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In situ compatibilization of polypropylene–polyethylene blends: a thermomechanical and spectroscopic study

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Polypropylene (PP) and low density polyethylene (LDPE) were melt blended in proportions of 75/25, 50/50 and 25/75 w/w, respectively. Poly(propylene-*g*-maleic anhydride) (PP-g-MA) with 0.8 mol% maleic anhydride content and poly(ethylene-*co*-vinyl alcohol) (EVAL) with 7.5 mol% vinyl alcohol content were added at a 50/50 w/w proportion as *in situ* reactive compatibilizers. Four series of compatibilized blends were produced containing 2.5, 5, 10 and 20 wt% compatibilizer in the final blend. The compatibilization reaction was followed by a torque increase during mixing and by *FT*i.r. spectroscopy. A notable improvement in tensile strength, elongation at break and impact strength was observed for all blends after compatibilization and, in particular, for the blends containing 10 wt% compatibilizer. Scanning electron microscopy (SEM), aided by micro-Raman spectroscopy, was used for investigating the morphology of the blends. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polypropylene (PP) is a non-toxic, recyclable polymer with excellent processability and relatively low cost. It has, however, poor impact properties, particularly at low temperatures. It is a pseudoductile polymer and its fracture behaviour and ultimate properties are currently studied extensively[1–15]. In order to improve its impact behaviour, PP can be rubber toughened by the addition, for example, of acrylonitrile-*co*-butadiene rubber (NBR)[2,3], ethylene–propylene–diene rubber copolymer (EPDM)[4–6], ethylene–propylene copolymers (EP)[7–11], butyl rubber together with styrene–butadiene–styrene copolymer[12,13] or styrene–ethylene/butene–styrene triblock copolymer (SEBS)[14], and ethylene vinyl acetate copolymer[15]. PP is toughened by mechanisms involving delocalization of shear yielding in the matrix and internal cavitation of the rubber particles[2]. An optimum rubber particle size is preferred for good toughening. However, strong interfacial adhesion between PP and the rubber is required as well[2,4].

Another common way to increase the impact resistance of PP is melt-blending with polyethylene (PE)[16–33]. Furthermore, such blends are of much interest, since in communal waste the main plastic components are the various types of semicrystalline PE and PP, which are used mainly for packaging applications[34]. The possibility of preparing a blend of these used polymers with acceptable mechanical properties would lead to a valuable material and be a useful recycling practice.

Because of the immiscibility (and incompatibility) of the two polymers, their blends have poor mechanical properties and a compatibilizer is needed. A compatibilizer consisting of two parts, each miscible or compatible with one of the polymers, is expected to be located at their interface. This results in an increase of adhesion between the phases and a decrease of interfacial tension, i.e. finer dispersion of the dispersed polymer (PE or PP) in the matrix of the other. Many studies have been conducted on improving the impact properties of PP–PE blends using block copolymers as compatibilizers. Ethylene–propylene block copolymer and styrene–ethylene/butylene–styrene triblock copolymer are commonly used[9,14,24,35–38]. EPDM is also used to compatibilize PP–PE blends[4,39]. The key factor in this method of improving the interfacial adhesion is the diffusion of component blocks of the block polymer into the corresponding homopolymer phase. This has been demonstrated by Cho *et al.*[40] who studied the effect of diblock polystyrene (PS)-*b*-poly(methyl methacrylate) (PMMA) on the adhesion properties between PS and PMMA.

The use of a copolymer as compatibilizer needs an additional separate step for producing and purifying it. Due to the lack of economically viable routes for the synthesis of suitable copolymers, compatibilization by preformed copolymers has not been used as extensively as its potential utility might suggest[3,41]. On the other hand, successful compatibilization can be the result of strong specific interactions between groups of two different polymers. Polyethylene graft modified with N-vinylimidazole by reactive extrusion has been successfully combined by ionic bonding corresponding to salt formation with acrylic acid modified polypropylene[42]. Structures of this type may have a compatibilizing effect analogous to that of block copolymers.

Graft or block copolymers acting as compatibilizers for polymer blends can be formed *in situ* through covalent or ionic bonding during the melt blending of suitable functionalized polymers[43–51]. *In situ* compatibilization between two polymers has gained significant interest during the last few years, the main reason being the economic advantages it has over compatibilization methods using a preformed compatibilizer. The extensive range of

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the reactive copolymers available in the market has contributed towards this direction. The main research efforts have focused on finding the appropriate functionalized copolymers which will react during the mixing period.

The basic requirements for the effectiveness of a reactive compatibilizing method are:

(1) a high degree of dispersion of one polymer in another;
(2) the presence of complementary groups to form a chemical bond;
(3) strong reactivities of the reactive groups to perform the interaction through the polymer melt;
(4) the chemical bond formed during the blending has to be stable to the subsequent processing conditions;
(5) small reaction times; i.e., smaller than the residence time in the extruder or the mixer.

In this work the *in situ* reactive blending technique has been used to form, during melt blending of polyethylene with polypropylene, their compatibilizer from poly(propylene-*g*-maleic anhydride) (PP-g-MA) and poly(ethylene-*co*-vinyl alcohol) (EVAL). The selected groups meet the above requirements 1–4. It is expected that the first graft copolymer component will be preferentially attracted by the polypropylene phase whereas the second is attracted by the polyethylene phase. The reaction of the maleic anhydride group with the hydroxyl group is expected to lead to a diminution of the interfacial tension and a fine dispersion of one polymer into the phase of the other. Improved physical properties of the blends are consequently expected.

Besides the classical studies of thermomechanical properties, i.r. spectroscopy and electron microscopy, we focus attention in this work on the application of micro-Raman spectroscopy in studying the morphology of the blends.

EXPERIMENTAL

Materials

The isotactic polypropylene (PP) used had a melting point of 168°C and degree of crystallinity 49% and was supplied by Montell. The low density polyethylene (LDPE) used was commercial grade with a melting point of 113°C and degree of crystallinity 25% and was supplied by Borealis. The materials used as *in situ* reactive compatibilizers were a poly(propylene-*g*-maleic anhydride) (PP-g-MA) copolymer (Fusabond MD-353), kindly supplied by Du Pont–Canada, with 0.8 mol% maleic anhydride content, as was measured by titration, and a poly(ethylene-*co*-vinyl alcohol) (EVAL) copolymer with 7.5 mol% vinyl alcohol content. This latter was obtained by hydrolysis–saponification[52] of a commercial poly(ethylene-*co*-vinyl acetate) copolymer (Alcudia) with 8 mol% vinyl acetate content.

