

Co-agent mediated functionalization of LDPE/iPP mixtures and testing as compatibilizer with WEEE-recovered PVC

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Abstract.

Mixtures of LDPE/iPP 80/20 w/w were functionalized in the melt by using maleic anhydride (MAH) as the functionalizing agent, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (L101) as the peroxide initiator and butyl 3- (2-furyl) propenoate (BFA) as a coagent suitable to prevent the degradation of iPP and to promote the inter-macromolecular reactions. The use of BFA aimed at favouring the control of radical-induced side reactions and the formation of interfacial graft copolymers. The functionalization degree (FD) and the modification of macromolecular architecture, which were

evaluated by selective solvent extractions combined with IR, DSC and SEM analyses, were modulated by varying the L101/MAH/BFA ratio in the feed. The optimized product in terms of FD value and processability was successfully tested as compatibilizer in a polyolefin/PVC mixture, where the PVC component resulted from the management of waste of electrical and electronic equipment (WEEE).

Keywords: LDPE/iPP blends, radical functionalization, recycling, WEEE, PVC blends

Introduction

Polyethylene, especially Low Density Polyethylene (LDPE), and isotactic Polypropylene (iPP) are the two main polyolefins used in packaging applications (for flexible and rigid issues, respectively) and thus the most important polymer components of urban plastic waste and industrial scraps. The two polymers are recognized as immiscible¹⁻³, even if limited evidences about their compatibility were found for low content of iPP⁴. To improve their compatibility, the mixing with a third polymer component used as compatibilizer was generally proposed and the resulting materials were tested by collecting morphological and thermomechanical responses. Ethylene-propylene-diene terpolymer (EPDM)^{5,6}, even functionalized with maleic anhydride (MAH)⁷, EPM copolymer⁶, polyethylene-polypropylene (PE-PP) block copolymer^{8,9}, PE and PP grafted with MAH¹⁰ (eventually ionically coupled by Zn acetate¹¹), SEBS copolymer¹² and crosslinked LLDPE-PP blends¹³, were used as polymer surfactants of PE/PP mixtures in physical compatibilization procedures. A certain improvement of the morphology and of the final properties were highlighted but, often, the employed systems were too structurally complex or required a previous expensive modification with a limited possibility to modulate the interfacial interaction and the final rheology with reference to the starting PE/PP blend composition.

Several papers aimed at the compatibilization of PE/PP mixtures by using reactive blending approaches. Generally peroxides initiated reactions^{14,15}, γ -irradiation¹⁶ or electron beam irradiation at different radiation doses¹⁷, also in the presence of liquid polybutadiene¹⁸ or EPDM¹⁹, were used to promote interfacial adhesion. However, even if inter-macromolecular reactions generating PE-PP graft copolymers were invoked, the occurrence of PE crosslinking and PP degradation influenced the final thermomechanical properties. Reactive compatibilizers, like liquid polybutadiene bearing fumaric acid end-groups²⁰ or LLDPE grafted with silane derivatives²¹, whose reactivity can be activated respectively by using peroxide during the mixing and by adding water after blending, were used to investigate the compatibility features as a function of the resulting branching degree. All

these papers were mainly devoted to improve the mechanical features of the resulting blends by optimizing the interactions at the interface between the two polymers, rather than to provide functionalized products suitable to be used as compatibilizers.

A really limited number of papers can be found in the literature discussing the radical functionalization of LDPE/PP blends and reporting, in particular, a discussion related to reactions mechanism. Li and al²² studied the maleic anhydride (MAH) grafting, peroxide-initiated, by varying the ratios between the polymers, the MAH and the peroxide amount. The grafting was proved by IR analysis and the functionalization degree (FD) was measured by back-titration. Extensive crosslinking of LDPE and degradation of PP were assessed to explain the viscosity evolution of the blends. This approach was recently employed in the preparation of plastic-wood composites with improved mechanical features²³; anyway not details concerning the characterization of grafted blends were reported and discussed. The use of a polyfunctional monomer, the trimethylol propane trimethacrylate²⁴, was introduced to favour inter-chain reactions thus obtaining increased compatibility. Krivoguz et al extensively studied the grafting of itaconic acid by changing the LDPE/PP ratio²⁵: the rheological behaviour of the products evidenced once again the occurrence of degradation and crosslinking assessing both collateral reactions difficult to be kept under control. The thermal and mechanical features of grafted LDPE/PP blends²⁶ suggested the lack of compatibility on the level of crystalline phases, while efficient interactions on the amorphous fractions were highlighted as proved by the variation of the glass transition temperatures (T_g).

Therefore, the conventional radical functionalization approach, which is successful in functionalizing single polyolefins, can be applied to polyolefin mixtures, even if extensive occurrence of side reactions (PE crosslinking by macroradical coupling reaction and PP degradation by β -scission reaction) is affecting the final properties. To overcome these drawbacks the tuning of optimized functionalizing monomer/peroxide ratio and the use of a suitable co-agent, the butyl 3-(2-furyl)propenoate (BFA), able to prevent the iPP degradation²⁷⁻³⁰ are here for the first time assessed.

The feasibility of this co-agent assisted radical functionalization process onto a LDPE/iPP 80/20 w/w blend is tested to provide materials with specific functionalities and controlled structure/architecture. The main target of this approach is to achieve improved compatibility between the two polymers by favouring inter-macromolecular reactions, but overall to provide a grafted product suitable, in terms of functionalization degree (FD) and processability, to be used as a polymer compatibilizer. In fact, such compatibilizers can be useful for improving the properties of recycled polymer blends³¹ with particular reference to those derived from Waste Electrical and Electronic Equipment (WEEE), whose availability is predicted to increase in near future. The plastic scrap recovered from electric wires is mainly constituted by polyvinylchloride, (PVC). The blending of such waste with polyolefins, also from recycled origin, can provide a sustainable recycling strategy. In an attempt to prepare polyolefins/PVC blends with improved compatibility, it should be considered that polyolefins with an increased content of carboxylic group³² or with other polar groups³³ were recently reported to be effective for their compatibilization. Hence in the present paper an optimized sample of functionalized LDPE/iPP blend is preliminary tested as compatibilizer in polyolefin/PVC (80/20 w/w) blends where the PVC component comes from WEEE recycling.

Experimental Part

Materials

Low density polyethylene (LDPE, Riblene FL34, Polimeri Europa) having MFI=2.1 g/10min, and density=0.924 g/cm³ and isotactic propylene homopolymer (Moplen HP501H, LyondellBasell) having MFR = 2.1 g/10' (2.16 kg/230°C) were used as received.

PVC grounded sample (PVC_R, by electric wire at the end of life) was collected from a prototype of separation device by University of Milan.

Maleic anhydride (99% MAH, Sigma-Aldrich) and 2,5-dimethyl-2,5-di-tert-butylperoxy hexane (Luperox101, L101, ARKEMA) were used as provided. Butyl 3-(2-furyl) propenoate (BFA) was synthesized as reported in literature³⁴.

Acetone (>99%, Sigma-Aldrich), n-heptane (>99%, Sigma-Aldrich), xylene (mixture of isomers, Carlo-Erba), Chloroform (>99%, Sigma-Aldrich) were used as received.

