

Glass-fiber reinforcement of *in situ* compatibilized polypropylene/polyethylene blends

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Polypropylene and low-density polyethylene (LDPE) were melt-blended at proportions 75/25, 50/50, and 25/75 w/w, respectively. These blends were reinforced with two types of glass fibers added at an amount of 20 wt %: the E-type fibers without any surface treatment and the M-type fibers, which were treated with γ -methacryloxy propyltrimethoxy silane coupling agent. Poly(propylene-*g*-maleic anhydride) with 0.8 mol % maleic anhydride content and poly(ethylene-*co*-vinyl alcohol) with 7.5 mol % vinyl alcohol content were added at a 50/50 w/w proportion as *in situ* reactive compatibilizers at an amount of 10 wt %. The thermoplastic composite materials have higher tensile strength as well as impact strength compared to the unreinforced blends. The simultaneous process of the *in situ* blend compatibilization, along with the incorporation of glass fibers in the thermoplastic matrix, leads to a significant improvement of the mechanical properties as compared to the properties of the composite materials with the uncompatibilized matrix. Scanning electron microscopy and micro-Raman spectroscopy have been used to study the adhesion of the thermoplastic matrix onto the glass fibers. Significantly better adhesion characteristics were observed in the composites containing M-type glass fibers, with LDPE adhering the most on the fibers. This better adhesion was reflected in the improved mechanical properties of the composites. © 1999 Kluwer Academic Publishers

1. Introduction

Glass-fiber reinforcement is often an attractive way to improve the mechanical properties of thermoplastic matrices, the improvement being attributed to the excellent mechanical properties of the fibers [1–3]. Many studies have been published concerning the rheology, processing conditions, and the properties of thermoplastics containing glass fibers [4–9]. The mechanical properties of these thermoplastic composites are significantly affected mainly by the interfacial adhesion between the glass fiber and the polymer matrix, the length and the diameter of the fiber, their concentration in the thermoplastic, the fiber orientations, and their distribution in the polymer composite [10–14]. On the other hand, there is an ever-increasing interest in the development of new polymer alloys and blends. In the last few years, much interest has also been shown in the fiber reinforcement of polymer alloys and blends [15–19].

Blending and alloying of polymers are effective methods for tailor-making materials that possess specific combinations of physical properties, processing characteristics, and cost. But because of the immiscibility and incompatibility of most polymers, the resulting

material has inferior mechanical properties when compared to the pure-component polymers. These properties could lie between the corresponding properties of the component polymers or even be inferior than either of the pure polymers. Polypropylene (PP) and low-density polyethylene (LDPE) are two of the most commonly used polymers, and their blends are of great interest. The possibility of preparing a blend of these polymers with acceptable mechanical properties would result in a valuable material and a useful recycling practice, because in communal waste the main plastic components are usually the various types of the semicrystalline PE and PP, which are used mainly in packaging applications [20].

Because PP and LDPE are incompatible, the use of a compatibilizer is always needed for the production of a blend with acceptable properties [21–24]. In a recent work, we studied the effect of polypropylene-*g*-maleic anhydride (PP-*g*-MA) and ethylene vinyl alcohol copolymers, as compatibilizers in PP/LDPE blends [25]. It was found that the above mixture of copolymers can act as an effective compatibilizer, increasing all mechanical properties, with a maximum observed at a composition of 10 wt % of compatibilizer in the final

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blend. The compatibilization action of this system was due to the reaction of the hydroxyl groups with maleic anhydride, which produced a block or graft copolymer acting as an emulsifier at the interface of the two polymers. Because of this emulsification action, a finer dispersion of one polymer into the matrix of the other could be obtained.

In the present work, the effect of glass fibers on the mechanical properties of the above compatibilized PP/LDPE blends was studied. For comparison purposes, identical glass-fiber reinforced blends, but without compatibilization, were also prepared.

2. Experimental procedure

2.1. Materials

Isotactic polypropylene was supplied by Montell and had a melting point of 168 °C and a degree of crystallinity of 48.8%. The LDPE was a commercial grade from Borealis with a melting point of 113 °C and a degree of crystallinity of 25.5%. The materials used as *in situ* reactive compatibilizers were a poly(propylene-g-maleic anhydride) (PP-g-MA) copolymer (Fusabond MD-353), supplied by Du Pont-Canada, with 0.8 mol % maleic anhydride content, as determined by titration, and a poly(ethylene-co-vinyl alcohol) (EVAL) copolymer with 7.5 mol % vinyl alcohol content. This latter copolymer was obtained by hydrolysis-saponification of a commercial poly(ethylene-co-vinyl acetate) copolymer (Alcudia) with 8 mol % vinyl acetate content.

E-glass fibers used for reinforcement had 6 mm average length and 13 μm average diameter and were obtained from Cristaleria Espanola (Madrid). The fibers were heat cleaned for 4 h at 500 °C before use. γ -Methacryloxy propyltrimethoxy silane (γ -MPS) coupling agent was used for the surface modification of E-glass fibers and was supplied by Dow Corning under the trade name Z-6030. The glass fibers were treated with γ -MPS in solution and cured for 12 h at 100 °C. These coated glass fibers will be referred to hereafter as M-type fibers.

2.2. Preparation of blends

PP and LDPE were reactive-blended at proportions 75/25, 50/50, and 25/75 w/w, respectively, containing also 10 wt % compatibilizer in the final blend. In the above blends, E- and M-glass fibers were introduced at an amount of 20 wt %. The same blends without compatibilizer were also prepared for comparative purposes. 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 . Prior to mixing, all polymers and E-type fibers were dried by heating in a vacuum oven at 75 °C for 24 h. The M-type fibers were also dried at 50 °C under vacuum for 6 h. The components were physically pre-mixed before being fed into the Rheomixer. Blending was performed at 200 °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. After preparation, the blends were immediately removed from the mixer, cooled to room temperature, milled, and placed in tightly sealed vials to prevent any moisture absorption.

2.3. 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 cross-head 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 conducted, and the reported results were their average. Prior to mechanical measurements, the samples were conditioned at $50 \pm 5\%$ relative humidity and at 23 °C for 48 h by placing them in a closed chamber containing a saturated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution in distilled water (ASTM E-104).

2.4. Thermal analysis

DSC measurements of samples were performed in a Shimadzu DSC-50Q fast quenching differential scanning calorimeter. Samples were placed in sealed aluminum cells, using a quantity of about 8 mg for each sample. The samples were initially heated with a heating rate of 20 °C/min to 200 °C in a nitrogen atmosphere and immediately quenched to remove any previous thermal history. The samples were subsequently rescanned with a heating rate of 20 °C/min, and from these thermograms the melting temperatures and heats of fusion were calculated.