Preparation of blends

PP and LDPE were reactive-blended in proportions 75/25, 50/50 and 25/75 w/w, respectively, along with the graft copolymers. Mixing was performed in a Haake–Buchler Rheomixer model 600, with roller blades and a mixing head with a volumetric capacity of 69 cm^3. Four series of compatibilized blends were produced with contents of 2.5, 5, 10 and 20% w/w compatibilizer (initial copolymers) in the final blend. Prior to mixing, all polymers were dried by heating in a vacuum oven at 75°C for 24 h. The components were physically premixed before being fed into the Rheomixer. Blending was performed at 185°C and 60 rpm for a period of 30 min. The melt temperature and torque were continuously recorded during the mixing period on a Haake Rheocord, model 5000. The blends, after preparation, were immediately removed from the mixer, cooled to room temperature, milled and placed in tightly sealed vials to prevent any moisture absorption.

FTi.r. spectroscopy

*FT*i.r. spectra were acquired in a Biorad FTS-45A *FT*i.r. spectrometer. For each spectrum 64 consecutive scans with 4 cm^{-1} resolution were coadded. Samples were measured in the form of thin films about 70 ± 2 μm thick. The films were prepared by hot press moulding at 200°C for 2 min at a pressure of 250 bar.

Differential scanning calorimetry (d.s.c.)

D.s.c. thermograms were recorded using a fast quenching differential scanning calorimeter (Shimadzu, model DSC-50Q). The instrument was calibrated using indium as a standard. About 8 mg from each sample were placed in sealed aluminium cells and were initially heated under a nitrogen atmosphere up to 200°C with a heating rate of 20°C min^{-1} to erase all previous thermal history. Subsequently, they were immediately quenched. The sample was rescanned under the same conditions and from this second recording the melting temperatures and heats of fusion were determined.

Mechanical properties

Measurements of the mechanical properties, such as tensile strength and elongation at break, were performed on an Instron mechanical tester, Model 1122, according to the ASTM D638 method. Measurements were done using a 5 mm min^{-1} crosshead speed. Six measurements were conducted for each sample, and the results were averaged to obtain a mean value.

Izod impact tests were performed on a Tinius Olsen instrument according to ASTM D256. For each sample six measurements were made and the results were their average value. Prior to mechanical measurements, the samples were conditioned at $50 \pm 5\%$ relative humidity and 23°C for 48 h by placing them in a closed chamber containing a saturated $Ca(NO_3)_2 \cdot 4H_2O$ solution in distilled water (ASTM E-104).

Scanning electron microscopy

The impact specimens were fractured and the revealed surfaces observed with a scanning electron microscope (JEOL, model JSM-840A). The surfaces of the fractured specimens were coated with gold to avoid charging under the electron beam.

Raman spectroscopy

The Raman spectra were recorded with a Renishaw Raman imaging microscope, model 1000. The incident laser excitation was 632.8 nm from a He–Ne laser source. All spectra were recorded with a resolution of 4 cm^{-1}, collection time 1 min, laser power 3 mW. The spectra were collected from fractured surfaces of impact specimens, using a 50 $\times$ objective.

RESULTS AND DISCUSSION

Reactive blending

PP-g-MA and EVAL copolymers, which were chosen to be used as compatibilizers, contain appropriate functional

groups capable of reacting with each other. The expected result is the formation of a new macromolecule which will act as compatibilizer. As has been reported in previous studies[53,54], these macromolecules produced during the melt reaction have an increased molecular weight while a simultaneous production of branched or crosslinked macromolecules occurs. An increase in melt viscosity usually appears, since all the above macromolecules have a higher flow resistance than low molecular weight and linear macromolecules. This increase in melt viscosity during blending is reflected in an increase in torque, which is measured during mixing, as can be seen in *Figure 1*.

The torque in the PP/LDPE 50/50 w/w blend without compatibilizer dropped continuously after the initial melting of the two polymers. In contrast, when compatibilizer was used at the 10 wt% level, after the initial complete melting (1.5–2 min) the torque started to increase again. This increase was recorded as a small peak but, as can be seen, the final torque also remains higher than that of the pure blend. This is a strong indication that a reaction between the reactive groups, i.e. the maleic anhydride and hydroxylic groups, has occurred, producing branched or crosslinked macromolecules.

The main problem with such reactions is to identify the new groups which are formed, especially when only small amounts of reactive groups are present, as in PP-g-MA (0.8 mol%). This problem becomes more difficult because this copolymer is used in very small amounts (1.25–10 wt%). Thus, the calculated concentrations of maleic anhydride in the blends will lie between 0.01 and 0.08 mol%. *FT*i.r. is a very sensitive spectroscopic technique and can be used to detect such small changes. However, to prove that the reaction actually takes place, a blend with only PP-g-MA and EVAL had to be produced and studied under the same conditions. In this blend, where the concentrations of the reactive groups are higher, the differences are more prominent and, thus, more easily detectable by *FT*i.r.

In *Figure 2* the carbonyl area spectrum of this blend is presented along with the spectrum of pure PP-g-MA copolymer. In the PP-g-MA spectrum, the two characteristic peaks at 1863 and 1787 cm^{-1} are attributed to the five-member saturated anhydride ring[55]. In blend spectra these two peaks are attenuated and a very broad peak appears between 1750 and 1680 cm^{-1}. A more careful examination of this peak reveals that there is a maximum at about 1727 cm^{-1}, which is attributed to ester groups formed by the reaction, and a shoulder at 1713 cm^{-1} due to carboxylic groups. The same reaction between PP-g-MA and EVAL occurred also in all PP/LDPE blends containing compatibilizer, as was verified by their *FT*i.r. spectra. These results prove that indeed a reaction between maleic anhydride and hydroxyl groups takes place during blending, as was assumed by the torque increase.

Differential scanning calorimetry

The *in situ* compatibilization between PP and LDPE could have an effect on the melting points of the two polymers as well as on their crystallinity. This was expected since the two polymer phases become smaller due to compatibilization and there may be a partial dissolution of a foreign substance (the compatibilizer) into the pure polymer phase. This possibility was examined with differential scanning calorimetry. The thermograms of PP–LDPE blends in different proportions indicate that the two polymers are immiscible, since two well distinguished endotherm peaks are always recorded. The first melting peak at 113°C is attributed to LDPE and the second, at 168°C, to PP. These two melt temperatures remain constant throughout the whole composition range.

Similar conclusions are drawn when the blends containing different amounts of compatibilizer are compared. The melting points of the two polymers remain constant and the differences measured are less than 1°C. Thus, it can be said that the added amount of compatibilizer in the blend does not affect the melt temperature of either LDPE or PP. However, it has been found that the amount of compatibilizer has a significant effect on the heats of fusion of the two polymers. From these heats, the degrees of crystallinity of the blends were calculated, taking into account the heat of fusion of the completely crystalline (100%) polymers, which is 290 J g^{-1} for LDPE[56] and 165 J g^{-1} for PP[57]. It is very important to know the degree of crystallinity, since it can affect considerably the mechanical properties of the blends.

