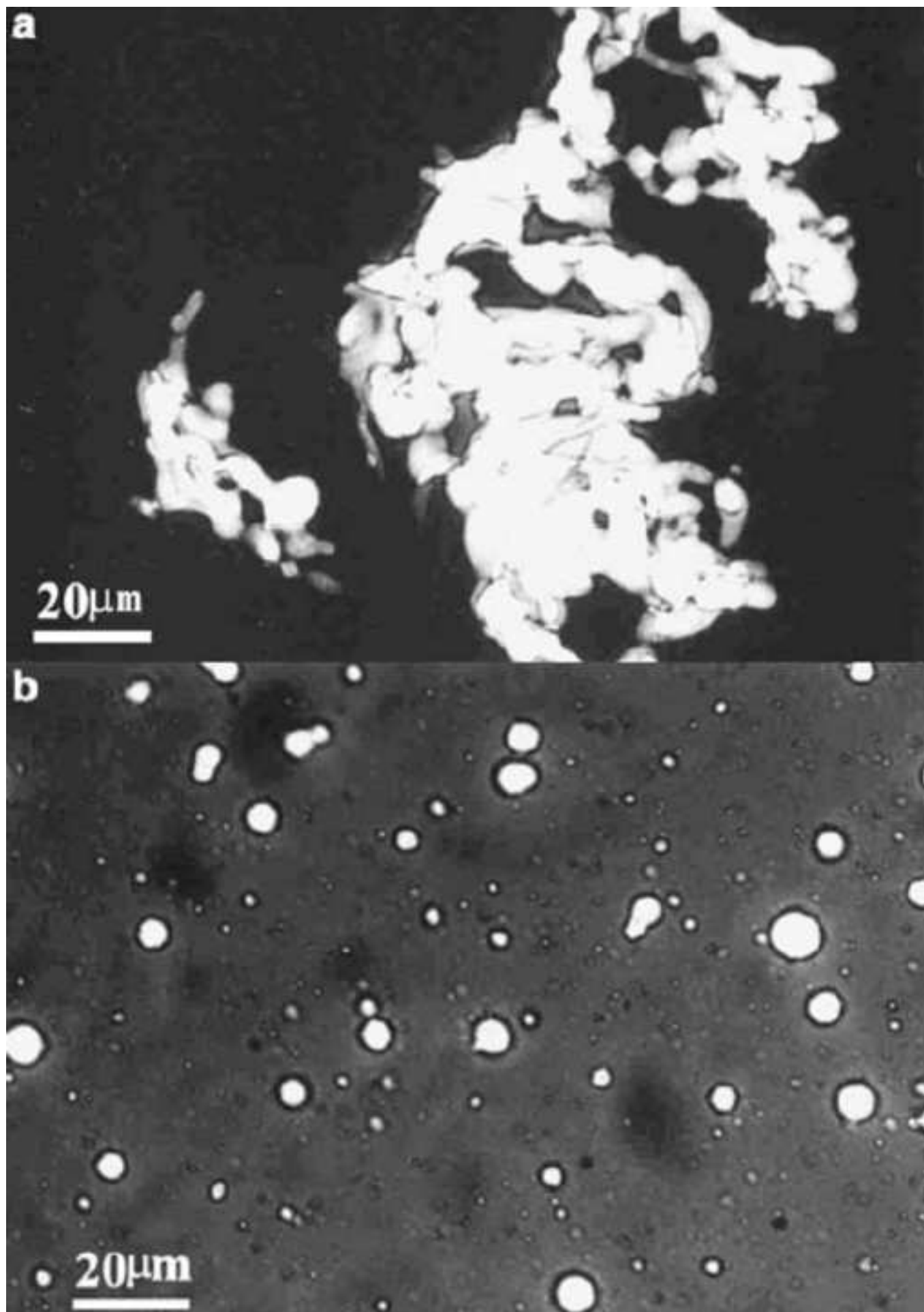


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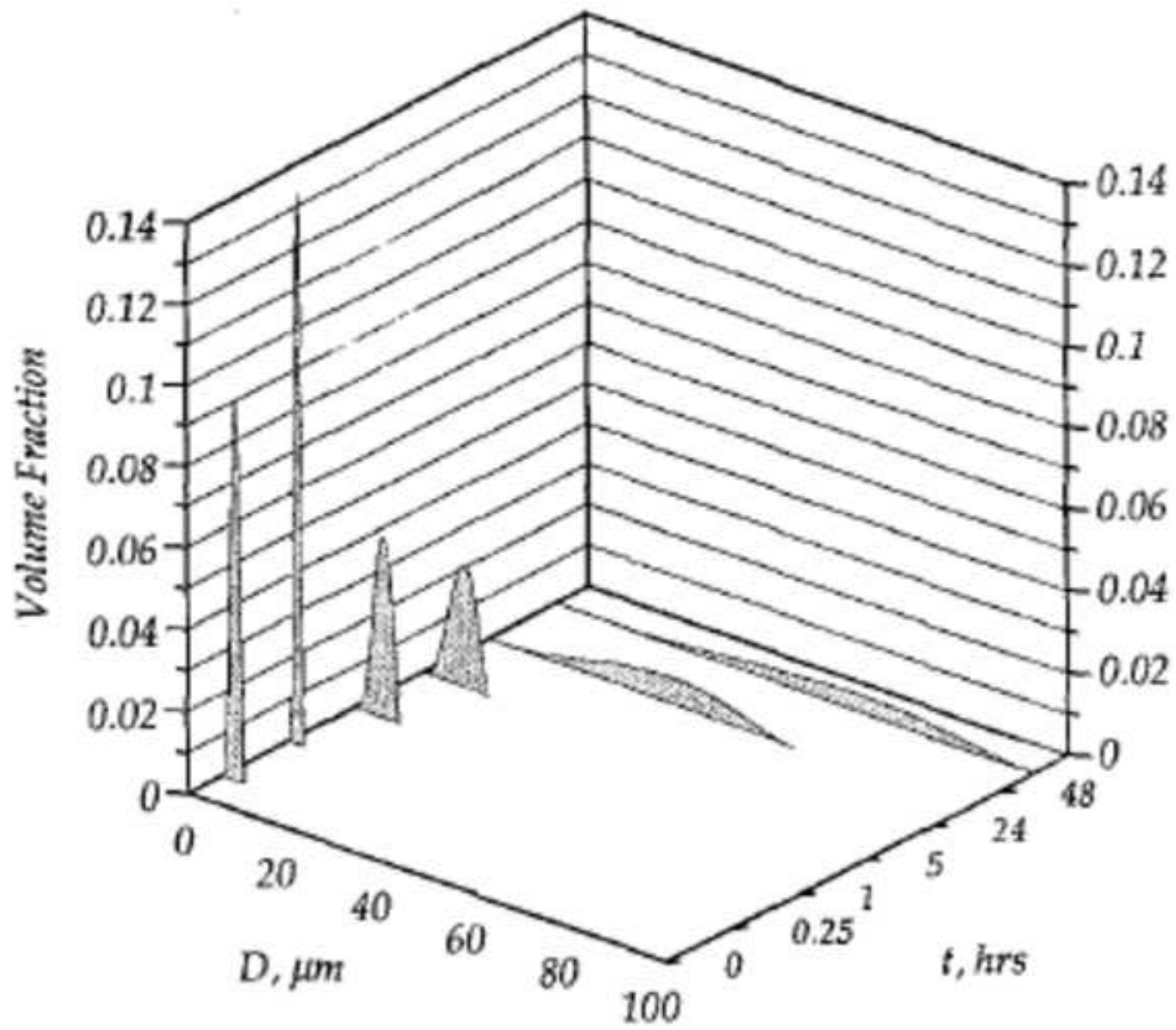