2.5. Scanning electron microscopy

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

2.6. Fourier transformation infrared spectroscopy

Fourier transformation infrared (FTIR) spectra were acquired in a Biorad FTS-45A FTIR spectrometer. For each spectrum, 64 consecutive scans with 4 cm^{-1} resolution were collected. Samples were measured in the form of thin films about $70 \pm 2 \mu\text{m}$ thick. The films were prepared by hot-press molding at 200 °C for 3 min and at a pressure of 250 bar.

2.7. Raman spectroscopy

The Raman spectra were recorded with a Renishaw Raman Imaging Microscope, Model 1000. The incident laser excitation wavelength 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, and laser power of 3 mW. The spectra were collected from fractured surfaces of impact specimens using a $50\times$ objective.

3. Results and discussion

3.1. Mechanical properties

The stress-strain curves of the various studied blends exhibit some characteristic differences between them. The unreinforced blends exhibit a clearly distinct yield point, especially those with 50 and 75 wt % LDPE composition. In contrast, glass-fiber reinforced blends break without yielding, and their behavior is similar to that of typical hard and strong polymers. An increase in yield strength appears in all reinforced blends. The effect of matrix composition on the tensile strength of reinforced and unreinforced blends is presented in Fig. 1.

As can be seen, in all blends there is a reduction in tensile strength as the concentration of LDPE increases due to the lower tensile strength (about 8 MPa) that LDPE has compared to that of PP (about 18 MPa). Due to the compatibilization effect of PP-g-MA/EVAL copolymers, the compatibilized blends have higher tensile strength compared to those without compatibilization. As already mentioned, the block and graft copolymers produced from the reaction between the maleic anhydride groups of PP-g-MA and the hydroxyl groups of EVAL can act as “emulsifiers” at the interface of the two polymer phases by reducing their interfacial tension [25].

The introduction of either type of glass fibers increases also the tensile strength of the blends for all polymer proportions compared to the corresponding uncompatibilized, as well as compatibilized, blends. This increase lies between 2–8 MPa with reference to the corresponding unfilled blends. Comparing the blends with different types of glass fibers, it can be seen that those with E-type fibers appear to have a smaller tensile strength increase than those containing the M-type fibers. In contrast to the non-polar characteristic of both PP and LDPE, the hydroxyl groups at the surface of the uncoated fibers give a hydrophilic character to the fibers, which results in a poor interfacial adhesion between PP or LDPE and E-type glass

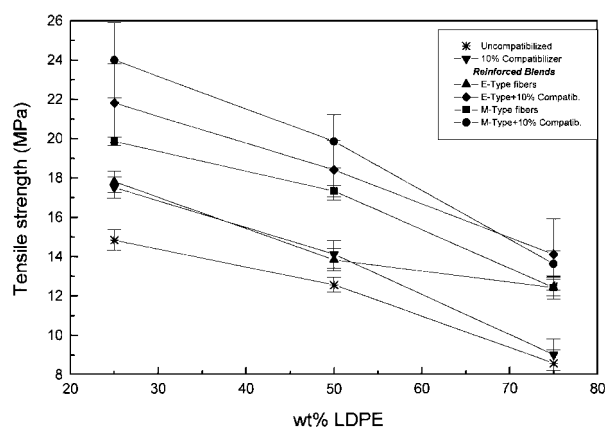


Figure 1 Tensile strength of compatibilized and uncompatibilized LDPE/PP blends containing different types of glass fibers.

fibers. Therefore, the improvement of the mechanical properties of the composites necessitates an appropriate control of the interfacial characteristics between the fibers and the polymer matrix.

The interfacial bonding strength between fibers and the polymer matrix can actually be controlled to a great extent by the use of suitable coupling agents. γ -MPS is such an agent, and it has already been found that it can promote the interfacial adhesion in glass-fiber reinforced polystyrene composites [26]. The observed substantial improvement of the mechanical properties in the blends containing M-type glass fibers can be attributed to the non-polar characteristic that γ -MPS can impart to the surface of the glass fiber. As a consequence, a better wetting of the fiber by the PP or LDPE matrix occurs, leading to an improved adhesion between the fiber and the polymer matrix, which in turn increases the tensile strength of the composite. γ -MPS also reduces the tendency of the fibers to aggregate and form clusters [27], and, thus, a better distribution within the polymer matrix can be achieved.

In comparing the tensile strength of the reinforced compatibilized and uncompatibilized blends, one additional factor comes into play: The reactive groups of the compatibilizer can react with the surface of glass fibers. Maleic anhydride groups of PP-g-MA can react with the hydroxyl groups of glass fibers (Fig. 2a). Such reactions have been assumed to take place in a similar system [28]. The carboxylic groups produced can form hydrogen bonds with the hydroxyl groups of the glass fibers. Another possibility is the formation of hydrogen bonds between the hydroxyl groups of EVAL copolymer and the hydroxyl groups of glass fibers (Fig. 2b). The latter is more pronounced because EVAL contains a higher amount of hydroxyl groups (7.5 mol %) compared to the maleic anhydride groups of PP-g-MA (0.8 mol %). All the above may lead to an increased adhesion between the polymer matrix and the uncoated glass fibers, which could explain why the compatibilized blends, reinforced with E-type glass fibers, have higher tensile strength than the uncompatibilized blends, reinforced even with M-type glass fibers.

To verify whether the above interactions take place, the blends were examined by FTIR spectroscopy. Spectra were collected for the compatibilized blends

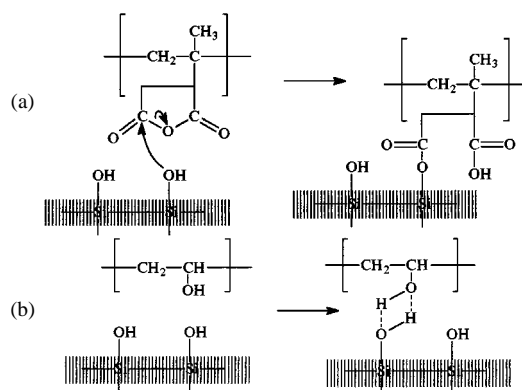


Figure 2 (a) Interactions between maleic anhydride groups of PP-g-MA and hydroxyl groups of glass fibers and (b) hydrogen bond formation between the hydroxyl groups of EVAL and glass fibers.