The degree of crystallinity for LDPE in the non-compatibilized blends depends on its amount in the blend. Increasing the amount also increases the crystallinity and, for the blend with 75 wt% LDPE, it is almost equal to the degree of crystallinity of pure LDPE. The same trend also appears in the blends containing different amounts of compatibilizer. Moreover, in the blends with 25 and 50 wt% LDPE, it appears that the degree of crystallinity increases as the amount of compatibilizer increases. These differences may be attributed to the EVAL copolymer used which is incorporated in the LDPE phase[58]. This copolymer has a melting point of 111°C (compared to 113°C for LDPE) and a heat of fusion of 110 J g^{-1} which is about 35 J g^{-1} higher than that of LDPE (25% crystalline). The heats of fusion for LDPE/PP 75/25 w/w blends compatibilized by 10 and 20% compatibilizer, however, indicated that LDPE had a lower degree of crystallinity than expected. The reduction of LDPE crystallinity in these blends is attributed to the greater extent of reaction between EVAL and PP-g-MA, which results in the production of a greater amount of branched and crosslinked macromolecules inhibiting crystallization.

In the uncompatibilized blends, the degree of crystallinity of PP shows a similar behaviour to that observed for LDPE. Increasing the amount of PP in the blend also increases the degree of crystallinity. When compatibilizer is added, the trend remains the same but, in all the blends, PP has a lower degree of crystallinity than the corresponding blends without any compatibilizer. Also, increasing the amount of compatibilizer decreases the degree of crystallinity. This behaviour is opposite to the effect of the compatibilizer on the crystallinity of LDPE. Comparing the heat of fusion of PP-g-MA, it can be seen that it is about 39 J g^{-1} lower than that of pure PP (49% crystalline). This is clear evidence that PP-g-MA is incorporated in the PP phase.

Mechanical properties

The main problem with most polymer blends is their inferior mechanical properties compared to those of the pure constituent polymers; this originates from the incompatibility of most polymers. In previous studies of uncompatibilized binary blends of linear low density polyethylene (LLDPE) and isotactic polypropylene it was postulated that the poor interfacial adhesion in these blends led to unsatisfactory mechanical properties[59–61]. *Figure 3* illustrates the tensile strength *versus* composition curves of LDPE/PP blends for various amounts of compatibilizer.
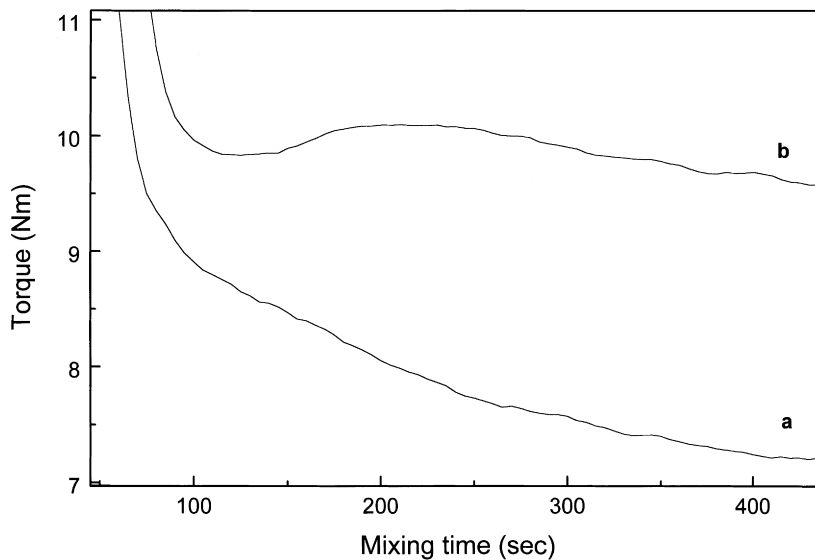
Figure 1   Melt torque of LDPE/PP 50/50 w/w blends: (a) without compatibilizer; (b) with 10 wt% compatibilizer
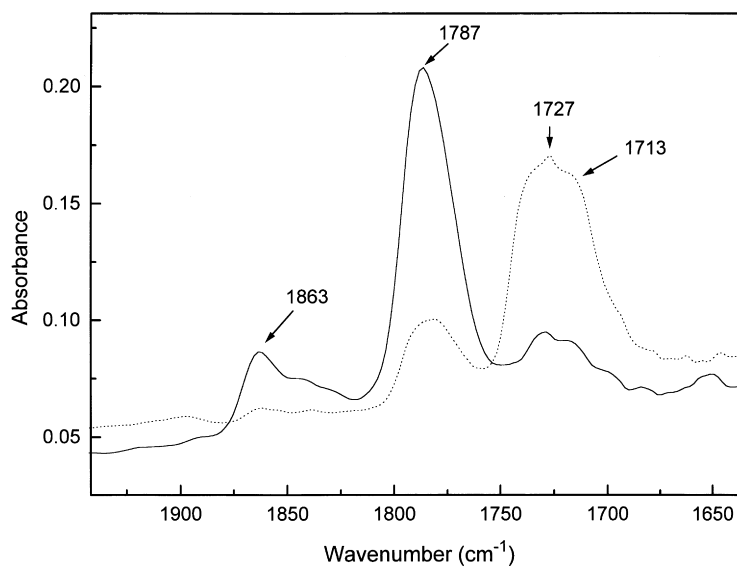

Figure 2   *FT*i.r. spectra of: (a) PP-g-MA; (b) the product of reaction between PP-g-MA and EVAL
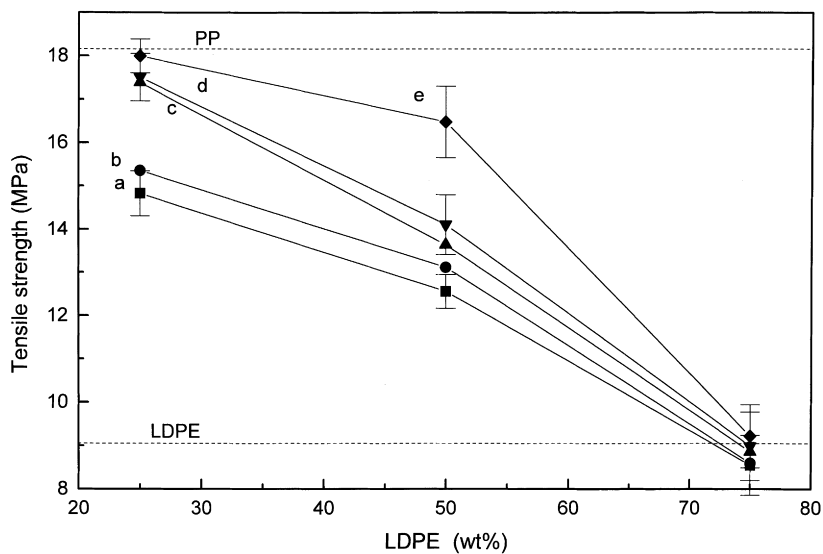