Functionalization experiments

The reactions of LDPE/iPP 80/20 w/w were carried out in the melt by using a Brabender Internal Mixer W30E at 200°C. The rotor speed was set at 50 rpm. Torque and temperature data were acquired by the Brabender Mixing software WinMix ver.1.0. All the experiments were performed by first introducing the polymers (a physical mixture of LDPE (14 g) and iPP (6 g)) in the pre-heated Brabender chamber and setting 15 min as total mixing time. After melting of the polymers (usually within 3 min), the functional monomer and the co-agent (MAH and BFA or their combination, Table 1) were added. The peroxide was introduced after 1 min.

The samples were collected from the mixer, and subjected to a solvent extraction procedure in Kumagawa; each solvent extraction was carried out for 16 hs. The acetone was used to remove unreacted functional reagents and by-products; the residual fractions were extracted sequentially with the n-heptane and xylene (used only for samples 9, 14 and 5).

PVC blending experiments

The blends of PVC_1 and PVC_2 were obtained by mixing the polyolefin mixture and PVC (80/20 w/w) in the Brabender Internal Mixer W30E at 180°C, for 8 min. First the polyolefin mixture LDPE/iPP 80/20 w/w was introduced in the mixer (16 g for entry PVC_1 and 14 g for entry PVC_2) and after 2 min 4g of PVC_R were added. In the case of the PVC_2 sample after 1 min 2 g of the sample 14 (Table 1) were introduced.

IR characterization

All the LDPE/iPP samples (and their solvent extracted and residual fractions) and PVC blends were analysed by IR spectroscopy. The FT-IR spectra of processable samples were recorded with a Fourier Transform Spectrometer “Perkin Elmer Spectrum Two” at room temperature on films prepared by compression moulding with a Carver 12 Ton Hydraulic Units, model 3912, working at 200°C. The thickness of each sample was about 30-60 μm . All the FT-IR spectra were recorded between 4000 and 450 cm^{-1} , at room temperature, with 16 scans. A few unprocessable samples were analysed by ATR FT-IR spectra by acquiring the spectra with the Perkin Elmer Spectrum Two FT-IR Spectrometer equipped with the Attenuated Total Reflectance accessory with diamond crystal. For all LDPE/iPP functionalized samples the FD determination was achieved by IR spectroscopy, by using the signal at 1376 cm^{-1} (scissoring $-\text{CH}_3$, iPP) as reference band for the LDPE/iPP mixtures by taking into account their composition. The determination of the integral absorptivity (ϵ) for this band was carried out according to a method usually adopted in our laboratory³⁵ (see Supporting Information, (SI) for additional details).

To calculate the functionalization degree (FD) of all the samples, a deconvolution procedure applied to the bands in the C=O stretching region of FT-IR spectra for MAH and MAH/BFA functionalized samples was used as described in a previous work^{27, 29} (see SI for additional details).

After the obtainment of the diagnostic band areas (calculated for three samples of the same run), FD was calculated (Table 1) as previously reported by taking into account the composition of the polymer blends and by knowing the integral absorptivity values for the reference band (see SI), and of all carbonyl stretching related to the absorption bands of BFA and grafted succinic derivatives^{27,29,36}.

The FD values for iPP and LDPE samples (runs LDPE_1 and iPP_1, Table 1) were determined by using the same methodology and for LDPE a calibration curve already used in previous work³⁷

DSC analysis

DSC analyses were carried out by using a differential scanning calorimeter Perkin Elmer DSC 4000, equipped with a Pyris Manager 9.0 software and connected to a intracooler for the low temperature operations. The instrument was calibrated with Indium (T_m : 156.6 °C, $\Delta H_m = 28.5$ J / g) and Lead (T_m : 327.5 °C).

For each sample 5-10 mg, placed in aluminium sealed pan were subjected to heating and cooling scans in an inert nitrogen atmosphere. The thermal program used for analysing LDPE/iPP mixtures of polyolefin and PVC_1 and _2 samples included a first heating from 30 °C to 200 °C, a subsequent cooling down to -100 °C while maintaining the latter temperature for 5', and a final heating from -100 °C to 200 °C. The speed of the each scan was 10 °C / min.

TGA analysis

Thermogravimetric analysis (TGA) of PVC_R sample was carried out using a Seiko, Parabiaco (Mi) Italy EXSTAR 7200 TGA/differential thermal analysis instrument. TG curve was collected on sample of 10mg in the temperature range from 30°C to 700 °C under nitrogen (N_2 flow= 200 ml/min), using a heating rate of 10 °C/min. (SI).

Tensile tests

The tensile tests for samples PVC_1 and PVC_2 were carried out by using INSTRON 4302 universal testing instrument (Canton, USA) on 7 specimens for each sample, at 10 mm / min with a load cell of 10 KN. The specimens were obtained by extruding in flush mode the material with a mini-screw extruder Haake MiniLab II TM Rheomex CTW 5 (Thermo Scientific Haake GmbH, Karlsruhe, Germany) at 180 ° C and 50 rpm and by recovering the material in the cylinder preheated to 200 ° C. The material was then injected at 200 ° C and at a pressure of 600 Bar in the mold of Haake TM MiniJet II mini-press (Thermo Scientific), for a holding time of 15 seconds, to obtain specimens Haake type-III.

SEM characterization

Scanning Electron Microscopy of the samples were carried out using the JEOL JSM-5600LV instrument (Tokyo, Japan), analysing surfaces cryogenically fractured and previously sputtered with gold.

<Table 1>

Results and Discussion

Functionalization of LDPE/iPP 80/20 w/w mixture

All the functionalization runs of LDPE/iPP 80/20 w/w mixture were carried out by using the same experimental procedure and different reagent ratios; in particular, while the functionalizing monomer MAH was used in higher ratio with respect to the peroxide concentration (up to 20 times for runs 13, 14, 5, corresponding to low values of the molar ratio between peroxide and maleic anhydride (R1, Table 1), the co-agent BFA was employed mostly in a stoichiometric ratio with respect to the primary radicals (considering 2 as the efficiency value for L101 primary radicals generation) or in a double concentration. One run was performed by using a molar ratio between BFA and primary radicals (R2) equal to 4 (run 14 in Table 1). For comparison purpose, two functionalization runs with either LDPE or iPP alone were also performed.

After cleaning with acetone to remove low molecular weight by-products and unreacted species, the samples were analysed by FT-IR to calculate the FD values (see Table 1). After, the acetone residue was extracted with n-heptane to tentatively separate the different polyolefin fractions.

The MAH grafting onto LDPE and iPP showed FD (and consequently grafting efficiency, GE) in agreement with previous studies^{27,28,30,34,36}. Indeed, by using the same feed conditions, higher GE was obtained for LDPE, with respect to iPP. Moreover, a high residual fraction of the functionalized

LDPE (59 % wt) was obtained by n-heptane extraction suggesting the occurrence of an extensive crosslinking, while iPP maintained almost unaltered its solubility. The sample 5 (LDPE/iPP 80/20 w/w treated with the same amount of reagents used for the functionalization of neat iPP and neat LDPE) showed an intermediate value of FD (0.47 % mol), and a residue to the n-heptane extraction (70.7 % wt) close to the expected value by considering the solubility of iPP (even after the functionalization process) and the quantity of insoluble polymer found for the functionalized LDPE. By increasing the amount of peroxide (sample 2), no significant variation of the n-heptane residue and of FD was envisaged, with an obvious decrease of the GE parameter. Lower FD values were obtained, instead, by decreasing the content of MAH as expected (samples 3 and 4), with a reduction of the quantity of the n-heptane insoluble fraction.