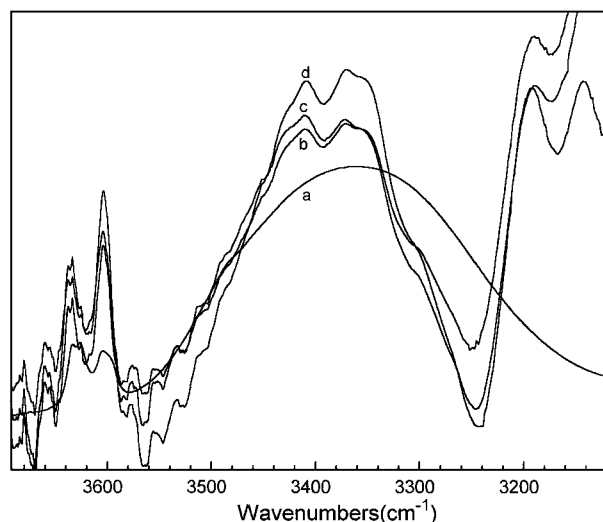


Figure 3 Hydroxyl region FTIR spectra of: (a) EVAL copolymer; (b) PP/LDPE 50 : 50 compatibilized blend without glass fibers; (c) PP/LDPE 50 : 50 compatibilized blend reinforced with E-type fibers; and (d) PP/LDPE 50 : 50 compatibilized blend reinforced with M-type fibers.

without fiber reinforcement with E-type and with M-type fiber reinforcement. All these spectra were similar in one appearance without any significant differences. There was a small peak at 1730 cm^{-1} , which was attributed to the ester group formation from the reaction of maleic anhydride group with the hydroxyl groups. But the magnitude of this peak was the same and in the compatibilized blend without glass fibers. This was expected, because the concentration of the maleic anhydride groups is very small and the greatest portion of them is consumed during reaction with the hydroxyl groups of EVAL. The exact amount that has reacted with the hydroxyl groups of glass fibers is difficult to determine from the above spectra.

The possibility of hydrogen bond formation was investigated by examining the hydroxyl region spectra shown in Fig. 3. As can be seen in Fig. 3, there are no significant differences, either in the hydroxyl area among the spectra for the blend without any glass fibers and for those containing E- and M-type fibers, respectively. It was expected that the compatibilizer was able to develop hydrogen bonds with the hydroxyls lying on the surface of the glass fibers, especially with the E-type fibers in which hydroxyls are not capped with silanes, as is the case with M-type fibers. Even in the case of M-type fibers, not all hydroxyls have reacted, and thus those remaining could also develop hydrogen bonds. These hydrogen bonds would partially explain the better mechanical properties observed in the compatibilized reinforced blends. However, the three spectra (b, c, and d) in this area appear almost identical with no extra peaks and peak shifts appearing in the spectrum of the reinforced blends. Of course, there is always the possibility that hydrogen bonds form, but because of bad overlap by other hydroxyl peaks they cannot be detected.

As was mentioned before, glass-fiber reinforcement leads to a drastic reduction of the ductility of the polymer blend. This is reflected in the elongation at break of the blends, as can be seen in Fig. 4.

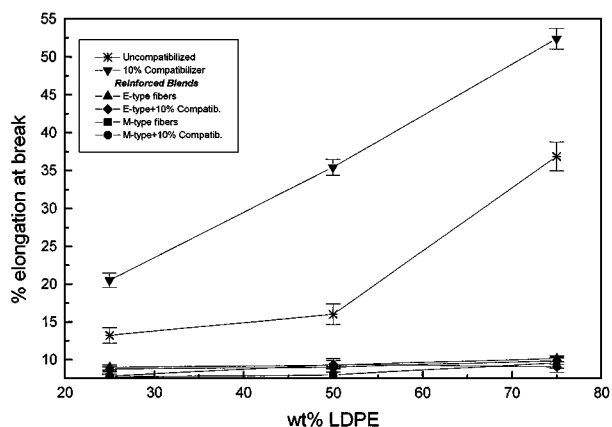


Figure 4 Elongation at break of compatibilized and uncompatibilized LDPE/PP blends containing different types of glass fibers.

In the blends without glass fibers, the elongation at break increases as the amount of LDPE increases. Furthermore, the compatibilized blends have higher elongations compared with the corresponding uncompatibilized blends. This is due to the reduction of the dispersed phase's size, introduced by the addition of compatibilizer. When glass fibers are introduced in the above blends, the elongation at break decreases drastically. In contrast with tensile strength, there are no large differences between the reinforced blends, as far as elongation at break is concerned, which lies between 8 and 10%, even in the blends containing 75 wt % LDPE. In general, the elongation at break of reinforced thermoplastics decreases as the concentration of the fibers increases [29].

The differences in the impact strength of the same blends are more clear, as can be seen in Fig. 5. It is known that in tough polymer matrices, the toughness usually decreases with the incorporation of glass fibers [2], while their addition in brittle matrices has the opposite effect [30–33]. Thus, the incorporation of E- and M-type glass fibers in PP increases their impact strength from 6 J/m to 14 and 16 J/m, respectively. In contrast, the incorporation of these fibers in the very tough LDPE transforms it into a rather brittle material.

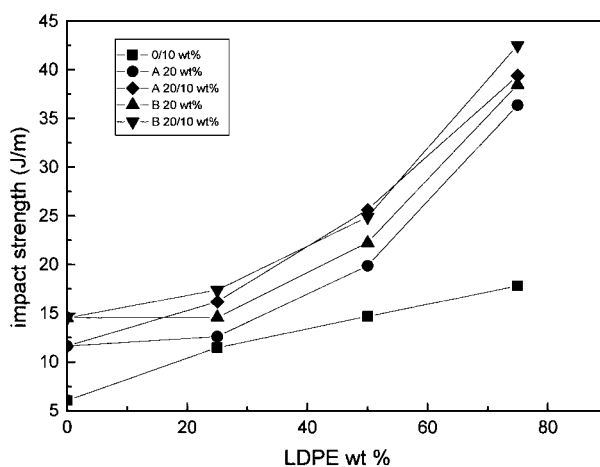


Figure 5 Impact strength of compatibilized and uncompatibilized LDPE/PP blends containing different types of glass fibers.

TABLE I Degree of crystallinity (%) of LDPE in blends

a/a	LPDE wt %	Uncompatibilized			Compatibilized		
		Unreinforced	E-type	M-type	Unreinforced	E-type	M-type
1	100	25.5	25.6	26.5			
2	75	25.1	24.6	25.3	24.6	23.9	25.4
3	50	22.3	23.5	22.8	23.5	24	23.9
4	25	17.6	24.1	24.4	21.9	23.4	25

TABLE II Degree of crystallinity (%) of PP in blends

a/a	PP wt %	Uncompatibilized			Compatibilized		
		Unreinforced	E-type	M-type	Unreinforced	E-type	M-type
1	100	48.8	49.2	54			
2	75	42	42.1	40.9	37.2	40	39.9
3	50	40	39.1	39.3	37.4	38.4	38.6
4	25	36.6	37.7	37.6	35.2	36.4	35.8

It is worth noting that all reinforced blends in Fig. 5 exhibit higher impact strength than the corresponding unreinforced blends. The effect of M-type glass fibers is also noticeable in both compatibilized and uncompatibilized blends. Compared to those containing the E-type fibers, it can be seen that in all cases, the former exhibit an impact strength 3–4 J/m higher except for the compatibilized blends where the impact behavior is the highest and practically the same for the two types of fibers. This is further evidence that the interfacial adhesion between the polymers and the glass fibers is higher in compatibilized blends. It is known that the ability of short glass fibers to absorb the mechanical impact energy depends, among other things, on the interfacial adhesion and on the composition of the interfacial fiber-matrix layer [15].