Figure 3   Degree of crystallinity of LDPE in the LDPE/PP blends *versus* wt% of LDPE in the blend containing different amounts of compatibilizer: (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt%, (d) 10 wt% and (e) 20 wt%
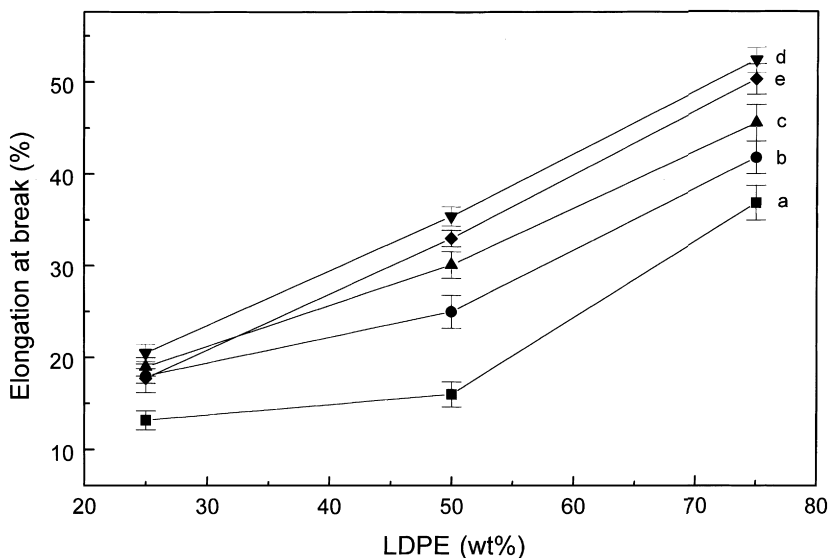
Figure 4 Elongation at break (%) for LDPE/PP blends containing different amounts of compatibilizer: (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt%, (d) 10 wt% and (e) 20 wt%
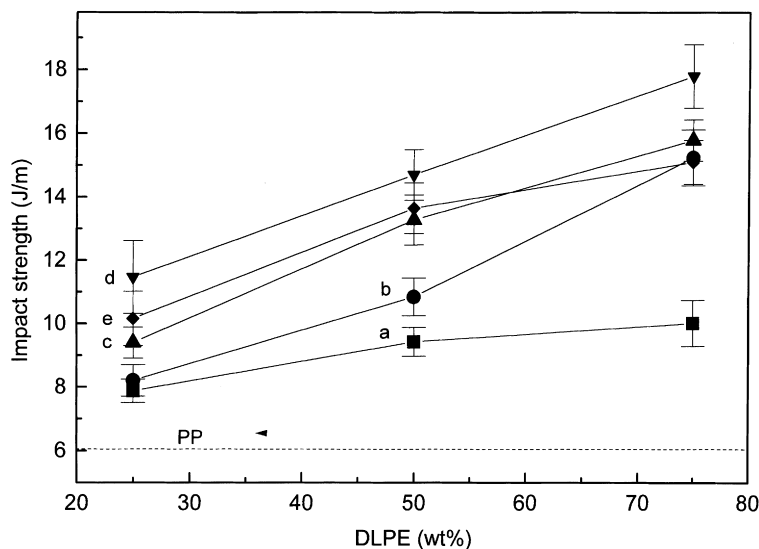

Figure 5 Impact strength of LDPE/PP blends for several compatibilizer contents: (a) 0 wt%, (b) 2.5 wt%, (c) 5 wt%, (d) 10 wt% and (e) 20 wt%

In all blends there is a reduction in tensile strength as the concentration of LDPE is raised, as a consequence of the fact that LDPE has a lower tensile strength (8.43 MPa) than PP (18.1 MPa). Actually the uncompatibilized LDPE/PP 75/25 w/w blends have lower tensile strength even than pure LDPE. In compatibilized blends, and regardless of the amount of compatibilizer, an increase in tensile strength is observed at all proportions studied. Blends with 20 wt% compatibilizer have the highest tensile strength. In the case of the 25/75 w/w LDPE/PP blend the tensile strength is similar to that of pure PP. Turcsanyi[42] found an analogous improvement in tensile strength for PP–LDPE blends compatibilized via imidazol–carboxyl interactions occurring between modified PP and PE.

If we examine more carefully the tensile strength variation, it can be seen that the amount of compatibilizer is not the only factor responsible for the tensile strength increase. As can be seen in *Figure 3*, the amount of compatibilizer affects much more the tensile strength of blends with 25 and 50 wt% LDPE and to a lesser degree that of the blends with 75 wt% LDPE. As pointed out earlier, in

the 25/75 w/w LDPE/PP blend an increase of the amount of compatibilizer does increase the overall crystallinity of the blend, resulting mostly from the increase of LDPE crystallinity. For this reason the highest increase in tensile strength appeared in this blend. The opposite was observed for the 75/25 blend, which has a lower degree of crystallinity than even the uncompatibilized blend.

In uncompatibilized blends the opposite behaviour appears for elongation at break, as shown in *Figure 4*. The elongation at break of the blends increases with the LDPE content. Lovinger and Williams[16] demonstrated that elongation at break of an uncompatibilized PP–HDPE blend exhibits a minimum at 25 wt% HDPE. Our blends show a similar trend. At higher HDPE contents the percentage elongation at break followed the increase of HDPE content. A similar trend was observed by Robertson and Paul[62].