The functionalization runs carried out with BFA showed the successful grafting of BFA with a FD value increase by raising the content of BFA (sample 6 versus samples 7 and 8), and with no effects exerted by the peroxide concentration. On the contrary, the peroxide significantly affected the content of n-heptane residue, which was lower by increasing the R2 parameter (sample 8).

By taking into account the runs carried out with MAH and BFA, it was evidenced, as a general trend, higher FD values for higher amount of MAH and lower grafting levels in the presence of the BFA co-agent with respect to the runs carried out without BFA (comparison between samples 2 and 9; samples 3 and 11) even if, the total FD value counts the BFA grafting (Table 1). A contemporary decrease of the insoluble n-heptane fraction could be envisaged. Both FD and n-heptane values level off for low amounts of peroxide (see sample 4 vs sample 15) (Figure 1a).

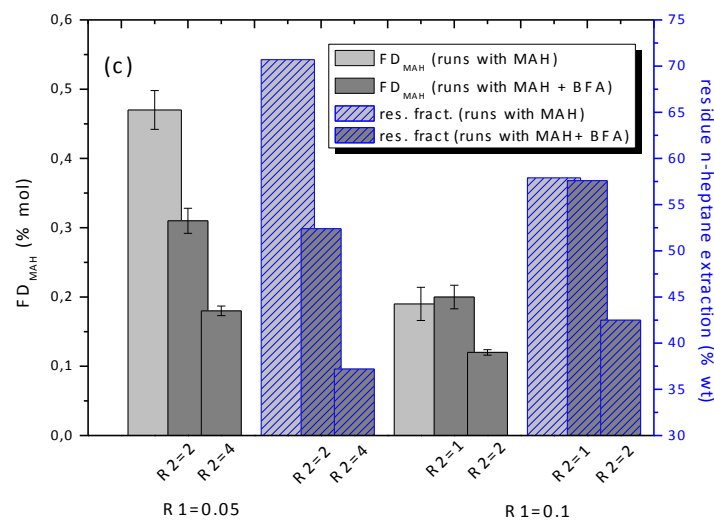
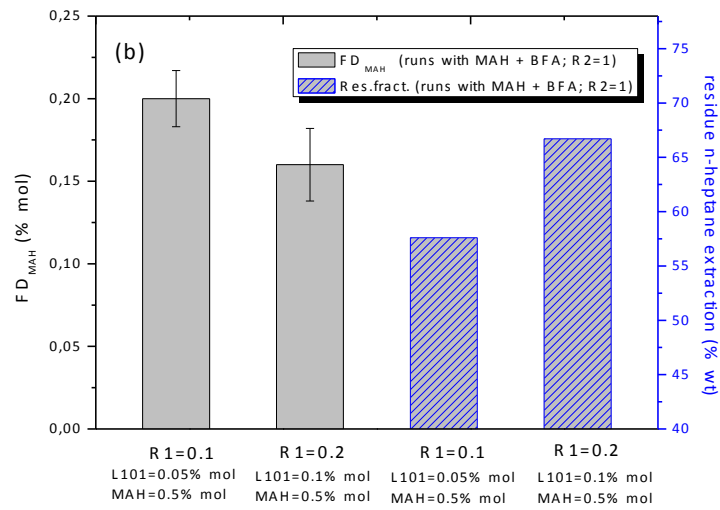
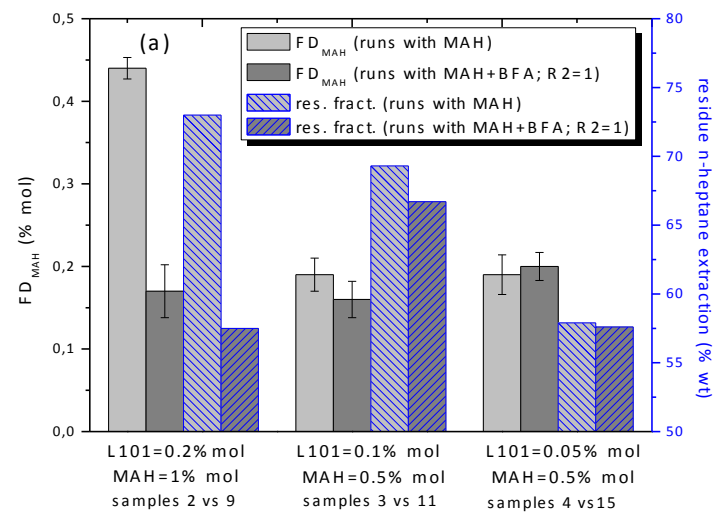


Figure 1: FD_{MAH} (% mol) and residue to n-heptane (% wt) extraction evolution as a function of feed composition; comparison between samples obtained (a) with MAH and MAH plus BFA; (b) by changing the R1 ratio and keeping constant R2; (c) with MAH and MAH plus BFA by increasing R2 at different R1 ratios.

By increasing the content of peroxide and keeping constant the MAH amount (samples 15 and 11), the FD values were not improved; instead, an increase of the insoluble n-heptane fraction was obtained (Figure 1b). By comparing the runs carried out increasing R2 (with the same R1 ratio), a decrease of FD values (samples 5, 13, 14 and samples 4, 15 and 12) was observed even if quite good results in terms of GE were reached (samples 13 and 14, Table 1). By using these feed conditions ($R2 = 2$ or 4) a substantially decrease of the n-heptane insoluble fraction was also achieved (Figure 1c).

The n-heptane extraction products were analysed by FT-IR spectroscopy to structurally investigate the fractionated portions and to evaluate the influence of the functionalization conditions on their relative amount (Figure 1). The FT-IR spectra of the soluble fractions evidenced vibrational bands due essentially to LDPE (as evidenced by comparing the FT-IR spectrum of the n-heptane soluble fraction of sample 14 with the spectrum of neat LDPE, Figure 2a), whereas the FT-IR spectra of the residues mainly showed bands specific of both LDPE and iPP (Figure 2b). This result confirmed that iPP did not change its solubility owing to functionalization procedure. Instead, a substantial quantity of LDPE ensued as insoluble after the functionalization (Figure 1a, b, and c); the amount of this fraction decreased in the presence of BFA and varied in function of the reagents ratio: a lower quantity of n-heptane insoluble polymer was obtained raising R2 (BFA/primary radicals) and lowering R1 (peroxide/MAH).