An important role in this interfacial adhesion and interfacial layer composition is played by the compatibilizer. Strong specific interactions, such as hydrogen bonding, or chemical interactions, such as those between maleic anhydride groups of the compatibilizer and the hydroxyl groups of glass fibers, across the phase boundaries, can control the overall performance of the polymer matrix composites [34]. In a previous study, it was found that the dominant crack propagation orientation is parallel to the glass fibers [35]. Because the fracture of the composite occurs near the fiber-matrix interface, the interfacial adhesion plays a very important role. When it is high, there is an efficient load transfer from the polymer matrix to the glass fillers. By improving the interfacial adhesion, the compatibilizer improves the impact strength of the composite material.

3.2. Thermal analysis

In a previous study, it was found that the introduction of compatibilizer in PP-LDPE blends affects the crystallinity of both PP and LDPE [25]. The degree of crystallinity in LDPE increases due to the incorporation of EVAL copolymer in the LDPE phase, whereas the crystallinity of PP decreases due to the incorporation of PP-g-MA in the PP phase. The use of glass fibers could also further affect the degree of crystallinity. It is

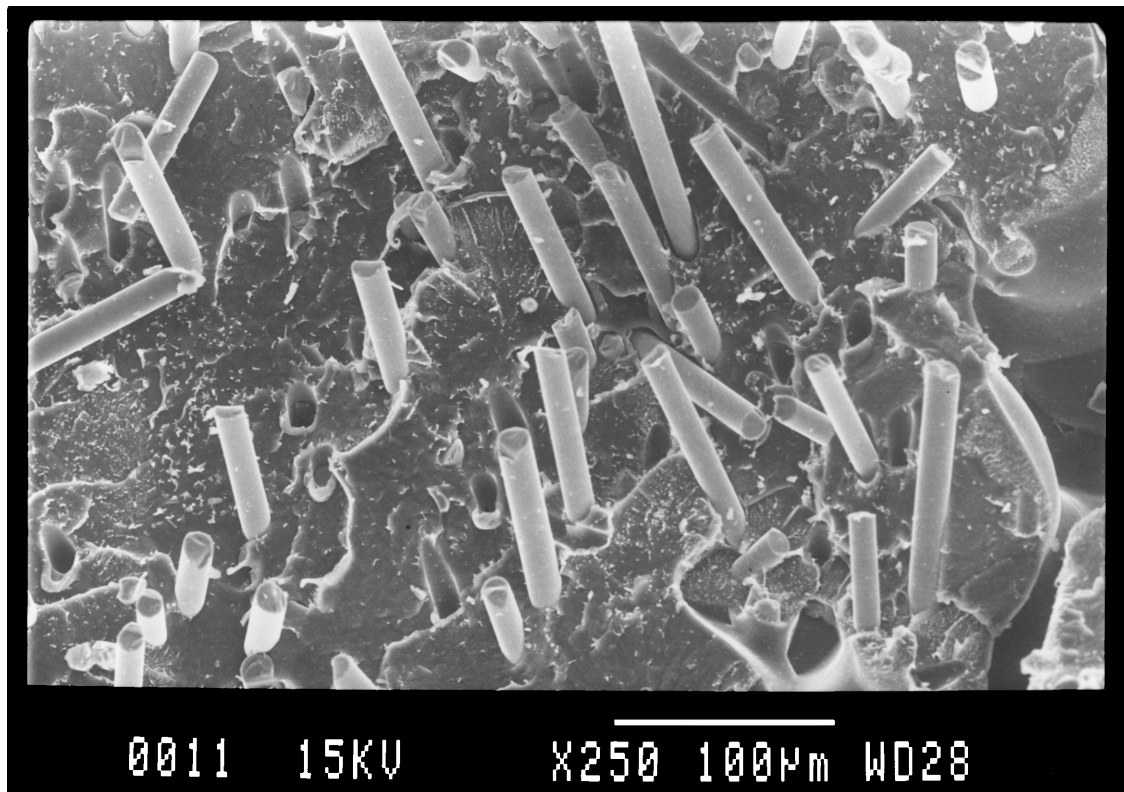
known that the surfaces of some fibers are provided for nucleating sites, which makes them act like nucleating agents and increase the rate of crystallization in pure PP [36]. The degree of crystallinity for each polymer in the blend was calculated from the heat of fusion taking into account the heat of fusion of completely crystalline (100%) polymers. For LDPE, this is 290 J/g [37] and for PP 165 J/g [38]. The crystallinity measurements are reported in Tables I and II. All reported data take into account the amount of each polymer in the blend.

In general, when glass fibers are added to polymer blends, they act as nucleating agents, and a noticeable increase in the crystallinity of the matrix polymer appears. However, it has been found that in polyethylene blends such as PBT-HDPE, the introduction of glass fibers had only a small effect on polyethylene's degree of crystallinity: In this case, the glass fibers were found to increase the degree of crystallinity of both polymers [16]. This could be explained by the fact that PBT is quickly crystallizable and that the degree of crystallinity depends on the rate of crystallization, as well. Nevertheless, in this study it seems that the incorporation of glass fibers has a very small effect on the degree of crystallinity of the polymer matrix. The enhancement of the mechanical properties of semicrystalline polymers, such as PP and LDPE, could in part be attributed to the changes in the morphology of the matrix, due to the presence of glass fibers acting as heterogeneous nucleating agents [39]. Because the changes in the degree of crystallinity in our blends are relatively small, the differences in the mechanical properties are mainly due to the increased adhesion between the polymer matrix and the glass fibers.