The addition of the compatibilizer improved the elongation at break of all blends. As can be seen in *Figure 4*, the improvement increases with increasing amount of compatibilizer, except for blends containing 20 wt% compatibilizer.
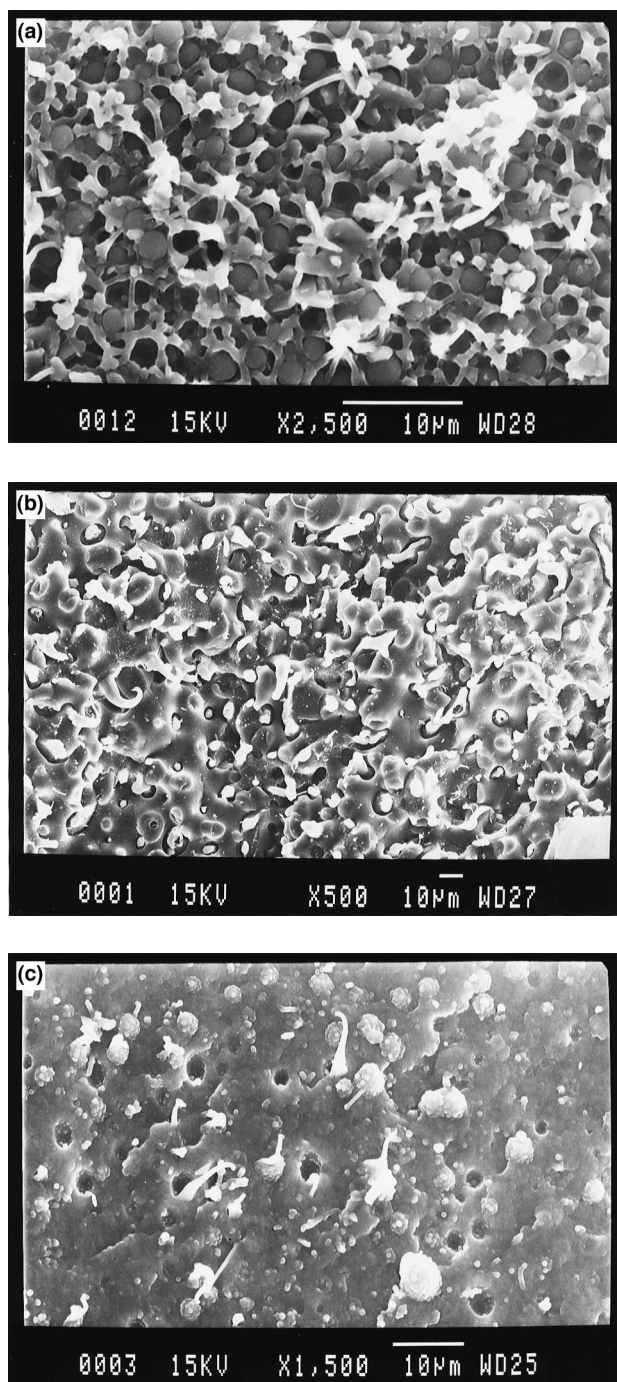
Figure 6 Scanning electron micrographs of fracture surface obtained from impact specimens of PP/LDPE blends: (a) 25/75 w/w, (b) 50/50 w/w and (c) 75/25 w/w

Since this was not observed for tensile strength, it can be concluded that the extent of crosslinking in these blends was higher. Crosslinked molecules have reduced mobility, which could increase the tensile strength but would significantly reduce the elongation at break[32]. The increase in elongation at break was higher in the blends with 75 wt% LDPE than in the blends with 25 wt% LDPE but, even in this case, it is much lower than the elongation of pure LDPE (about 600%).

An improvement was also found in the impact strength for all compatibilized blends, compared to the uncompatibilized ones. As illustrated in *Figure 5*, this increase depends also on the amount of the added compatibilizer.

Blends with a higher amount of compatibilizer had higher impact strength values except for those containing 20 wt%. The blends with 10 wt% compatibilizer had the highest impact strength values. In these blends the impact strength improved from 50%, for the LDPE/PP 25/75 w/w blend, up to 100% for the LDPE/PP 75/25 w/w, as compared to the respective uncompatibilized blends. The observations made for impact strength are similar to those made for elongation at break.

The amount of the added compatibilizer is of key importance in the improvement of the mechanical properties of the compatibilized blend and, as a consequence, the extent of the reaction for its *in situ* formation must be very well controlled. In a previous study[52], it was found that the extent of the reaction between two reactive groups during melt mixing depends on their concentration and molar ratio in the blend, and on the reaction time. High reaction times and molar ratios result in the production of macromolecules with higher degrees of crosslinking. However, in this case the macromolecules may lose their ability to act as compatibilizers[63]. To avoid such problems, in the present study a very low molar ratio between maleic anhydride and hydroxyl groups (about 0.1) was chosen. EVAL copolymer contained a high amount of hydroxyl groups which were in a tenfold excess compared to maleic anhydride groups of PP-g-MA. This means that, even in the case that all the maleic anhydride groups had reacted, a high amount of hydroxyl groups would remain intact. As a result, the remaining hydroxyls can react with or develop hydrogen bonds with the carboxylic groups produced by the opening of the maleic anhydride ring[64]. This could further increase the compatibility between PP and LDPE without the need for production of more crosslinked macromolecules. But even in this case, when 20 wt% of compatibilizer was added, the extent of the reaction between the two components of the compatibilizer was too high, leading to the production of more branched and crosslinked macromolecules. For this reason the produced macromolecules had a negative effect, mainly on elongation at break and impact strength. Taking into account all the above considerations, it can be concluded that an amount of 10 wt% compatibilizer represents an optimum concentration as far as impact strength and elongation at break are concerned.

Blend morphology

Uncompatibilized blends. It can be pointed out once again that good mechanical behaviour (including impact strength) depends on interfacial adhesion for efficient transfer of stress between the component phases[65]. The role of the adhesion for toughening a brittle polymer is clearly determined[2], while the role of interfacial chemical bonding in toughening a pseudoductile matrix polymer is not as clear, though there are suggestions which indicate that toughening with a copolymer via reactive blending does not result from particle size reduction but rather from an interfacial adhesion effect[66]. From the morphological studies presented below, it can be said that in our compatibilized blends the reaction between PP-g-MA and EVAL led to better adhesion between PP and LDPE and, consequently, to higher mechanical properties than in uncompatibilized blends.

The morphology of polymer blends is primarily affected by two factors: interfacial tension and rheological properties[67]. Scanning electron micrographs from uncompatibilized PP–LDPE blends are shown in *Figure 6*.
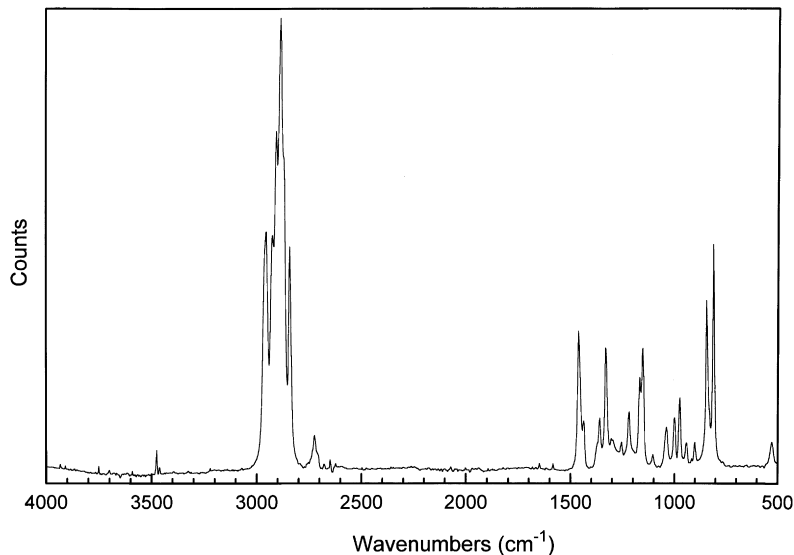
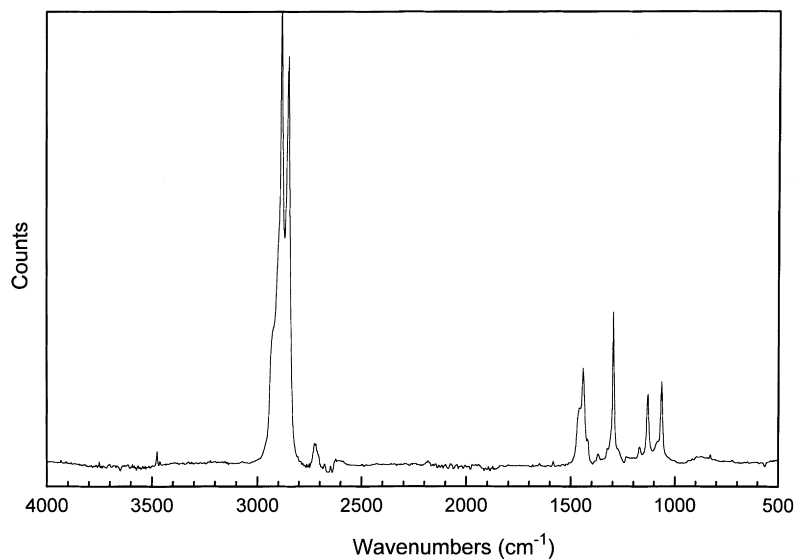**Figure 7**   Raman spectrum of pure PP