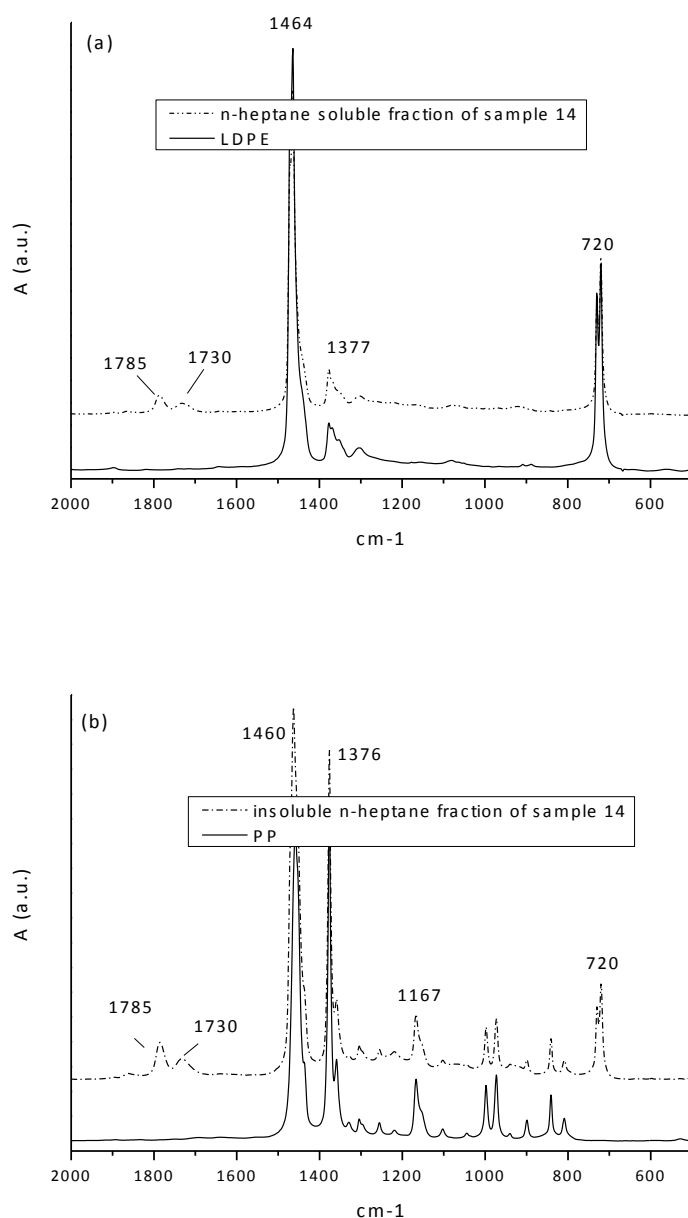


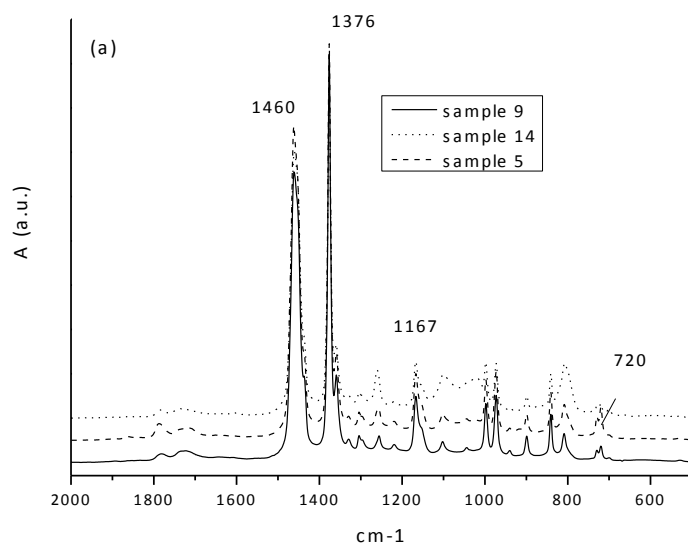
Figure 2: IR spectra of soluble (a) and insoluble (b) fractions to n-heptane extraction of sample 14. iPP and LDPE spectra are reported as reference. All the spectra are normalized to the band at 1376 cm⁻¹ (scissoring of -CH₃)

The absorption bands in the carbonyl stretching range, shown in the spectra of all the fractions, accounted for the functionalization. The determination of the FD for the soluble fractions evidenced lower values with respect to the whole samples: as example it accounts for 0.1% mol in the case of

the extracted portion of the sample 14 while the starting FD was 0.18 % mol; consequently, higher grafting level has to be assumed for the insoluble fractions. This experimental evidence can be rationalized considering that the fractionation likely took place not only on the basis of chains molecular weight, but also on the FD level that affects the polymer chains solubility by polar intermacromolecular interactions²².

To further separate the polyolefin fractions contained in the n-heptane residues, selected residual fractions were further extracted with boiling xylene. This solvent is, indeed, able to completely solubilize iPP and all linear polyethylene-based homopolymers and copolymers, even with block/graft structure.

To compare samples prepared in different experimental conditions, the samples 5, 9 and 14 were selected.



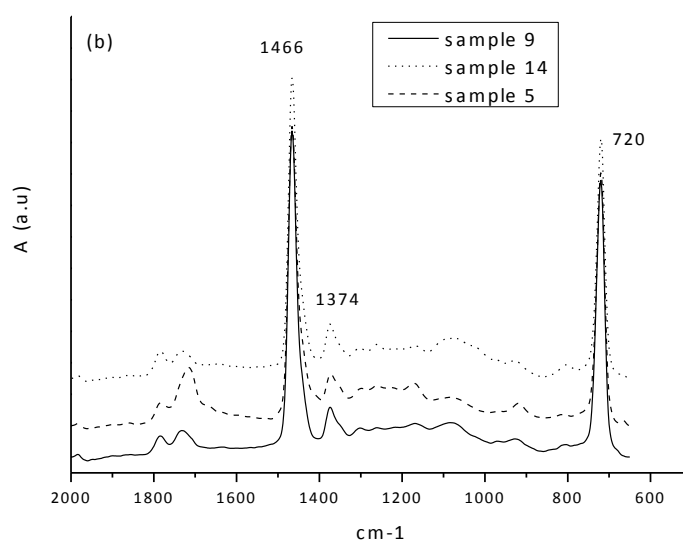


Figure 3: a: FT-IR spectra of the xylene soluble fractions of samples 5, 14 and 9, b: ATR spectra of xylene insoluble fraction of samples 5, 14 and 9. All the spectra are normalized to the band at 1376 cm⁻¹ (scissoring of -CH₃)

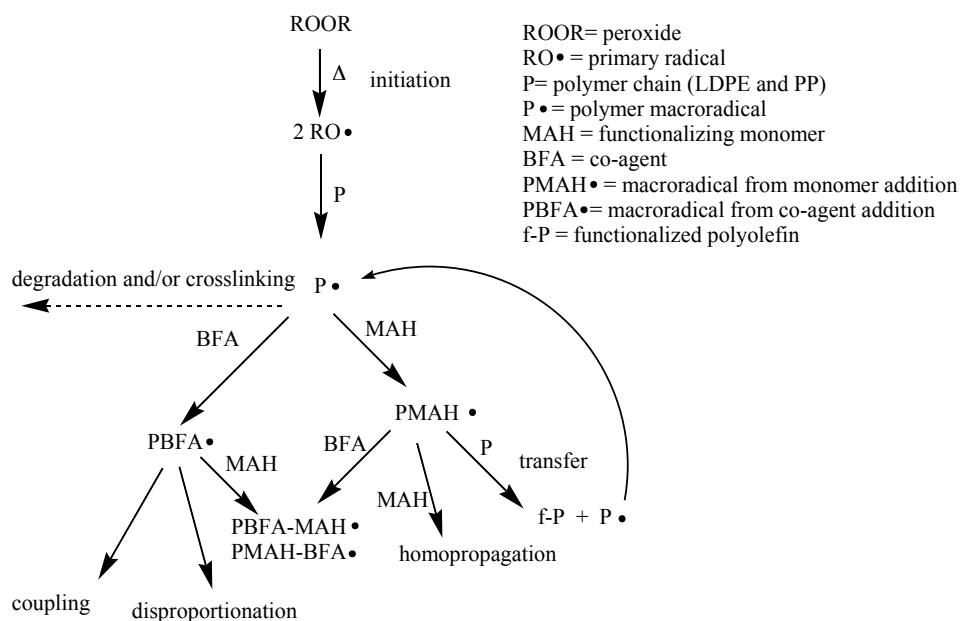
The results showed a soluble functionalized fraction consisting of both of iPP and LDPE (figure 3.a), whose insolubility in n-heptane (particularly with respect to the starting LDPE component) can be attributed to chain extension reactions and to the possible formation of a graft copolymer iPP-LDPE. The FT-IR spectrum of this xylene soluble fraction appeared particularly rich in iPP as evidenced by the ratio of the characteristic bands of the two polymer phases (-CH₂ bending at 1460 cm⁻¹ and -CH₃ scissoring at 1376 cm⁻¹ as well as the -CH₃ rocking mode at 1167 cm⁻¹).