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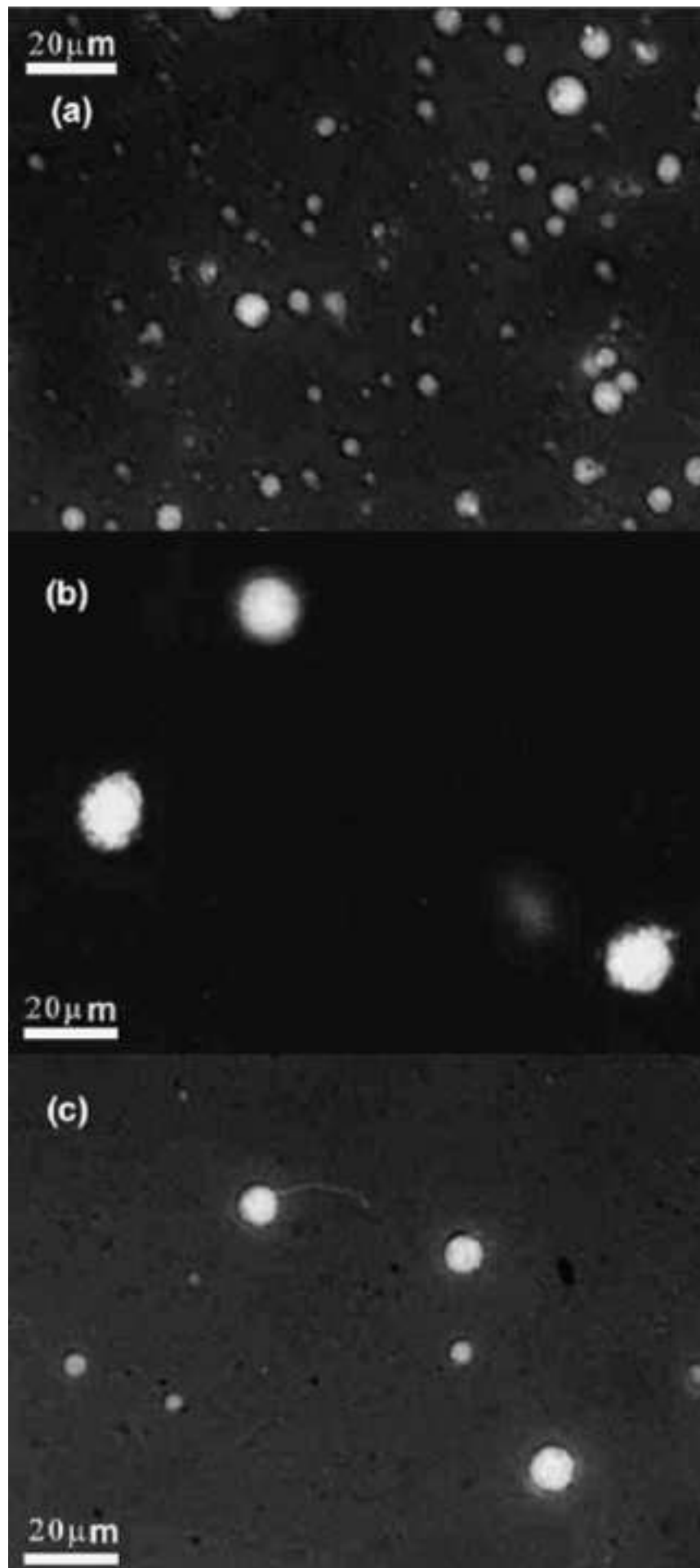


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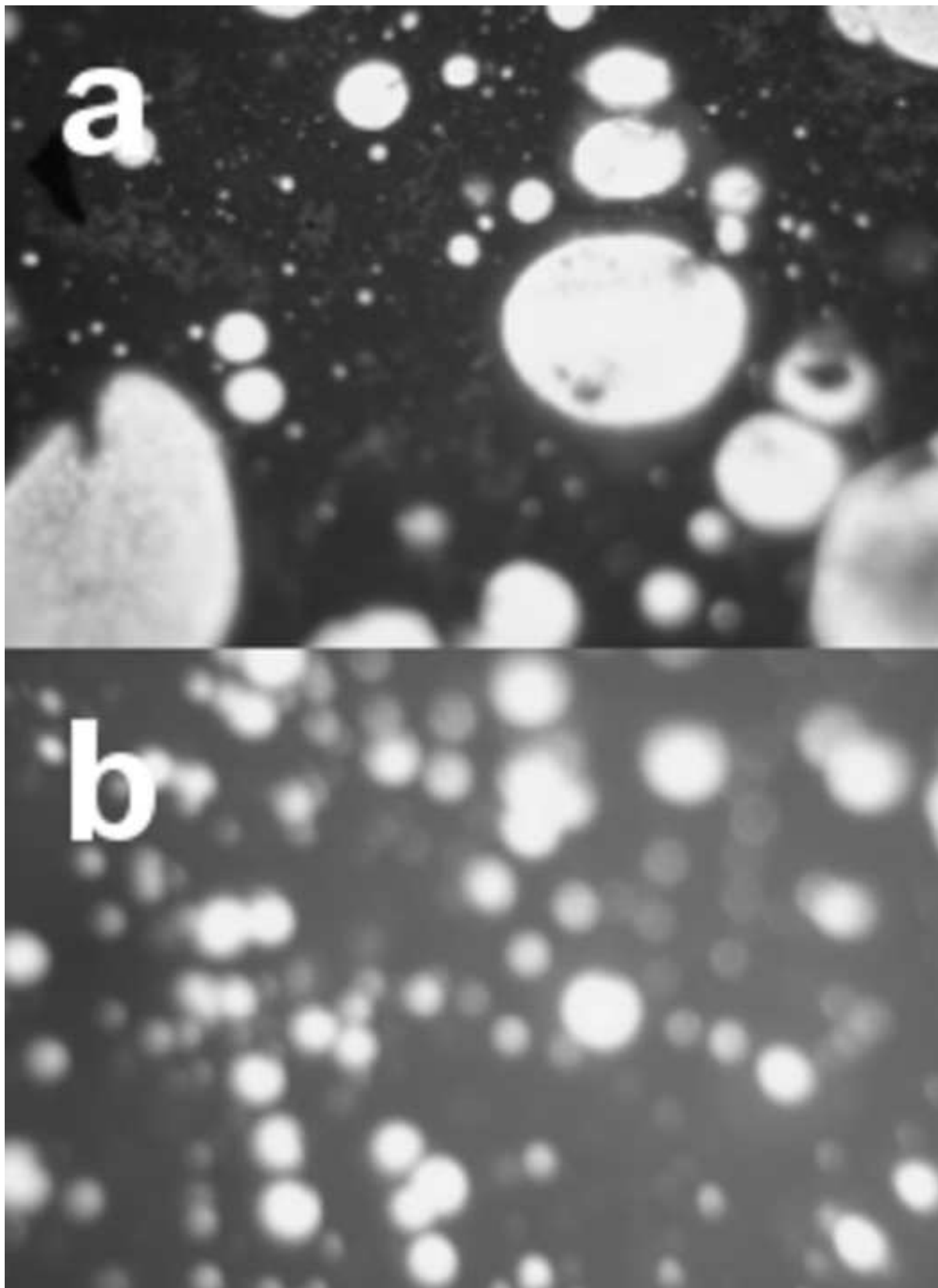