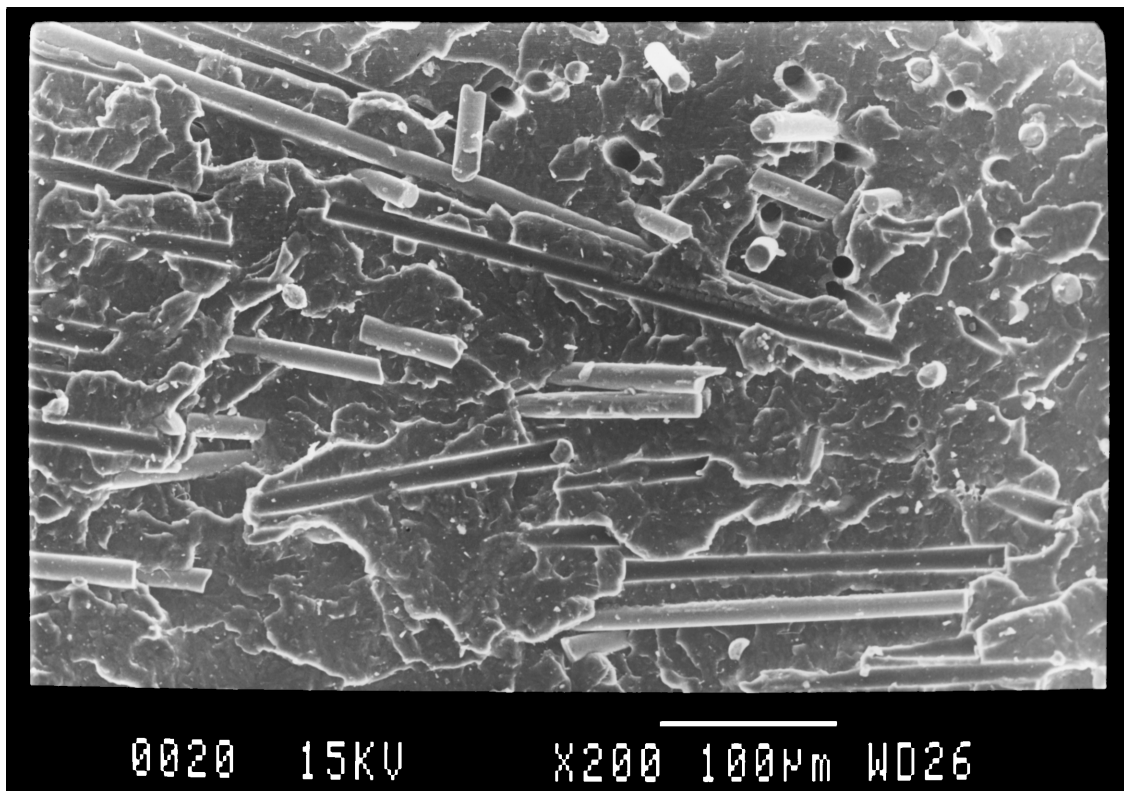
3.3. Scanning electron microscopy

The improved interfacial adhesion has been confirmed in the present investigation by direct examination of impact fracture surfaces by SEM. In Fig. 6, the SEM micrographs of pure PP and LDPE, containing different types of glass fibers, are presented.

In the fractured surfaces, the glass fibers are projected out from the polymer matrix. They appear to be



(a)

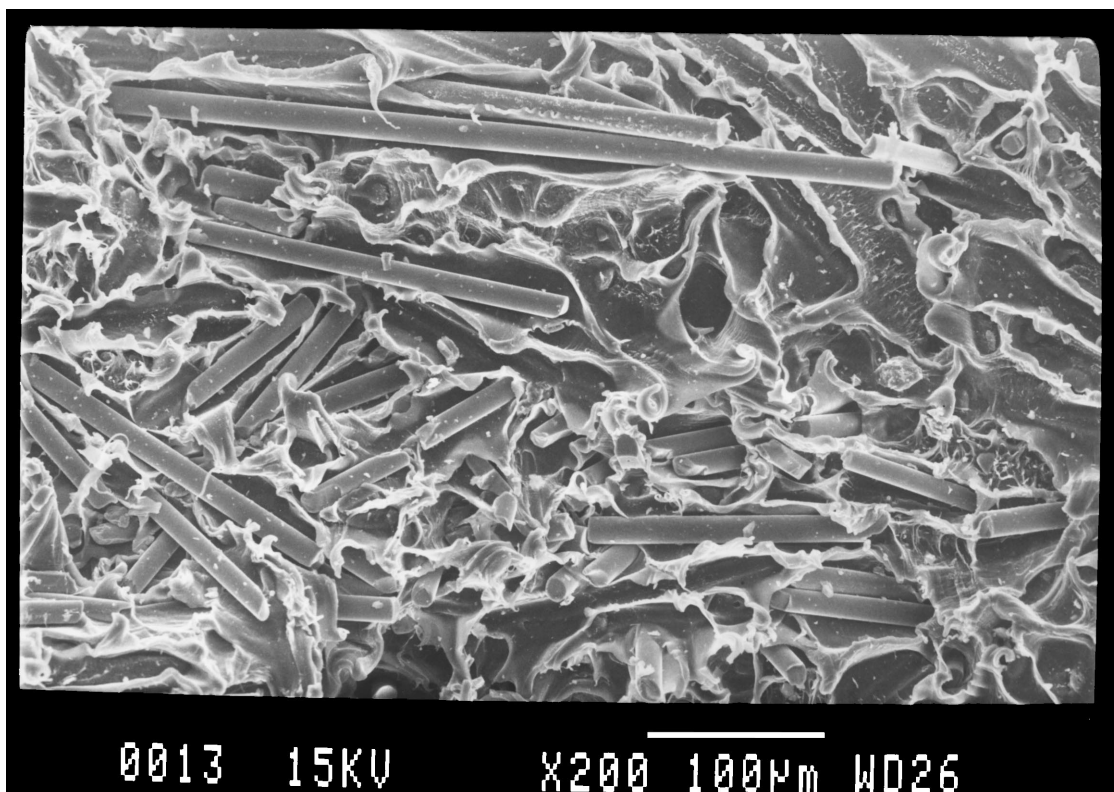


(b)