The residual fractions (Figure 3b), quantitatively lower for the sample treated with a lower amount of peroxide (sample 9 versus sample 14, Table 2), but significant because it constituted more than the half of the residue to the n-heptane extraction, consist of LDPE and a low quantity of iPP, presumably as iPP-LDPE graft copolymer, by considering that iPP is completely soluble in xylene, even after the functionalization. In fact, the characteristic bands of the iPP, with particular reference to the mode at 1167 cm⁻¹, are difficult to be distinguished suggesting that this polymer is contained in

a negligible quantity. In the presence of BFA and at a constant peroxide concentration, the quantity of this insoluble fraction strongly decreased. By considering the composition of this fraction (mainly constituted by insoluble functionalized LDPE chains) this evidence suggested a beneficial effect of BFA on the crosslinking side reactions of LDPE, particularly by lowering the peroxide content (Table 2).

<Table 2>

These results can be rationalized on the basis of a very simplified functionalization mechanism (Scheme 1). Both the macroradicals formed via hydrogen abstraction from LDPE and iPP can react with MAH and BFA. By taking into account previous results and considering the intrinsic macroradicals stability (those with grafted BFA moieties are resonance-stabilized^{29,34}), the formation of PBFA• is likely favoured^{27,28,33}. This implies, as a first effect, a good control of the degradation reactions of iPP as proved by its unchanged solubility. The resulting functionalized macroradicals have different reactivity: while PMAH• provides new P• by H-transfer reaction thus raising the amount of macroradicals and then favouring the functionalization reactions by improving GE values, the PBFA• is likely subjected to termination reactions. This explains the lower FD values obtained in the presence of BFA (Figure 1a); at the same time by considering that the crosslinking due to macroradical coupling reactions is favoured by P• generation (it is indeed a bi-molecular reaction), a lower instantaneous concentration of P• decreases the incidence of such reactions with particular reference to the LDPE fraction (Figure 1a and Table 2). By raising R2 (that means higher BFA content) and lowering R1 (meaning low peroxide content) the macroradicals instantaneous concentration was lowered, thus optimizing the FD and the final processability of the samples (Figure 1b, 1c and Table 2).



Scheme 1: Simplified functionalization mechanism of polyolefin mixture (P) with MAH in the presence of BFA.

Both the xylene soluble and insoluble polymer fractions resulted functionalized, as proved by absorption bands in the carbonyl stretching region, and the insoluble fractions appeared more functionalized, even if the insoluble nature of the materials (which is highly crosslinked) did not allowed an accurate spectroscopic comparison; the unprocessable polymer fractions were, indeed, analysed by ATR mode. Anyway we observed an apparently different distribution of functionalities structure (Figure 4).

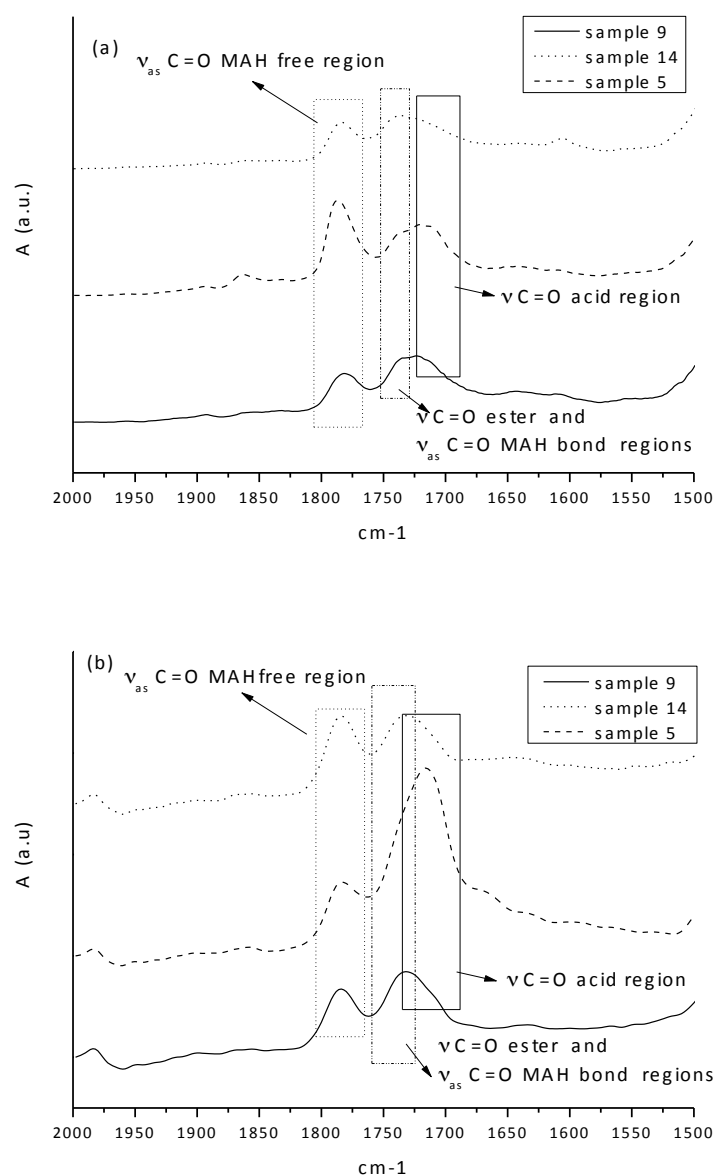


Figure 4: Enlargements of carbonyl stretching region of IR spectra of (a) soluble fractions (FT-IR) and (b) insoluble fractions (ATR) to xylene fractionation of selected samples

While for the samples obtained in the presence of BFA the ratio between the area of the absorption peaks assigned to the different species is mostly unchanged in the two fractions (comparison between Figure 4a and 4b, for samples 9 and 14, respectively), an increase of the peak intensity in the 1730-1690 cm^{-1} region was noticed for the xylene insoluble fraction of the sample 5; an accumulation of acid groups as a result of the hydrolysis of the grafted anhydride groups appeared evident for sample