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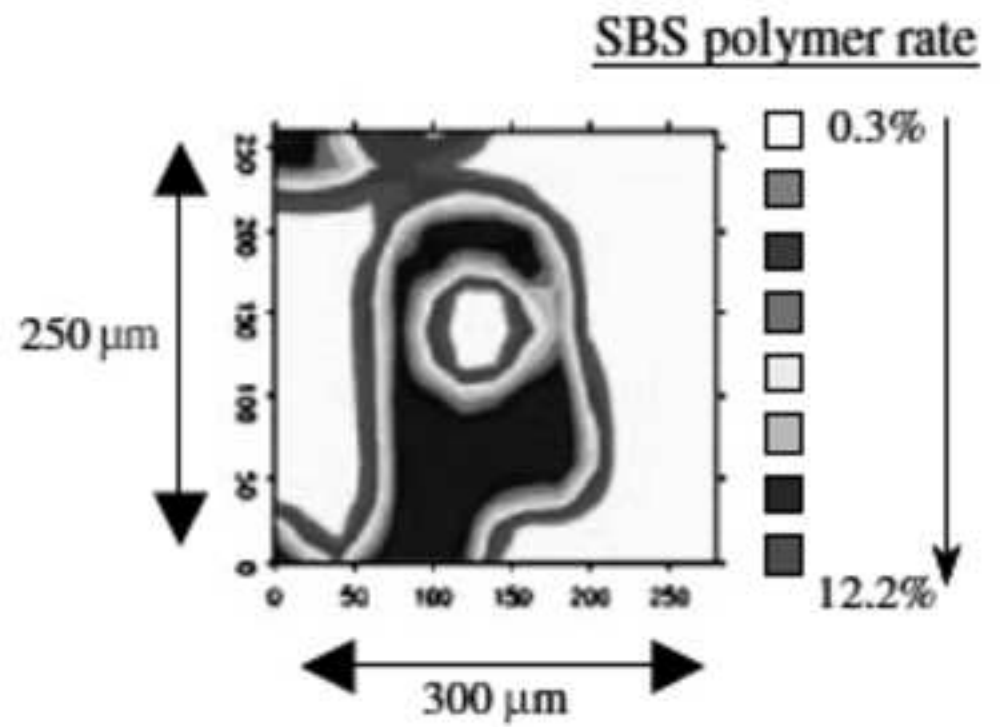


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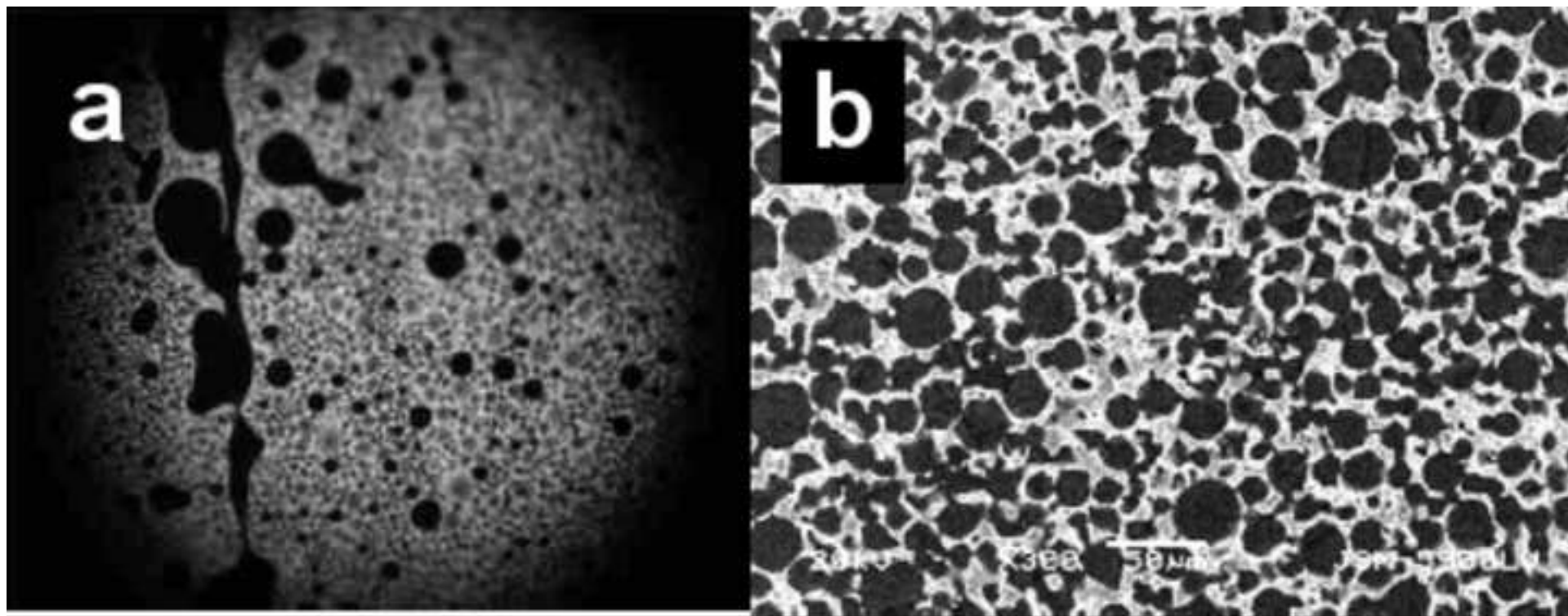