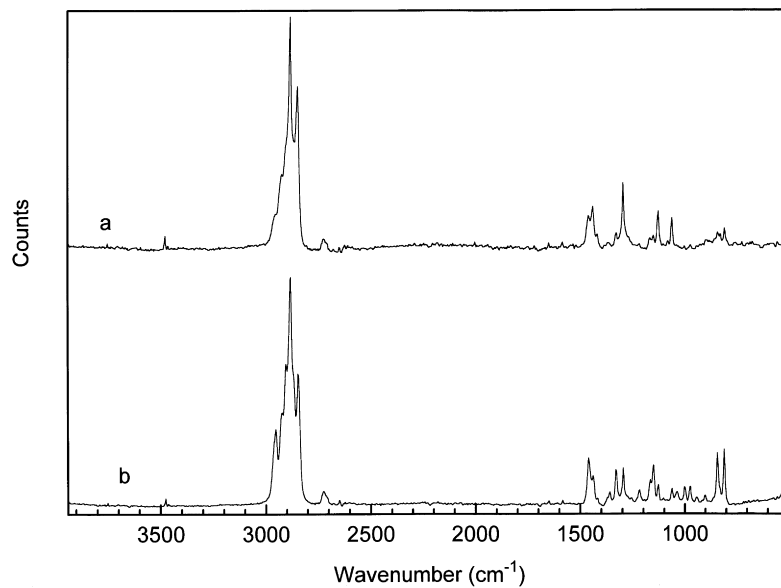**Figure 8**   Raman spectrum of pure LDPE

Figure 9   Raman spectra of PP/LDPE 25/75 w/w blend focusing on: (a) spherical parts; (b) continuous phase
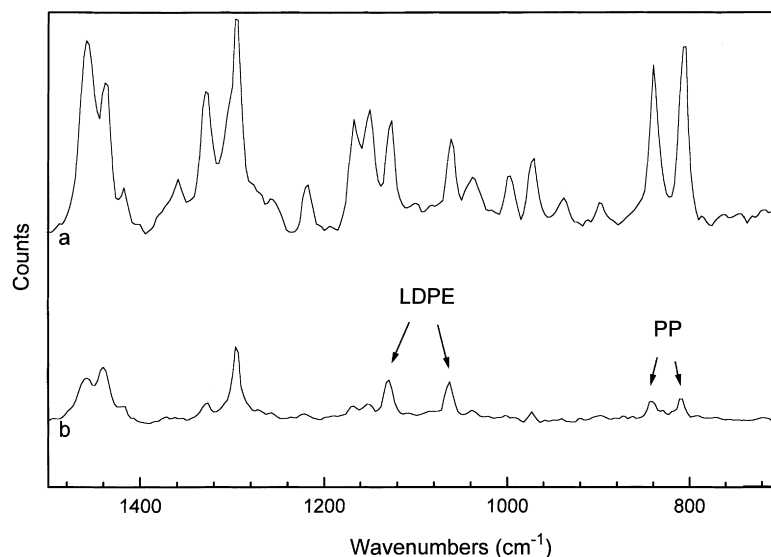
Figure 10 Raman spectra of PP/LDPE 75/25 w/w blend focusing on: (a) continuous phase; (b) spherical domains

The microstructure also depends, of course, on the composition of the blend. At higher LDPE content (PP/LDPE 25/75 w/w, *Figure 6a*) spherical PP domains of constant size of the order of 2.5 μm in diameter are present. The two polymers seem to be mutually insoluble and the phases can be clearly discerned. The blend morphology was verified by micro-Raman spectra recorded by focusing on the dispersed spherical microphases and the continuous matrix phase around the spherical domains. This is an important complement to the SEM feature that micro-Raman spectroscopy offers: besides morphological observations, modern Raman microscopy with spatial resolution of the order of 1 μm enables us to identify which polymer is the dispersed and which is the continuous phase[68]. One may also verify whether the microstructure conforms with that expected from the different rheological behaviour of the mixed pure polymers. The aid of micro-Raman spectroscopy is particularly important in the case of blends of polymers with similar shear viscosities, as is sometimes the case with PP/LDPE blends[21].

The Raman spectra of PP and LDPE before blending were recorded as a reference guide for further examination of PP–LDPE blends and are presented in *Figures 7 and 8*. The spectrum of polypropylene has characteristic vibrations at 1105 and 810–860 cm^{-1}. The most important vibrations of polyethylene are at 1128 and 1062 cm^{-1} (vC–C), as illustrated in *Figure 8*.

From the spectra, which were collected from each area separately, it was found that the spherical parts are PP and the continuous phase is LDPE, since their spectra are identical to those of the pure polymers (*Figure 9*). Focusing straight to a spherical domain, the PP characteristic peaks were recorded at 1105 cm^{-1} and at 810–860 cm^{-1} (double peak, *Figure 9b*). Moreover, if the peak at 2810–2950 cm^{-1} is compared with the corresponding peak of pure PP, it is verified that the spherical particles are polypropylene. By focusing on the flattened area around the spherical particles in the same blend, the spectrum illustrated in *Figure 9a* was recorded. The characteristic peaks of polyethylene at 1128 cm^{-1} and at 1062 cm^{-1} were present. In addition, the double peak at 2820–2940 cm^{-1} is the same as the corresponding one in pure LDPE. Thus it can be claimed that the spherical particles are surrounded by polyethylene,

i.e. the matrix is LDPE. This finding confirms the intuitive rule from emulsions that in polymer blends the minor component forms the dispersed phase and the major the matrix.