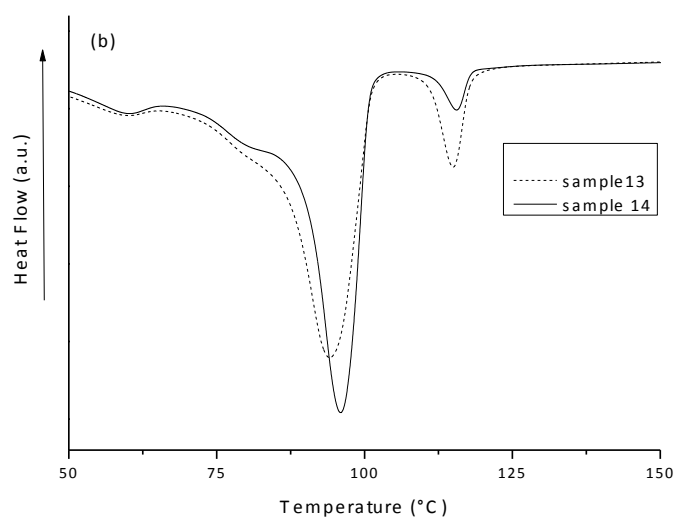
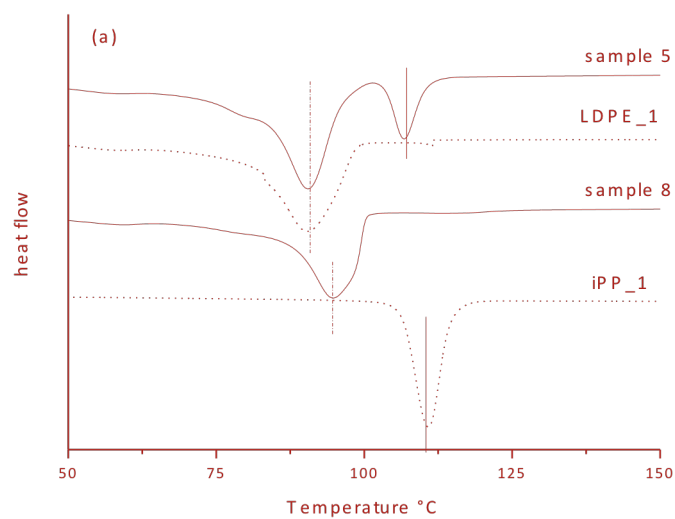
5, obtained in the absence of the co-agent. This result was attributed to the higher functionalization degree and the presence of grafted oligomers that generates a higher content of not isolated acid groups (see Scheme 1). These oligomers are characterized by strong absorption in the C=O stretching region due to the formation of associated forms through hydrogen bonds^{38,39} responsible of material unprocessability; on the other hand the coupling reactions of functionalized macroradicals can certainly improve the content of crosslinked polymer portion. The ability of BFA to control the transfer and the homopropagation of MAH keeps the same distribution of the functionalities in the various fractions, thus indirectly controlling the homogeneity of the grafted functionalities.

DSC characterization of functionalized samples

Two well-evidenced melting transitions were observed for all the samples, attributable to fractions containing mainly LDPE or iPP and characterized by temperatures and associated enthalpy values in agreement with composition or processing conditions. Instead, the cooling scans revealed the presence of peaks not always ascribable to structurally recognized polymer phases and only one crystallization enthalpy value was taken into account (see Table S2).

The comparison of unfunctionalized starting polyolefins (LDPE and iPP) with runs LDPE_1 and iPP_1, and even with the functionalized blends, evidenced, as a general trend, that LDPE phase crystallized slower (the T_c decreased). This effect can be explained by the growing of LDPE melt viscosity during functionalization^{22, 25, 26} as revealed by the presence of crosslinked materials, mostly composed by polyethylene fraction. By comparing the crystallization path of the samples functionalized by using MAH and peroxide in the same reagent ratio ($R1=0.05$, runs LDPE_1, iPP_1 and sample 5), we observed a decrease of T_c associated to the iPP phase (or to a phase iPP rich), (Figure 5a) suggesting a co-crystallization effect presumably owing to intermacromolecular reactions occurrence (macroradicals and functionalized macroradicals, derived from both iPP and LDPE, coupling reactions, see even Scheme 1). This effect was really magnified for the samples grafted

with BFA alone (see as example run 8, Table S2 and Figure 5a) confirming that the macroradicals derived from BFA addition are more reactive toward coupling and thus they favour the cross-phases reactions in the fraction able to crystallize.



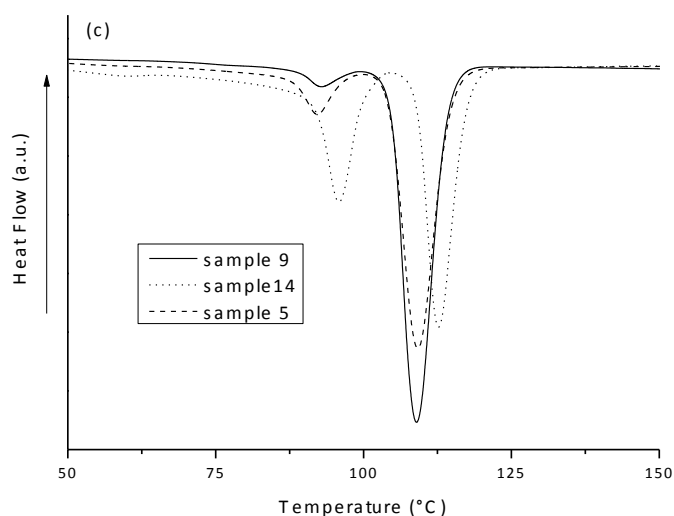


Figure 5: DSC cooling scans of selected samples after cleaning with acetone (a) and (b) and xylene extracted phases (c).

The functionalization reactions carried out with both MAH and BFA provided samples with two distinct crystallization peaks, even if evident co-crystallization effects decreasing the enthalpy of the transition at higher temperature was noticed for the runs carried out with high content of BFA (see Figure 5b). All the soluble and insoluble fractions to different solvent extractions were analysed by DSC. The results confirmed that the composition of the crystalline phases reflects those of the whole samples: n-heptane soluble and xylene residual fractions evidenced melting and crystallization peaks mostly ascribable to polyethylene phases. The xylene soluble portions contained both the polymer phases, even if their DSC curves are characterized by evident differences in T_c and associated enthalpy with respect to the LDPE and iPP starting polymers. In particular, the sample 14 obtained by using a high R2 ratio showed the higher content of phase resembling the LDPE crystalline fraction or more packed in crystallites (Figure 5c).

Thus, the DSC results suggested that, despite the incompatibility between the polymer phases, the samples obtained by the functionalization process underwent to co-crystallization effects reflecting the composition (at least for the extracted and residual fractions) and the interchains reactions extent

(crosslinking and/or iPP/LDPE graft copolymer formation). This effect is evident in particular in the presence of BFA and confirms intensive interactions or the trigger of intermacromolecular reactions taking place between the functionalized polyolefin phases assisted by the presence of the co-agent.

SEM analysis of functionalized samples

The morphological analysis (Figure 6) of the pristine mechanical mixture confirmed the incompatibility of the polymers. Indeed, the dispersed phase (reasonably iPP) has a spherical shape of 2-3 μm . The lack of adhesion to the LDPE matrix can be observed and in agreement several holes in the main matrix were evident due to iPP detachment. The functionalization carried out with the peroxide and the MAH led to a visible decrease in the diameter of the iPP phase, independently of the reagents ratio in the feed. The domains have dimensions of about 200-500 nm and resulted completely embedded in the matrix (samples 2, 9 and 5). In spite of the good results in terms of morphology, these samples resulted unprocessable as proved by the pictures on the right in Figure 6 showing the probes obtained by compression moulding of the analysed samples. Films containing a low content of infusible gels and able to be remould were obtained only for those samples that have a n-heptane insoluble fraction lower than 50 wt % (as sample 14).