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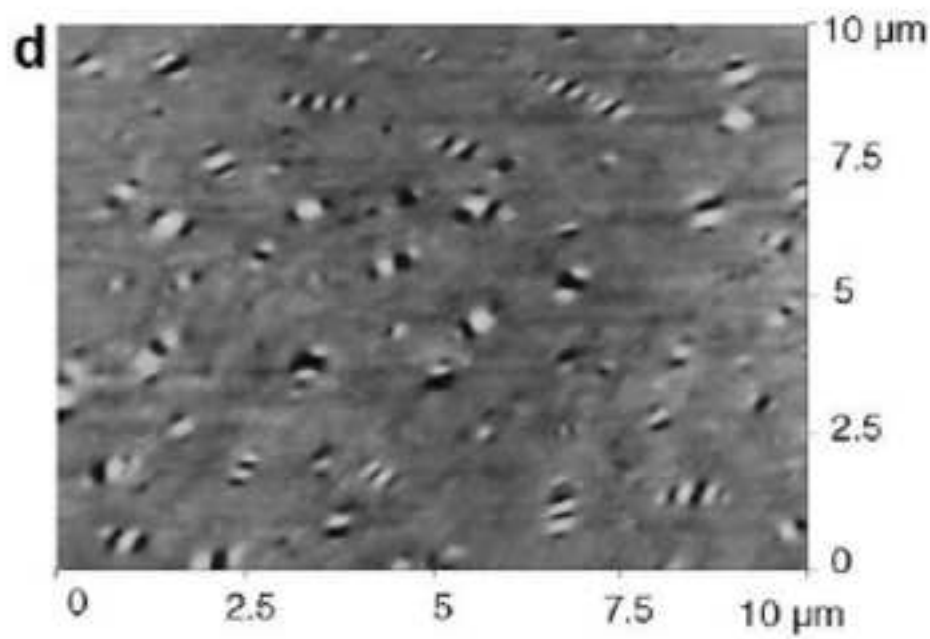
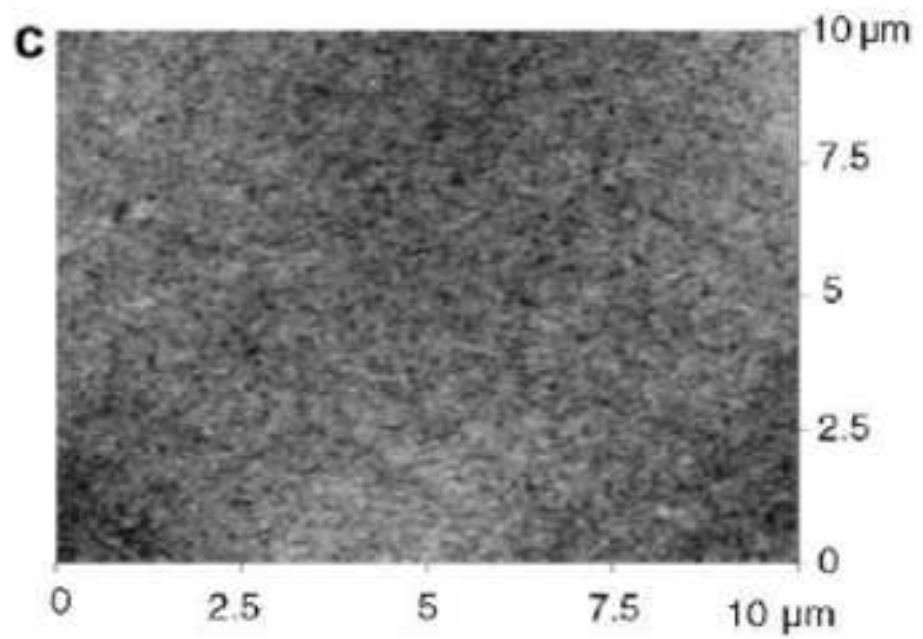
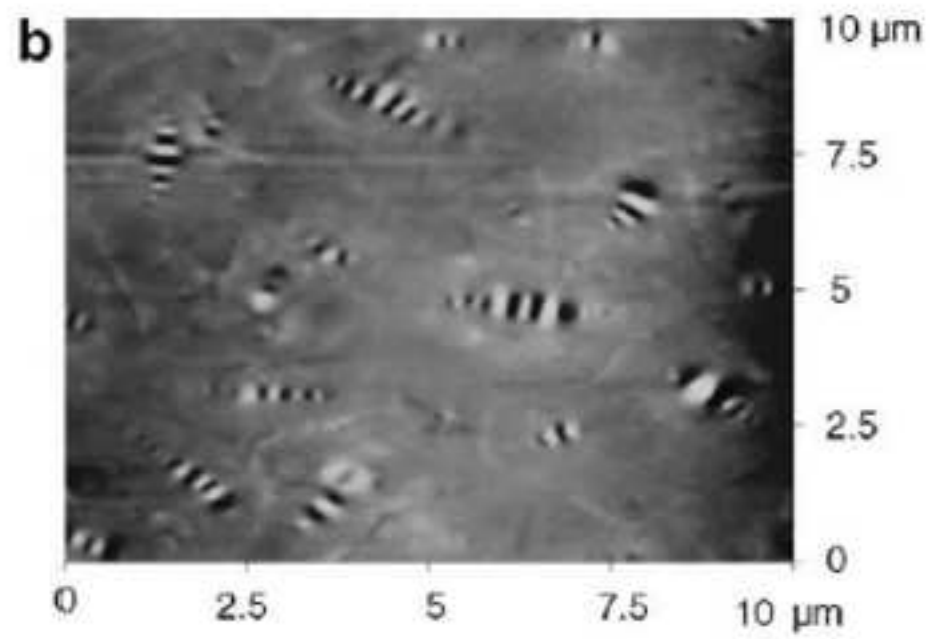
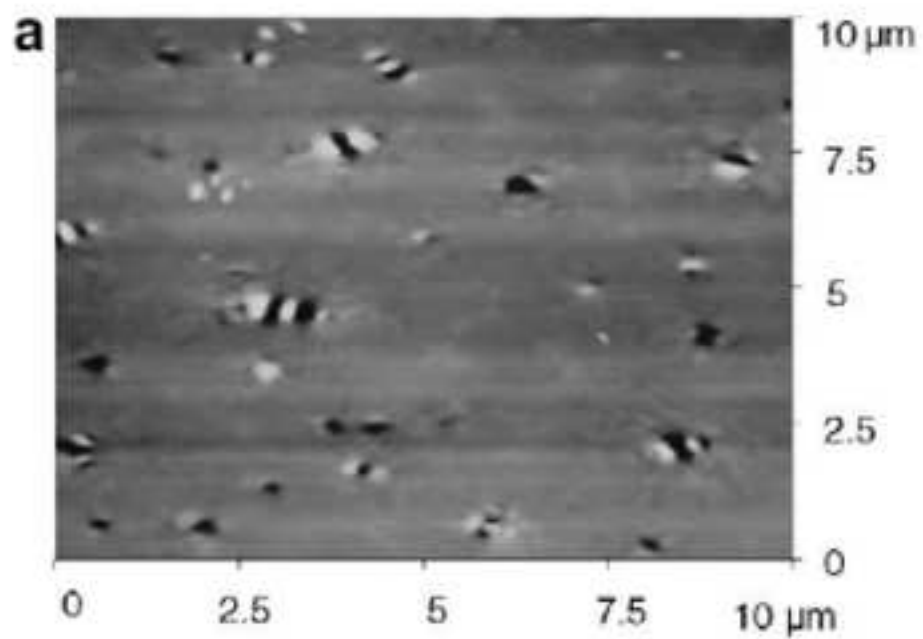


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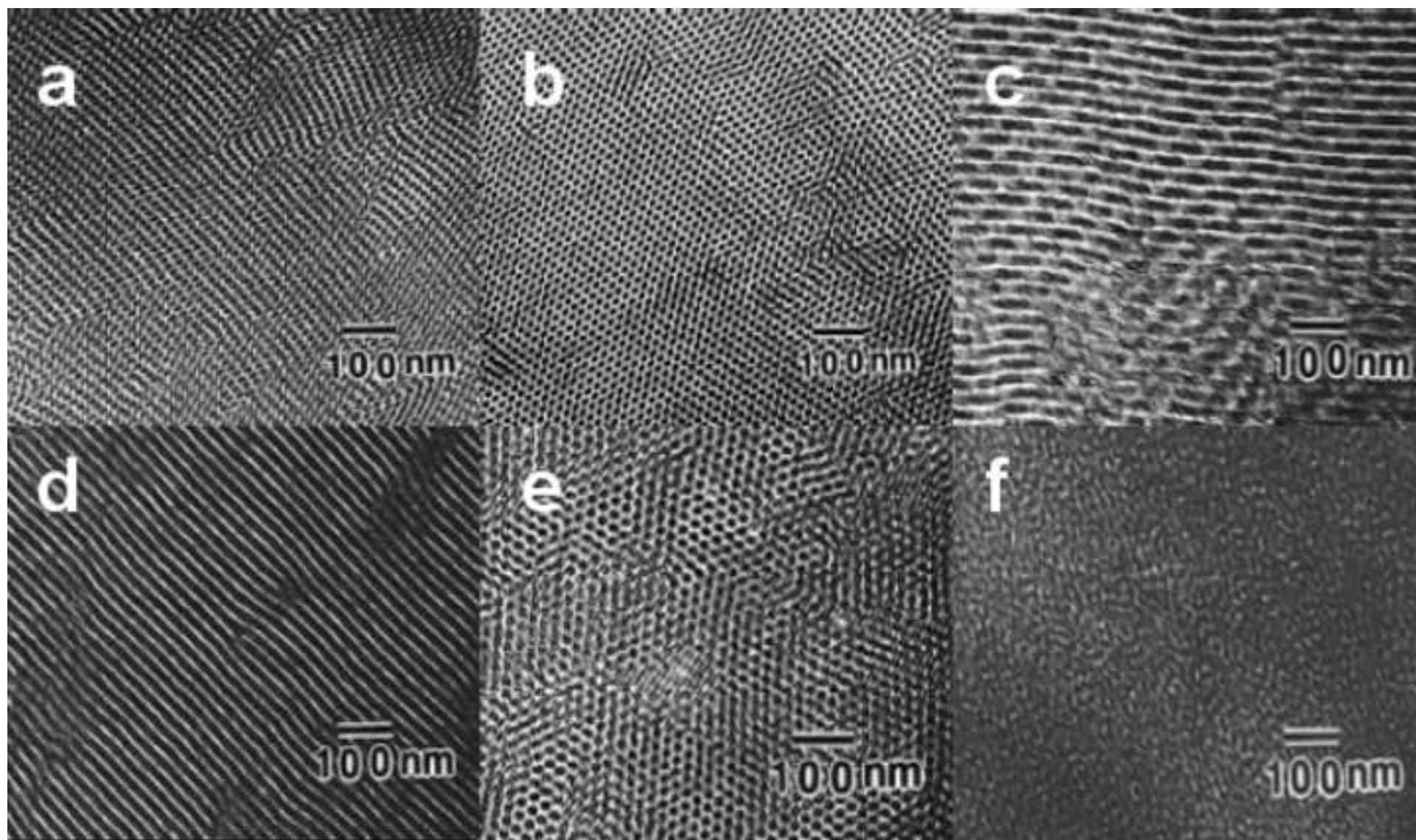