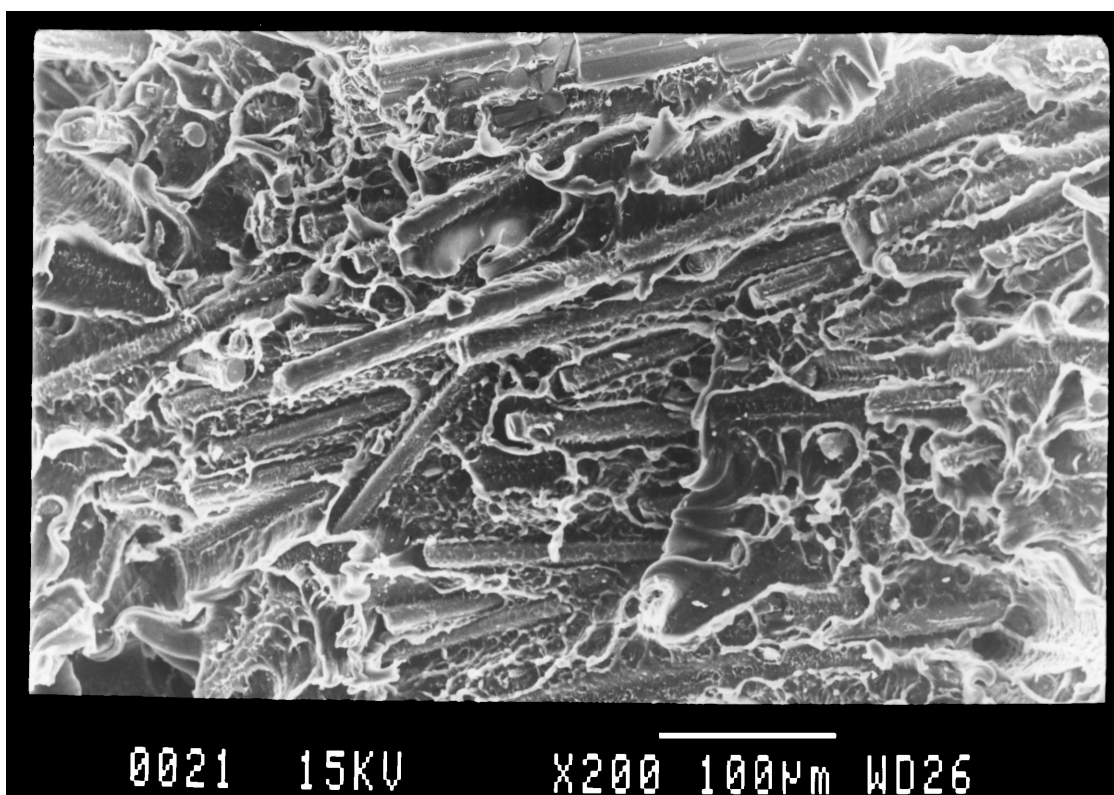
Figure 6 SEM micrographs of impact fracture surfaces of pure polymers, containing different types of glass fibers: (a) PP with E-type; (b) PP with M-type; (c) LDPE with E-type; and (d) LDPE with M-type. (Continued).

randomly dispersed without any apparent orientation or difference between the two types of the fibers. For the E-type fibers, the glass surfaces are very clear in both polymers. Also, the surfaces of the hollow cylinders or cavities in the polymer matrix, which were created from the pulled-out glass fibers, are smooth. Because

neither of the two main polymers can interact with this type of fiber, the interfacial adhesion is very poor. The same behavior appears when the M-type is incorporated within PP. The cohesion remains poor. On the contrary, in LDPE the fibers are covered with a thin layer of polymer. The treatment of the glass fibers with



(c)



(d)

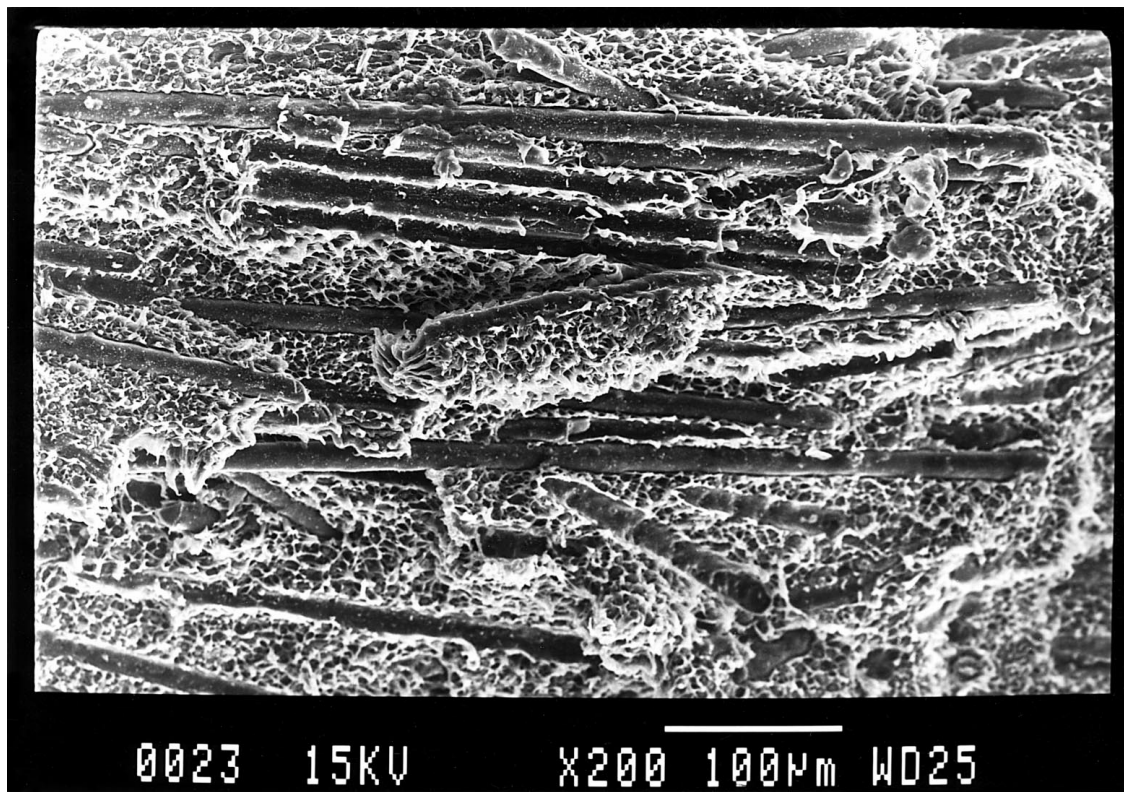
Figure 6 (Continued).

the silane coupling agent γ -MPS turns them non-polar, leading to an improvement of the interfacial adhesion between the fibers and LDPE. As observed in Fig. 6d, LDPE is tightly adhered to all fibers in the micrograph.

Uncompatibilized blends show a similarity to pure polymer behavior regarding their adhesion to the glass

fibers. Only in the blends containing the M-type glass fibers does a surface coating by polymer appear, as can be seen in Fig. 7a. This coating should primarily be LDPE.

When a compatibilizer was used in the blends, both types of glass fibers were covered by a polymer layer,



(a)