The decrease of LDPE concentration (PP/LDPE 50/50 w/w) affected the microstructure of the blends (*Figure 6b*). The phase boundaries are easier to discern and some globules are formed also. The 'cavities', initially occupied by the dispersed phase, are smooth and featureless. The main problem, when the two polymers are in equal amounts, is to identify which one is the dispersed phase and which the matrix. If one of them is soluble in a solvent (which is non-solvent for the other), it can be extracted and then it is easy to find its placement in the polymer blend by SEM. In the case that we cannot find such a solvent, we may obtain useful information by means of micro-Raman by focusing in different areas and studying the collected spectra. Study of the resulting spectra showed that the dispersed phase was PP, as in the blend with 25 wt% PP, while LDPE was the continuous phase.

In blends with high PP concentration (PP/LDPE 75/25 w/w, *Figure 6c*) there are spherical domains of 2.5–5 μm in diameter dispersed in the continuous matrix. These domains consist of small particles in the order of 0.5 μm in diameter, which can be better observed in the inner side of the cavities created when bigger spherical particles were pulled out during fracture. The assemblies, which were not pulled out from the matrix during the breaking of the specimen, are difficult to discern. A very high proportion of these spherical domains is also dispersed throughout the whole matrix. Since LDPE is in a lower concentration than PP it was initially assumed, after studying the SEM micrographs, that the large spherical domains were LDPE. Surprisingly, the Raman spectrum of this area was that of PP. This leads to the conclusion that they are PP domains. Similar spectra were also collected from the continuous phase. It remains to be resolved where the LDPE is dispersed to. Examining more carefully these spectra (*Figure 10*), it can be seen that the characteristic peaks of both polymers exist in all areas. However, in the continuous phase the PP peaks dominate, whereas in the small spherical domains those of LDPE are more prominent.

It has been mentioned that in a similar blend, consisting

of polypropylene and linear low density polyethylene (LLDPE) at a 70:30 w/w ratio, LLDPE is the dispersed phase, as was identified by SEM microscopy[69]. Also, a fine LDPE dispersion has been identified in another blend of isotactic polypropylene and LDPE, containing 75 wt% polypropylene[70]. This seems to be the case in our blends as well. LDPE forms very small spherical particles which are less than 1 μm in diameter, as can be seen in SEM micrographs. Since this size is smaller than the spatial resolution of our Raman instrument, it is impossible to collect the spectrum from an isolated LDPE-rich domain

Figure 11 Scanning electron micrographs of fracture surface obtained from impact specimens of PP–LDPE blends compatibilized with 10 wt% compatibilizer: (a) PP/LDPE, 25/75 w/w; (b) PP/LDPE, 50/50 w/w; (c) PP/LDPE, 75/25 w/w

and thus the spectrum contains also the contribution of the surrounding PP-rich matrix.

Compatibilized blends. The morphology of compatibilized blends containing 10 wt% compatibilizer depends mainly on the blend composition, as does that of uncompatibilized blends. SEM micrographs of these blends are illustrated in *Figure 11*.

The micrograph of the compatibilized blend containing 75 wt% LDPE (*Figure 11a*) clearly demonstrates that the compatibilizer influences the morphology of the final product. It is remarkable that in this blend the compatibilizer effected the greatest improvement of impact strength (80%) while it also improved the tensile strength. The boundaries of the domains are not difficult to discern, but there are many differences when compared with the corresponding uncompatibilized blend (see *Figure 6a*). The PP spheres seem to be bigger. Examining these particles more carefully, it can be seen that they contain on their surface many smaller spherical particles with sizes less than 1.5 μm. Also, there is a fine distribution of the same particles over the whole matrix which seem to be smaller than those of the uncompatibilized blend. Raman spectra recorded from the large spherical domains and the flattened surfaces surrounding them showed that a small amount of LDPE exists within the PP phase and vice versa.

As can be seen from *Figure 12*, in the spectra of spherical domains of the uncompatibilized blend (*Figure 12c*) the two characteristic peaks of LDPE at 1128 and 1062 cm^{-1} appear with a very small intensity. Since these peaks do not exist in the spectrum of PP, it can be concluded that the two polymers exhibit a limited mutual solubility. Similar evidence is given by Kryszewski *et al.*[71]. In the spectrum of the same particles after compatibilization (*Figure 12d*), the intensity of these two peaks is increased. This can be attributed mainly to EVAL copolymer which has approximately the same spectrum as LDPE and is placed at the interface along with the PP-g-MA blocks. The presence of the compatibilizer causes, of course, an increase in mutual solubility of the two polymers.

Similar observations were made for the continuous phase. As shown in *Figure 13c*, the characteristic absorption of polypropylene at 810–860 cm^{-1} (weak, double peak) was recorded when focusing on the flattened area around the PP domain. This means that a small part of the polypropylene was present even in the flattened area surrounding the spherical domain.

At equal PP and LDPE proportions in the compatibilized blend, it is difficult to determine which phase is PP and which is LDPE, in contrast with the uncompatibilized blend. The white spots observed in the micrographs (*Figure 11*) of this blend are not a separate polymer phase. They are inclined planes of the polymer formed after specimen rupture which were not completely covered by gold during preparation of the specimen for SEM microscopy. The Raman spectra are similar to those collected for the PP/LDPE 75/25 w/w blend, where the characteristic absorbances of both polymers were simultaneously present, since the sizes of each phase are lower than 1 μm—the spatial resolution of the micro-Raman unit.