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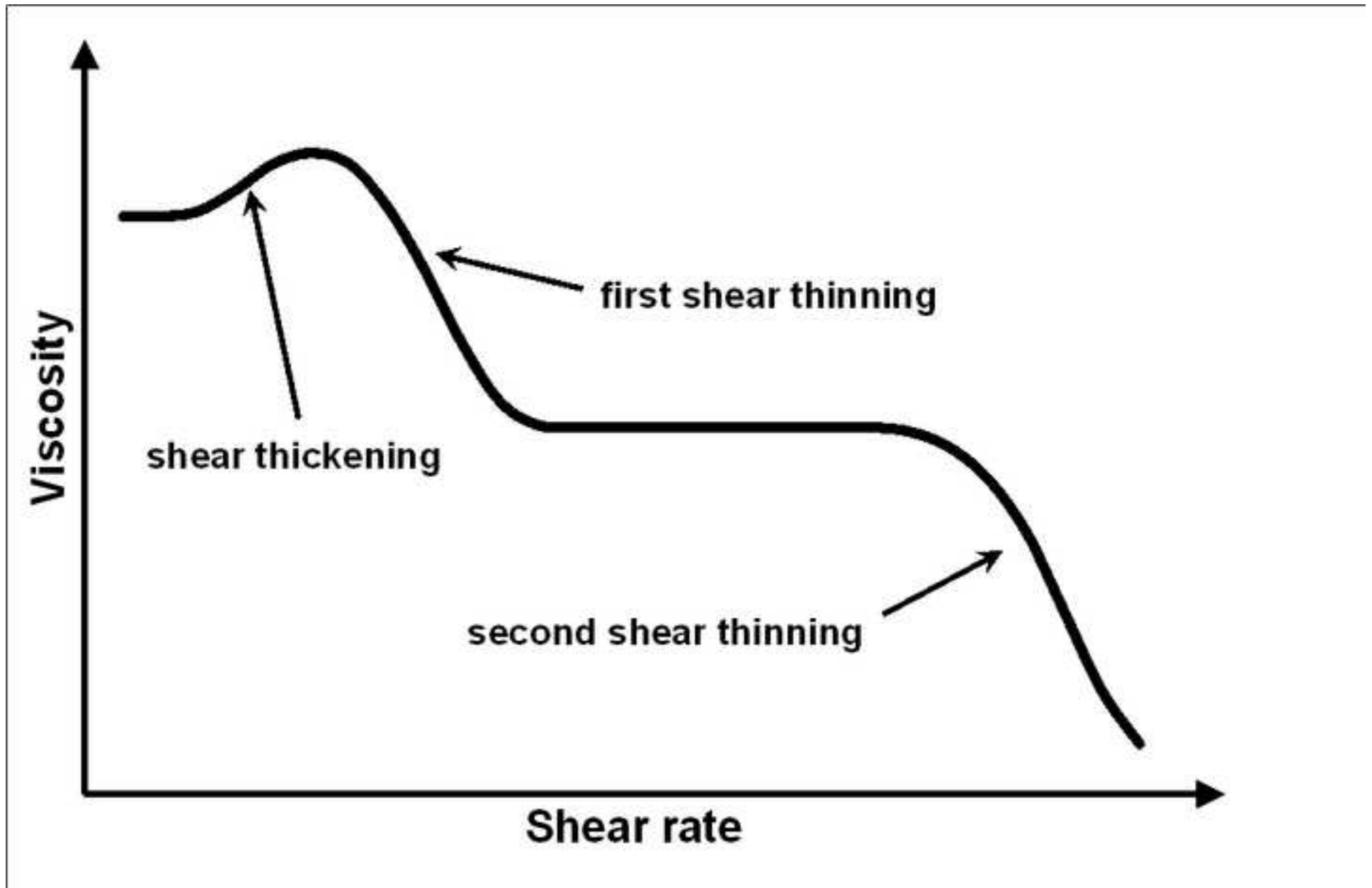


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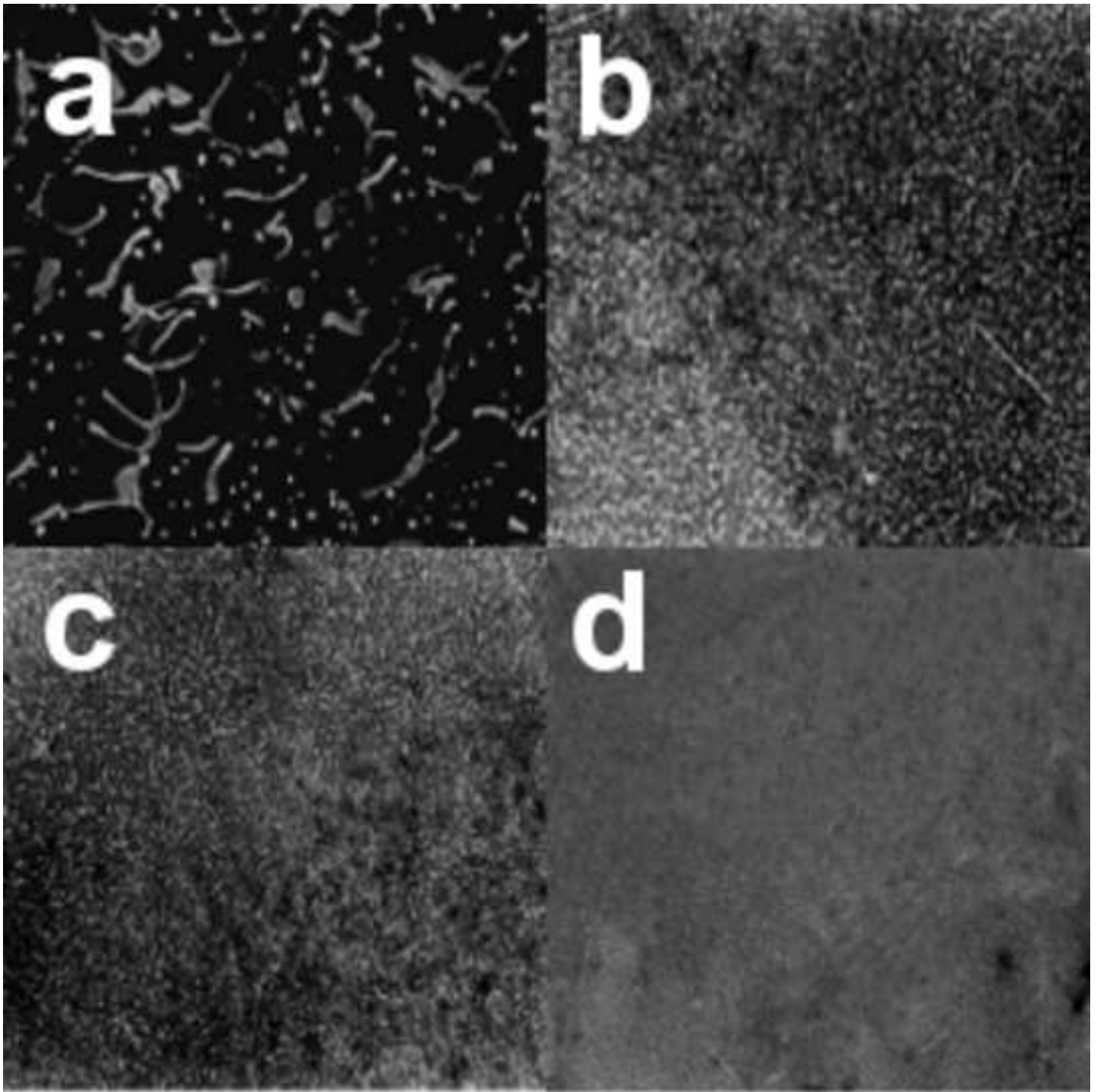