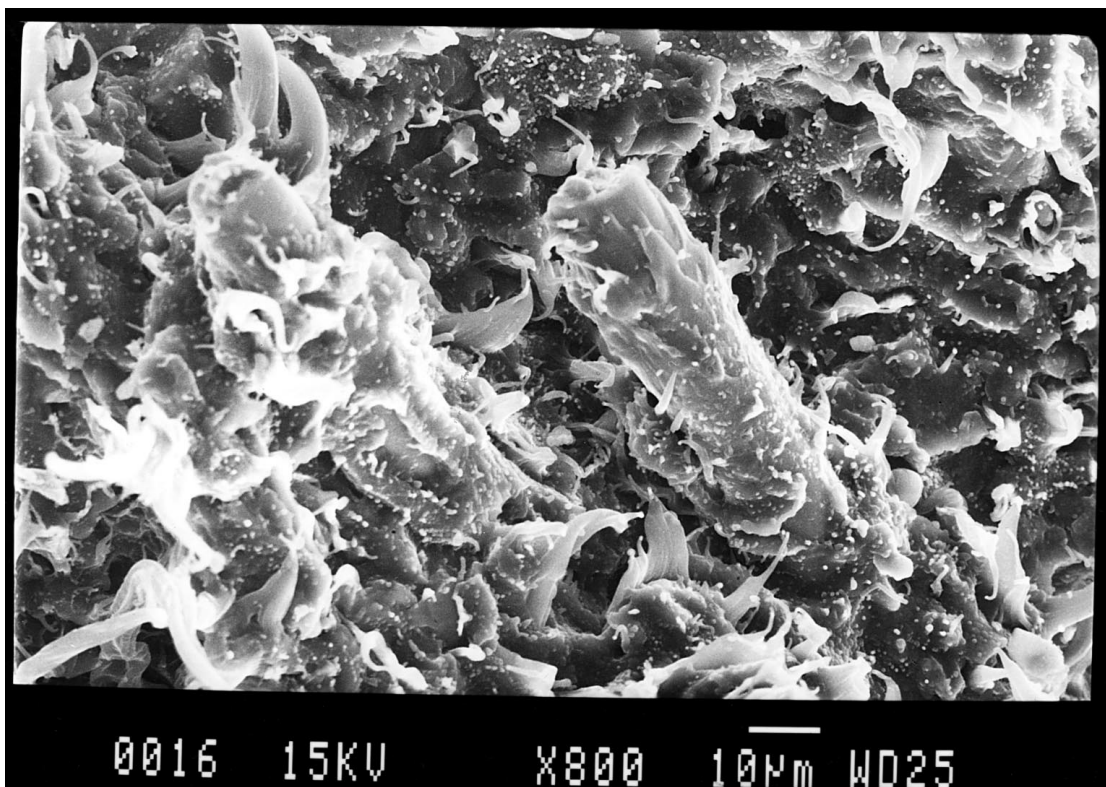


(b)

Figure 7 SEM micrographs of impact fracture surfaces of PP/LDPE 25/75 w/w blends, containing different types of glass fibers: (a) uncompatibilized blend with M-type fibers; (b) compatibilized blend with M-type fibers; and (c) compatibilized blend with E-type fibers. (Continued).

as can be seen in Fig. 7b for the M-type fibers and in Fig. 7c for the E-type fibers. Because neither of the two polymers interacts with the E-type fibers, the SEM findings give indirect but strong evidence that interactions can take place between the compatibilizer and the glass fibers. These cannot be the others than those men-

tioned before (Fig. 2). It has been found that grafting of polypropylene [15] or polyethylene [5] with acrylic acid was affecting the microstructure of the composite due to the increased interactions between the acidic acrylated compounds and the basic centers (hydroxyls) on the fiber surface. The increased adhesion that



(c)

Figure 7 (Continued).

was found in all compatibilized blends can explain the superior mechanical properties that these blends show compared to the uncompatibilized ones. The transmission of the applied load through the matrix to the fibers depends on the state of the bonding between the matrix and the fibers. The strong hydrogen bonds of the hydroxyls of the compatibilizer with the hydroxyl groups at the fiber surface on the one hand, and the strong adhesion of the same compatibilizer to the main polymers of the polymer matrix on the other, keep the fibers tightly bound to the matrix and in proper orientation, thus facilitating the transfer and distribution of the applied load among fibers.

3.4. Raman spectroscopy

The Raman spectra of pure PP and LDPE were recorded as reference spectra for further examination of PP-LDPE blends and are presented in Fig. 8.

The spectrum of polypropylene has characteristic vibrations at 1105, 810–860 (double peak), and 2953 cm^{-1} . The most important vibrations of polyethylene, which do not appear for PP, are at 1128 and 1062 cm^{-1} (vC–C), as illustrated in Fig. 8. The Raman spectra of the copolymers used as compatibilizers were similar without significant differences.

The micro-Raman technique has the ability to collect spectra from very small areas, in the order of 1 μm . Thus, it is easy to collect the spectra from the polymer, which is the thin coating, by focusing at the glass surface, because the average diameter of the glass fibers is 13 μm . The main problem with these spectra was the high fluorescence associated with the glass fibers. In Fig. 9a, the Raman spectra collected from the M-type

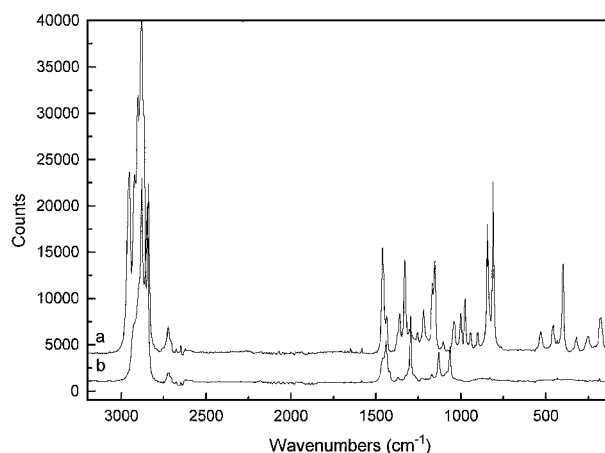


Figure 8 Raman spectra of (a) pure PP and (b) LDPE.

glass fiber surfaces, in compatibilized and uncompatibilized PP/LDPE 25/75 w/w blends, are presented.

From the spectra, which were collected from the uncompatibilized blend, one can see clearly the characteristic peaks of LDPE. This is in agreement with SEM micrographs because only LDPE can form a thin coating on the surface of M-type glass fibers. In the spectra collected from the compatibilized blend, besides the LDPE peaks, one can clearly see the characteristic peaks at 1105 cm^{-1} , at 810–860 cm^{-1} , and at 2953 cm^{-1} , as well, which are attributed to PP. Because pure PP cannot interact with this type of glass fiber, this is further evidence that the peaks are due to the compatibilizer, which has adhered to the surface of the glass fibers.

The same observations can be made in the collected spectra from the compatibilized blends containing the

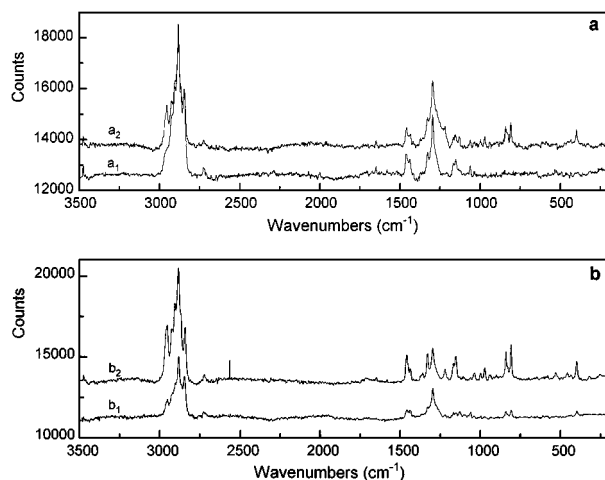


Figure 9 (a) Raman spectra of uncompatibilized (a_1) and compatibilized (a_2) PP/LDPE 25/75 w/w blends containing M-type glass fibers; (b) Raman spectra of compatibilized PP/LDPE 50/50 w/w (b_1) and 75/25 w/w (b_2) blends containing E-type glass fibers.