At lower LDPE content (25 wt%), the agglomerated spherical particles (*Figure 11c*) are fewer in the compatibilized blend than in the corresponding uncompatibilized one. The spherically shaped imprints on the matrix and the phase boundaries were not as sharp and well defined as in the corresponding uncompatibilized blend. Also, the
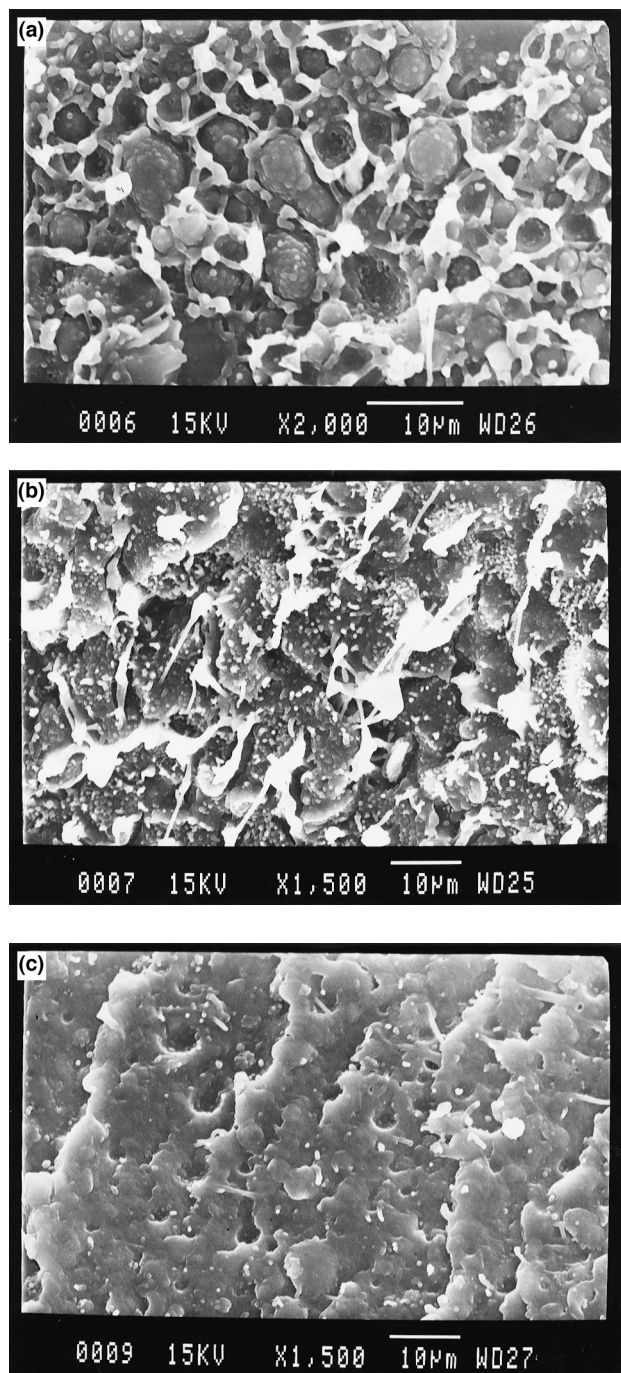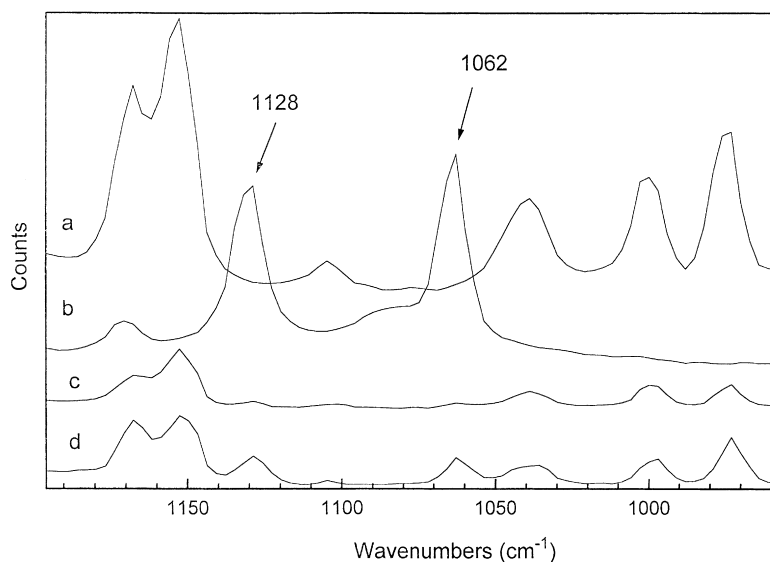
Figure 12 Raman spectra in the region 1200–950 cm^{-1} of PP/LDPE blends: (a) pure PP; (b) pure LDPE; (c) spherical domains in PP/LDPE 25/75 w/w blend without compatibilizer; (d) spherical domains in PP/LDPE 25/75 w/w blend with 10 wt% compatibilizer
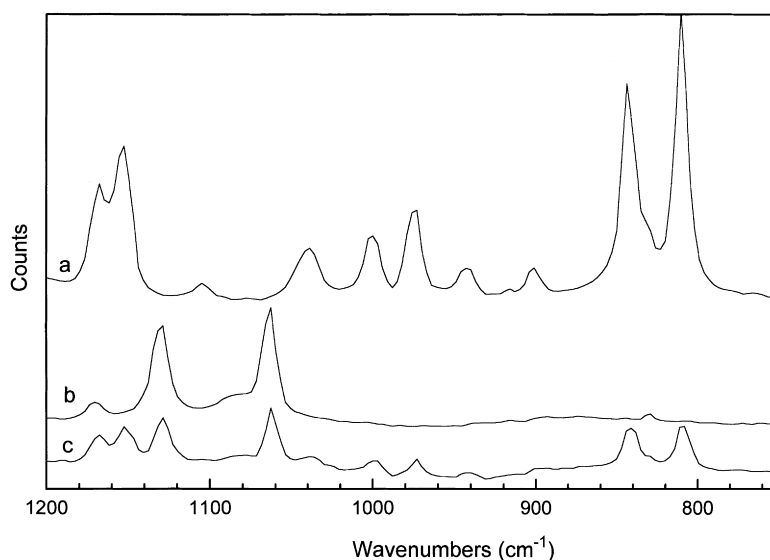

Figure 13 Raman spectra in the region 1200–750 cm^{-1} of PP/LDPE blends: (a) pure PP; (b) pure LDPE; (c) flattened area in PP/LDPE 25/75 w/w blend with 10 wt% compatibilizer

dispersed LDPE particles are of smaller size, due to compatibilization.

CONCLUSIONS

(1) Micro-Raman spectroscopy seems to be a valuable tool for studying polymer blend morphology. This technique has verified that PP and LDPE are immiscible polymers with marginal mutual solubility and has allowed a clear identification of the dispersed phase.

(2) The esterification reaction between PP-g-MA and EVAL for the *in situ* formation of compatibilizer macromolecules was verified by the melt torque increase recorded during blend mixing, and by *FT*i.r. spectroscopy.

(3) The compatibilizer's constituents, PP-g-MA and EVAL, are mainly incorporated in the PP and LDPE phases respectively. EVAL has a higher degree of crystallinity than LDPE and PP-g-MA a lower degree than PP. The consequence of this is the increase of the LDPE degree of crystallinity and the reduction of the PP degree of crystallinity observed in the compatibilized blends.

(4) The addition of compatibilizer also improves the mechanical properties (tensile strength, elongation at break and impact strength) of the blends. Higher tensile strength was obtained by addition of 20 wt% compatibilizer, whilst higher impact strength was obtained by addition of 10 wt% compatibilizer. This improvement is due to the increased interfacial adhesion between the two polymers, leading to a better dispersion of the minor component into the matrix, as was shown by SEM microphotographs.

(5) Adding LDPE to PP in the presence of even small amounts of compatibilizer improves significantly the poor impact strength of PP.

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