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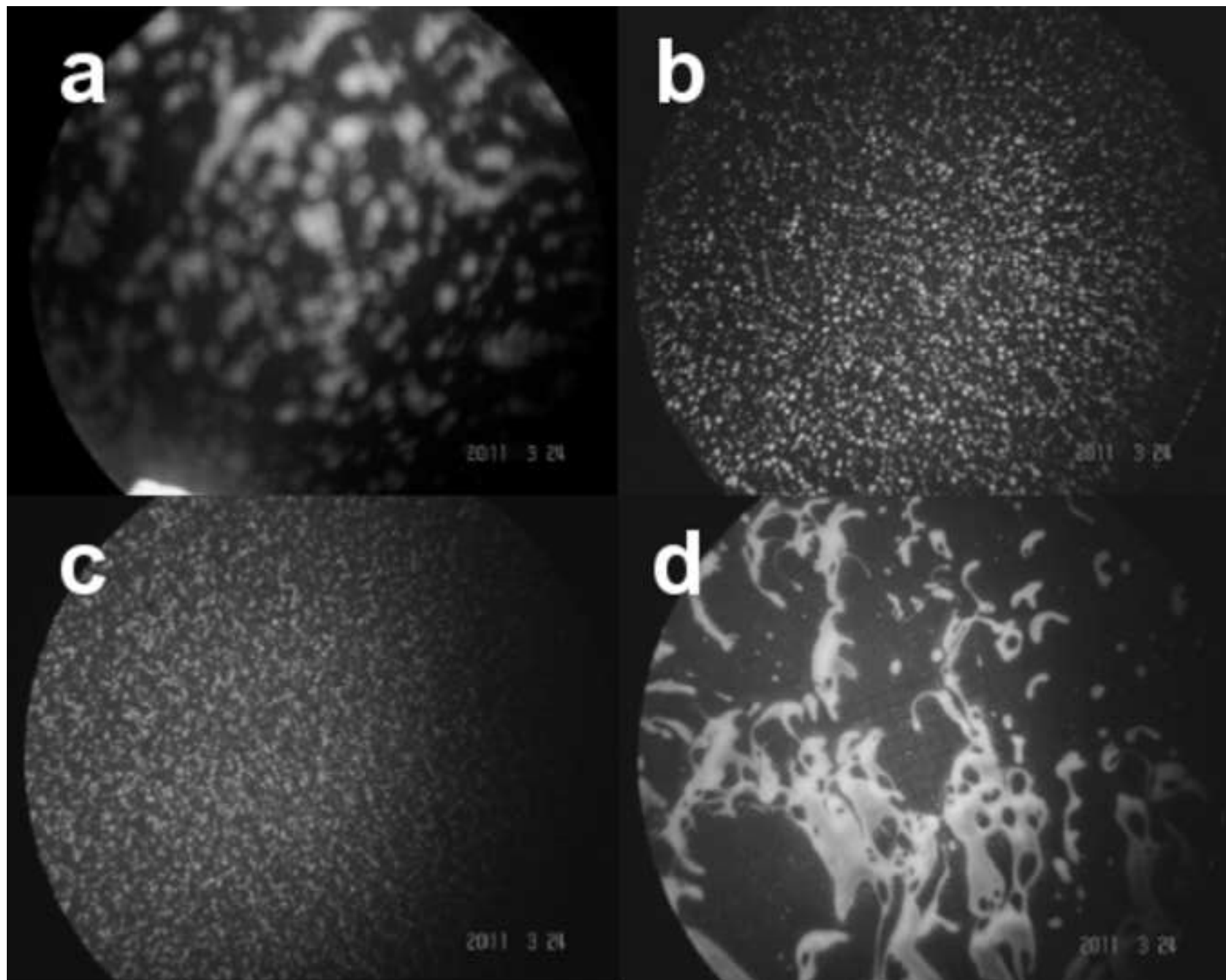