E-type glass fibers (Fig. 9b). The characteristic peaks for LDPE and PP polymers can clearly be seen in these spectra, as well. But, as already mentioned, none of the pure polymers can adhere and form a thin coating on the surface of this type of glass fiber. Thus, the characteristic peaks observed are due to the compatibilizers, which can interact with the surfaces of the glass fibers and produce a better interfacial bond between the matrix and the fiber. Of course, these compatibilizers may act as bridges bringing the main polymers into contact with the glass fibers.

4. Conclusions

E-type glass fibers have a very poor interfacial adhesion with both PP and LDPE. Their surface treatment with the silane coupling agent γ -MPS has increased the interfacial adhesion, but only in the case of LDPE. Apparently, polypropylene needs some other coupling agent. The glass-reinforced blends showed better mechanical properties, such as tensile strength and impact strength, than the corresponding unreinforced blends. The presence of a compatibilizer has further improved the above mechanical properties. This observation was attributed to the strong specific or chemical interactions that can take place between the reactive groups of compatibilizers, such as maleic anhydride and hydroxylic groups, with the hydroxyl groups of the glass fibers. The extent of the interfacial adhesion of the polymer matrix onto the fibers was revealed by SEM. SEM micrographs have revealed the presence of a coating layer on both types of glass fibers in the case of compatibilized blends. Micro-Raman spectroscopy has revealed the composition of this surface layer and the role that the compatibilizer plays by adhering to the surface of the glass fibers.

Acknowledgements

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References

1. W. H. BOWYER and M. G. BADER, *J. Mater. Sci.* **7** (1972) 1315.
2. F. RAMSTEINER and R. THEYSON, *Composites* **10** (1979) 111.
3. P. F. BRIGHT and M. W. DARLINGTON, *Plast. Proc. Appl.* **1** (1981) 139.
4. K. FRIEDRICH, *Colloid Polym. Sci.* **259** (1981) 808.
5. I. KAMEL, M. J. KOCZAK and R. D. CORNELIUSSEN, *J. Appl. Polym. Sci. Polym. Sympos.* **23** (1974) 157.
6. L. CZARNECKI and J. L. WHITE, *J. Appl. Polym. Sci.* **25** (1978) 1089.
7. P. T. CURTIS, M. G. BADER and J. E. BAILEY, *J. Mater. Sci.* **13** (1978) 377.
8. J. U. OTAIGBE and W. G. HARLAND, *J. Appl. Polym. Sci.* **36** (1988) 165.
9. J. P. TANCREZ, F. RIETSCH and J. PABIOT, *Eur. Polym. J.* **30** (1994) 789.
10. V. B. GUPTA, R. K. MITTAL and P. K. SHARMA, *Polym. Compos.* **10** (1989) 16.
11. L. CERCONE, *ibid.* **12** (1991) 81.
12. C. K. MOON, J. LEE, H. H. CHO and K. S. KIM, *J. Appl. Polym. Sci.* **45** (1992) 443.
13. M. J. FOLKES, in "Short Reinforced Thermoplastics," edited by M. J. Bevis (Research Studies Press, Chichester, 1985).
14. M. RATZCH, in "Interfaces in Polymer, Ceramic and Metal Matrix Composites," edited by H. Ishida (New York, 1988).
15. I. KELNAR, *Angew. Macromol. Chem.* **189** (1991) 207.
16. M. JOSHI, S. N. MATITI and A. MISRA, *Polymer* **35**(17) (1994) 3679.
17. A. K. GUPTA, K. R. SRINIVASAN and P. K. KUMAR, *J. Appl. Polym. Sci.* **43** (1991) 451.
18. A. K. GUPTA, V. B. GUPTA, R. H. PETERS, W. G. HARLAND and J. P. BERRY, *ibid.* **27** (1982) 4669.
19. M. ARROYO and F. AVALOS, *Polym. Compos.* **10** (1989) 117.
20. J. E. GUILLET, in "Degradable materials, Perspectives, Issues and Opportunities," edited by S. A. Barenberg, J. L. Brash, R. Narayin and A. E. Redpath (The First International Scientific Consensus Workshop, C.R.C., Boca Raton, FL, 1990).
21. I. FORTENLY, E. NAVRATILOVA and J. KOVAR, *Angew. Macromol. Chem.* **188** (1991) 195.
22. J. W. THE, *J. Appl. Polym. Sci.* **28** (1983) 605.
23. F. STEHLING, T. HUFF, C. S. SPEED and G. WISSLER, *J. Appl. Polym. Sci.* **26** (1981) 2693.
24. J. W. BARLOW and D. R. PAUL, *Polym. Eng. Sci.* **24** (1989) 525.
25. C. TSELIOS, D. BIKIARIS, V. MASLIS and C. PANAYIOTOU, *Polymer*, submitted.
26. J. JANG, J. Y. LEE and J. K. JEONG, *J. Appl. Polym. Sci.* **59** (1996) 2069.
27. R. G. RAJ and B. V. KOKTA, *Polym. Eng. Sci.* **31** (1991) 1358.
28. K. K. KALP KOGYO, *Jpn. Kokai Tokkyo Koho, JP 60, 23, 432; C.A.* 103: 23335x (1985).
29. K. GIANNIKOURIS, *Diploma thesis*, University of Thessaloniki (1996).
30. L. H. LEE, *Polym. Eng. Sci.* **9** (1969) 213.
31. F. G. KRAUTZ, *Adv. Chem.* **99** (1971) 452.
32. M. A. ALI and F. J. GRIMER, *J. Mater. Sci.* **4** (1969) 389.
33. D. GAWTHORNE and B. HARRIS, *Composites* **6** (1975) 25.
34. M. XANTHOS, *Polym. Eng. Sci.* **28** (1988) 1392.
35. J. U. OTAIGBE and W. G. HARLAND, *J. Appl. Polym. Sci.* **37** (1989) 77.
36. E. DEVAUX and B. CHABERT, *Polymer Commun.* **31** (1990) 391.
37. Z. SONG and W. E. BAKER, *J. Appl. Polym. Sci.* **44** (1992) 2167.
38. S. CANEVAROLO and F. CANDIA, *ibid.* **57** (1995) 533.
39. J. O. IROH and J. P. BERRY, *Polymer* **34** (1993) 4747.

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