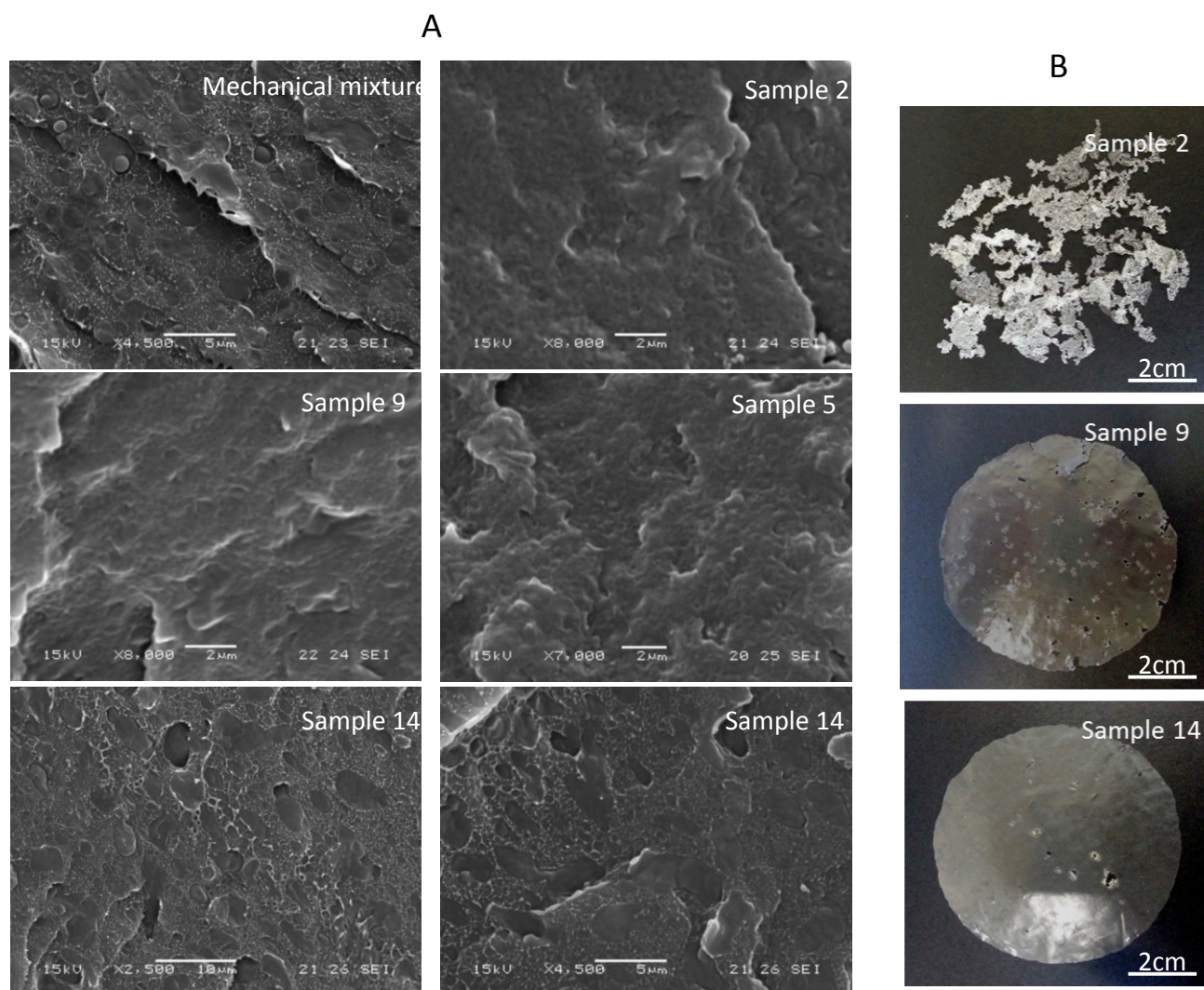


Figure 6: A: SEM micrographs of samples functionalized by using different reagents ratio and B: pictures of materials as obtained by hot-pressing (200°C and 2 tons)

With reference to this last sample obtained for low R1 and high R2 ratios a different morphology was achieved. Actually the dimensions of the iPP are larger than those of previous samples: an increase of the apparent average diameter as well as of its standard deviation is evident. In addition, the dispersed domains are no longer spherical but elongated and, most likely, interconnected. This result as well as the loss of sphericity can likely be attributed to the compatibilization between the polymers, which determines a reduction of interfacial tension³⁸.

Preliminary testing the functionalized LDPE/iPP mixture as compatibilizer in polyolefin/PVC blends

By considering all the results in terms of FD values, compatibilization occurrence and processability, the sample 14 was selected to be tested as compatibilizer in the mixture polyolefins/PVC_R 80/20 w/w where the polyolefins were composed by LDPE/iPP in the same ratio (80/20 w/w) employed for the previous functionalization runs.

The PVC_R sample used for this part of the work was derived from WEEE and before its use in the mixtures with the polyolefins an accurate structural analysis was performed⁴¹ (see SI).

After the mixing with the LDPE/iPP 80/20 w/w the resulting samples were analysed by SEM, DSC and tensile analysis (Table 3).

The morphological analysis of PVC_1 confirmed the incompatibility between the polymer components⁴²; Figure 7 shows the presence of domains with dimensions ranging from 5 to 20 μm whose larger aggregates with a sharper surface were ascribable to the inorganic filler contained in the PVC_R (as supported by TGA analysis) and the smaller with a smooth surface are attributable to the PVC phase. The presence of sub-micrometric domains (indicated by arrows) can also be evidenced, probably attributable to the iPP domains. The addition of the sample 14 (10% wt on the whole mixture) for PVC_2 run brought a beneficial effect onto the morphology: the larger dispersed phase drastically reduced its dimensions to less than 5 μm and appeared strongly interconnected with the matrix; the smaller domains disappeared or were completely embedded in the polyolefin matrix, confirming the role of compatibilizer played by the sample 14 on both the PVC/LDPE and LDPE/iPP interfaces.