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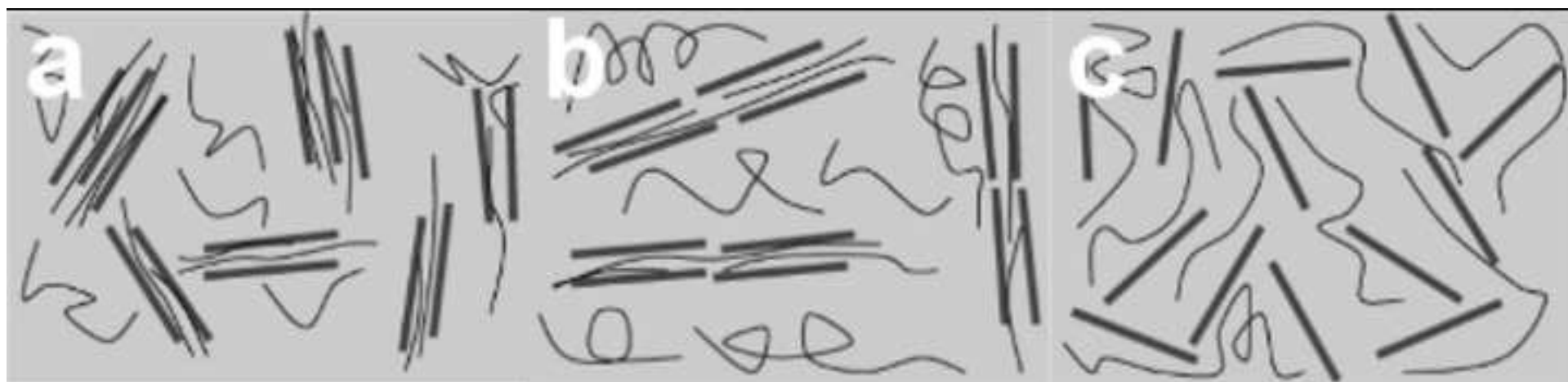
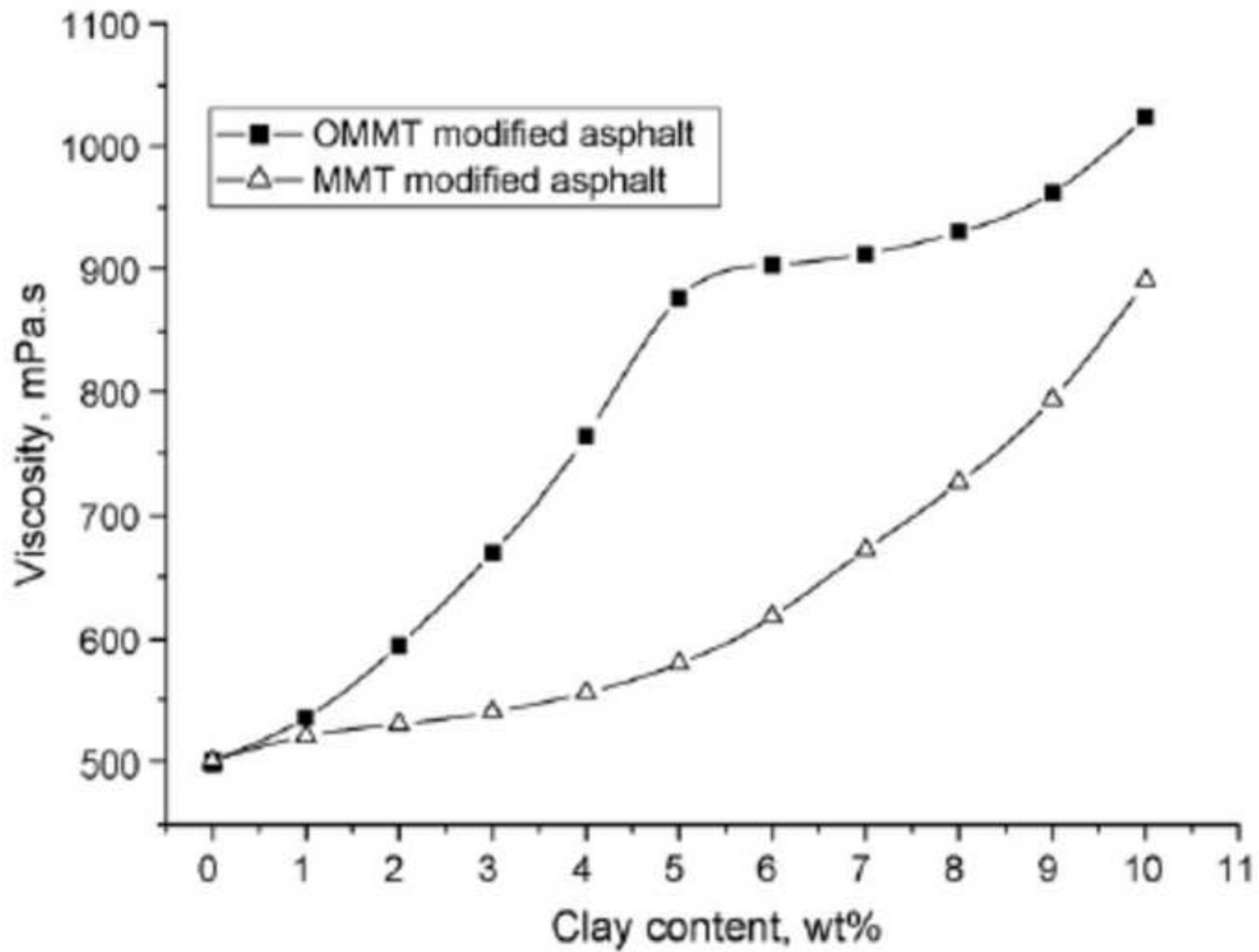
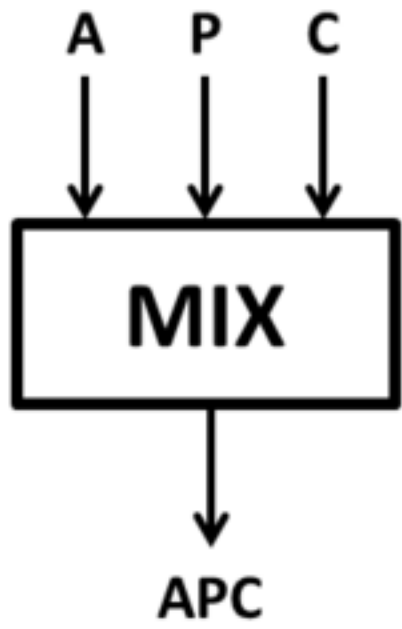
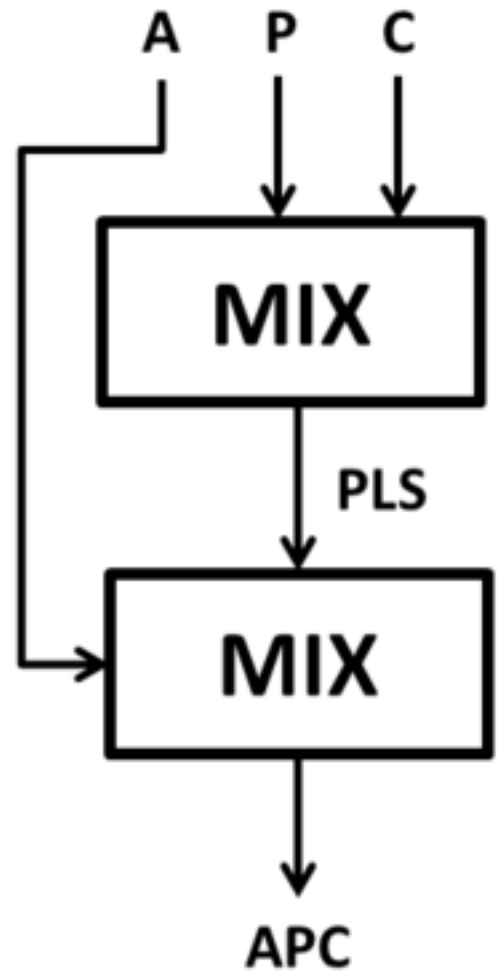


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Physical Mix



Master Batch

Figure 23

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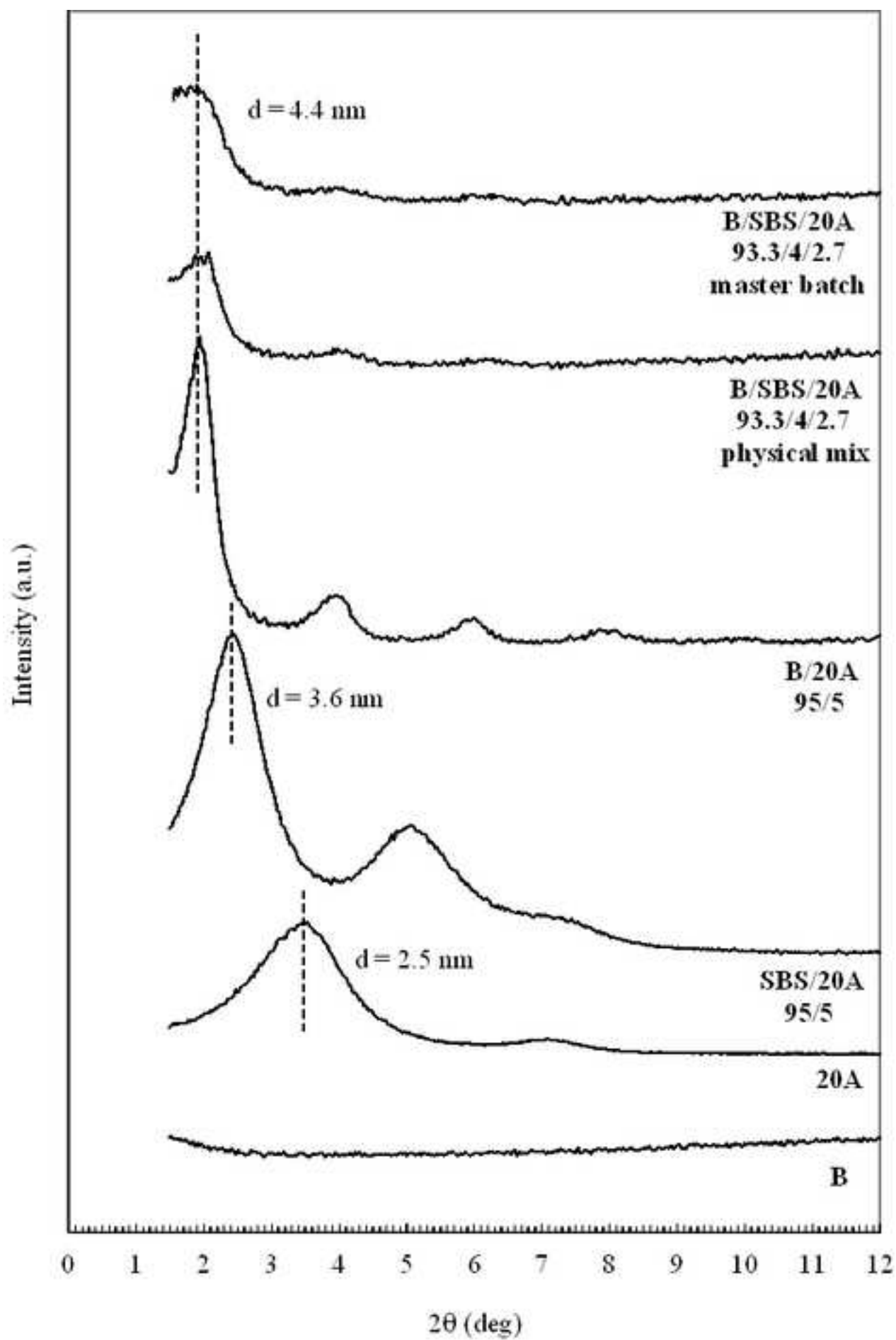


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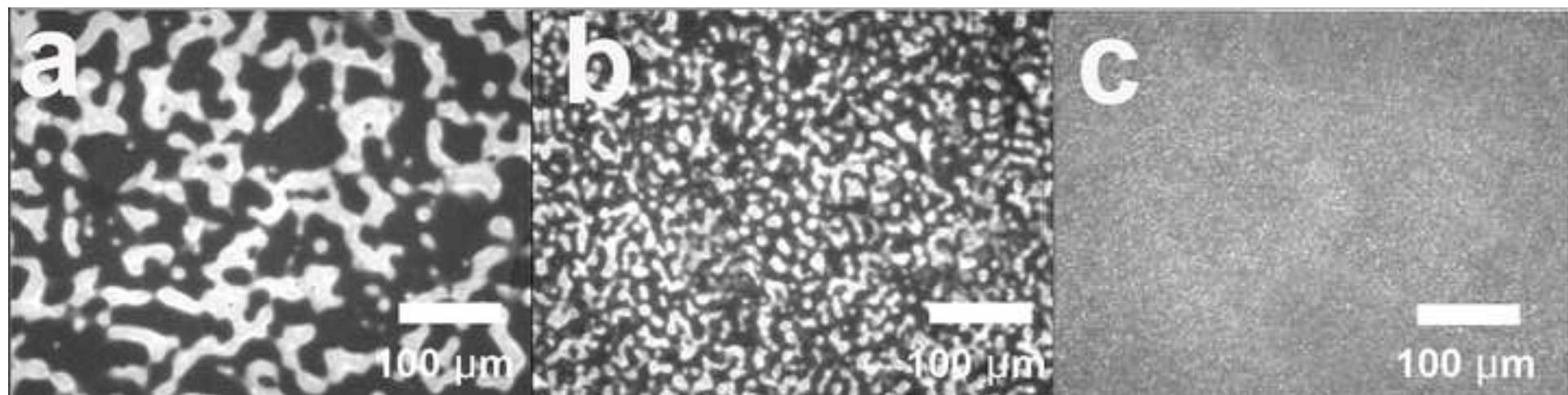


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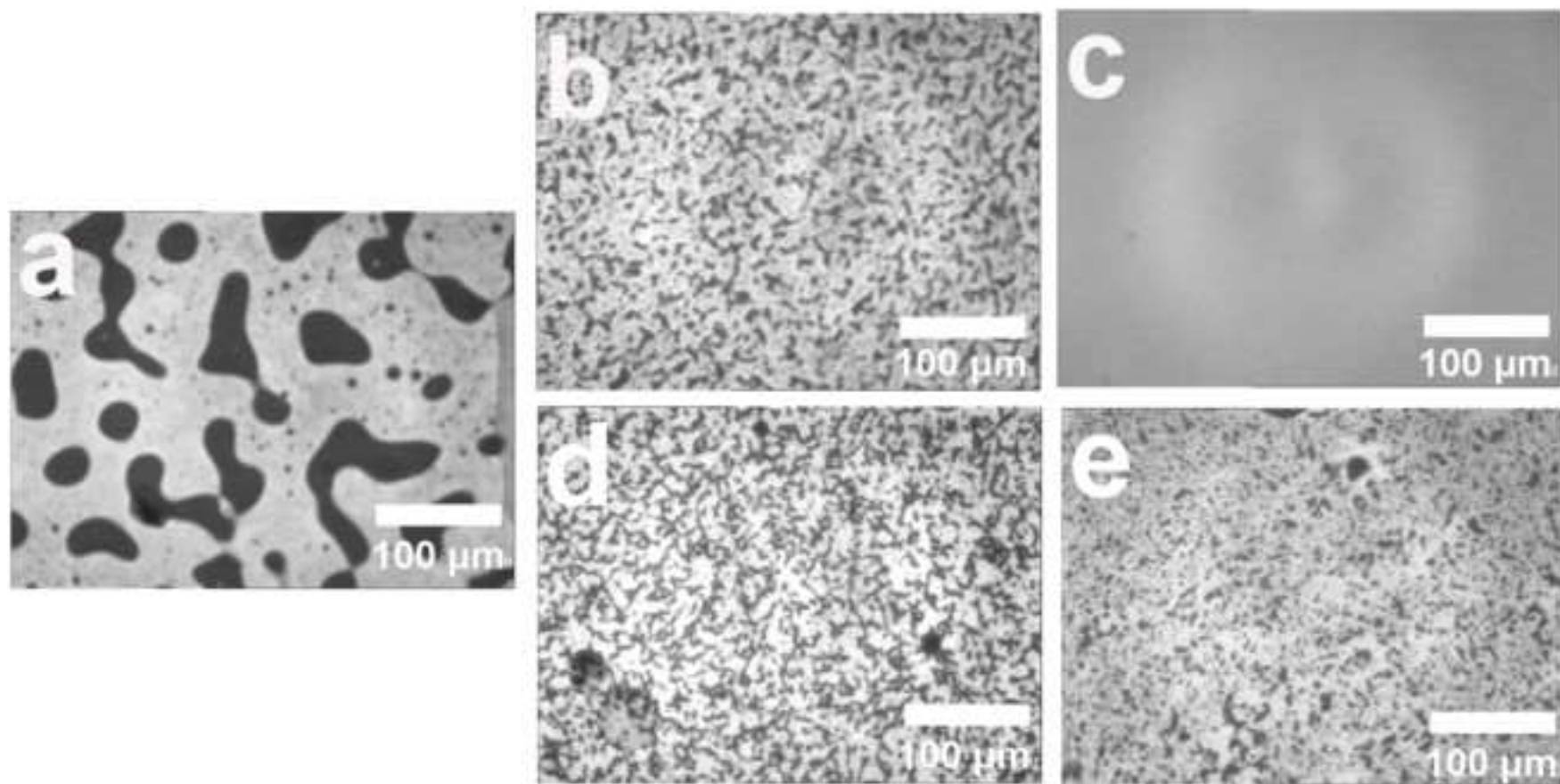


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