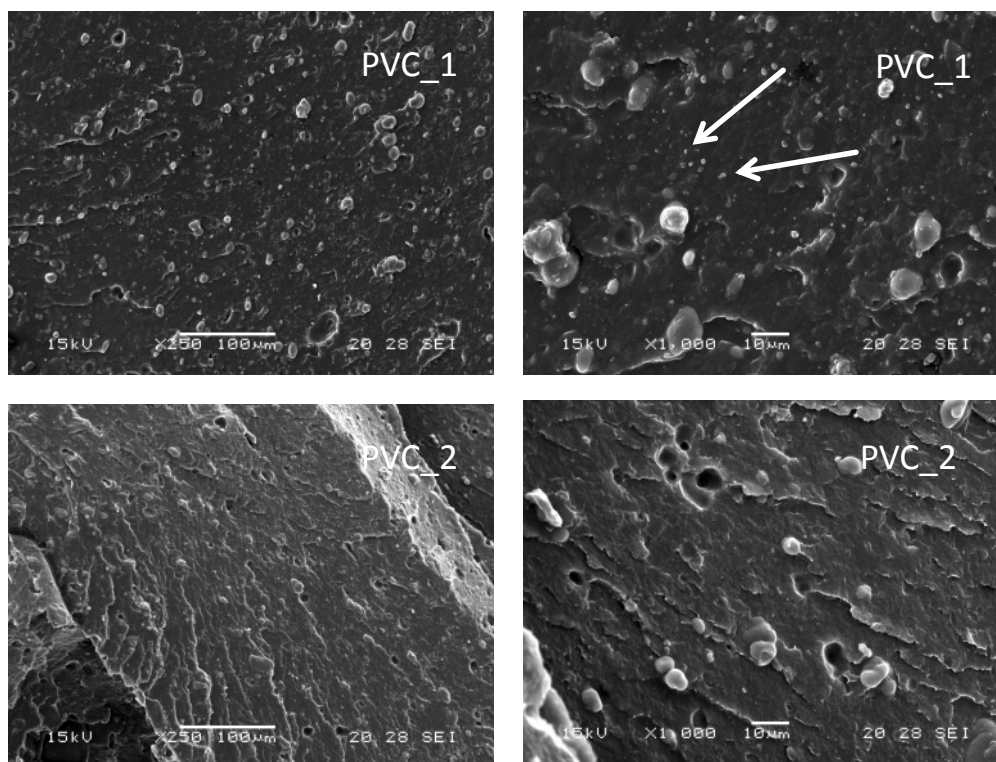


Figure 7: SEM micrographs of PVC_1 and PVC_2 samples

Even if the DSC analysis can explore only the crystalline phases of polyolefin fractions, the evident co-crystallization effect for the PVC_2 sample (Figure S3) particularly at lower temperatures suggested stronger interfacial interactions even between the LDPE and iPP phases in the PVC_2 blend. In fact the presence of the compatibilizer generates a broader crystallization, confirming its miscibility/solubility in both polymer phases, owing presumably to graft-copolymer (LDPE-iPP) formation. In addition the presence of carboxylic groups grafted on the iPP and LDPE interacting with H-C-Cl moieties granted the compatibility improvement of the PVC/polyolefin blend⁴³. As a result, this may lead also to an increased ductility of the material. In fact the tensile tests (Table 3, Figure S4) evidenced a significant gain of elongation at break for the compatibilized sample (PVC_2) and unchanged mechanical features in terms of modulus and stress at break values, confirming the profitable role played by the compatibilizer.

<Table 3>

Conclusions

The radical functionalization of LDPE/iPP mixtures carried out with MAH and peroxide and mediated by the use of BFA allowed obtaining functionalized polyolefin mixtures by controlling the side reactions and the functionalities distribution among the different phases. iPP degradation and LDPE crosslinking were kept under control by tuning the chemicals ratios and the resulting grafted functionalities distribution ensued more homogeneous with respect to samples obtained without BFA. In addition, the cross-phases reactions seemed to improve copolymers formation acting as surfactant at interface and producing functionalized, but even processable and compatibilized blends. The use of such product as compatibilizer in blending PVC sample from WEEE and polyolefins mixture constituting the matrix, was clearly beneficial in terms of morphology and final mechanical properties.

This work proved that by using a conventional polyolefin radical functionalization process, but in the presence of a chemical (BFA) able control the macroradicals stability and reactivity, the interfacial interactions are promoted through functionalities grafting and intermacromolecular reactions. This approach is then a good tool to prepare products with improved high-added value even starting from recycled polymer mixtures thanks to the possibility to control the final rheological and mechanical features.

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Table 1: Feed composition, solvent extraction results and FD values for functionalization runs^a

Entry	L101 (% mol) ^b	MAH (% mol) ^b	R1 ^c = L101/MAH	BFA (% mol) ^b	R2 ^d = BFA/pr.rad	Acetone extracted fraction (% wt)	Residue to n- heptane extraction (% wt)	FD _{MAH} (% mol) ^e	FD _{BFA} (%mol) ^e	GE ^f
LDPE	-	-	-	-	-	-	0	-		
iPP	-	-	-	-	-	-	94.9			
LDPE 1	0.05	1.0	0.05	-	-	0.9	59.0	0.55±0.06	-	11.0
PP 1	0.05	1.0	0.05	-	-	1.0	93.8	0.18±0.01	-	3.6
1 ^g	0.2	-	-	-	-	-	58.6	-		
2 ^g	0.2	1.0	0.2	-	-	1.1	73.1	0.44±0.01	-	2.2
3 ^g	0.1	0.5	0.2	-	-	0.6	69.3	0.19±0.02	-	2.0
4 ^g	0.05	0.5	0.1	-	-	0.8	57.9	0.19±0.02	-	4.0
5 ^g	0.05	1.0	0.05	-	-	0.7	70.7	0.47±0.03	-	9.4
6 ^g	0.2	-	-	0.4	1	0.9	55.6	-	0.20±0.024	1.0
7 ^g	0.1	-	-	0.2	1	0.7	60.1	-	0.11±0.002	1.0
8 ^g	0.05	-	-	0.2	2	0.8	38.0	-	0.12±0.004	2.4
9 ^g	0.2	1.0	0.2	0.4	1	1.5	57.5	0.17±0.03	0.02±0.005	1.0
10 ^g	0.1	1.0	0.1	0.2	1	0.4	63.4	0.20±0.01	0.04±0.003	2.4
11 ^g	0.1	0.5	0.2	0.2	1	0.5	66.7	0.16±0.02	0.05±0.004	2.0
12 ^g	0.05	0.5	0.1	0.2	2	0.8	42.5	0.12±0.02	0.05±0.028	3.4
13 ^g	0.05	1.0	0.05	0.2	2	0.5	52.4	0.31±0.02	0.04±0.001	7.0
14 ^g	0.05	1.0	0.05	0.4	4	1.5	37.2	0.18±0.01	0.07±0.007	5.0
15 ^g	0.05	0.5	0.1	0.1	1	0.3	57.6	0.20±0.02	0.03±0.009	4.6

a: runs carried out at 200°C, 50 rpm, 20 min

b: moles of molecule (reagent) per 100 moles of monomeric units (calculated on the basis of the average molecular weight of monomeric unit, by considering the composition of the blend)

c: R1=molar ratio between peroxide and maleic anhydride

d: R2= molar ratio between BFA and primary radicals

e: FD= moles of grafted functional monomer (MAH plus BFA) per 100 moles of monomeric units

f: GE=grafting efficiency which represents the moles of grafted functionalities per mole of peroxide

g: LDPE/iPP 80/20 w/w

Table 2: Solvents extractions results for selected samples

Entry	L101	MAH	BFA	Acetone		n-heptane ^a		xylene ^b	
	(%mol)	(%mol)	(%mol)	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble
				(% wt)	(% wt)	(% wt)	(% wt)	(% wt)	(% wt)
5	0.05	1.0	-	99.3	0.7	70.2	29.1	45.7	24.5
9	0.2	1.0	0.4	98.5	1.5	56.6	43.4	37.9	18.6
14	0.05	1.0	0.4	98.5	1.5	36.6	61.9	20.2	16.4

a: solvent extraction results with respect to acetone insoluble residue

b: solvent extraction results with respect to n-heptane insoluble residue

Table 3: Blends composition and stress-strain results

Run	Composition w/w	Elastic	Stress at	Elongation at
	Polyolefins/PVC_R/Compatibilizer	Modulus (E, GPa)	break (σ_b , MPa)	break (ϵ_b , %)
PVC_1	80/20/0	0.37±0.05	13.9±0.3	36±6
PVC_2	70/20/10	0.32±0.04	13.0±0.8	50±10