Effect of Inclusions and Blending on the Mechanical Performance of Recycled Multilayer PP/PET/SiO$_x$ Films

Y. WYSER,* Y. LETERRIER, J.-A. E. MÅNSON

Laboratoire de Technologie des Composites et Polymères (LTC), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

ABSTRACT: Extending the useful life of materials through recycling has proven to be an efficient means of reducing natural resource use and limiting the production of waste. In the case of polymer-based materials, in general, and of packaging materials, in particular, material recovery is complicated by the presence of incompatible polymers, as well as *a priori* undesirable contaminants such as inorganic inclusions. This article investigated the recycling of multilayer packaging material systems, based on polypropylene and silicon oxide-coated poly(ethylene terephthalate). In particular, the effect of a compatibilization of the blend using maleic anhydride-grafted polypropylene on the mechanical properties of the recycled material was examined. Without a compatibilizer, and at low compatibilizer concentrations, the blend exhibits a coarse morphology and is brittle. At a concentration of 5% wt of the compatibilizer, a fine morphology is obtained, and the blend shows excellent ductility. Beyond this concentration, a brittle interphase forms between the blend constituents, with a corresponding decrease in ductility. These results were confirmed by a study of strain-induced crystallization in the blend. Furthermore, the size of the SiO$_x$ inclusions, resulting from the fragmentation of the oxide coating during reprocessing, had no detectable influence on the mechanical properties of the recycled blend, providing that their concentration is lower than 2×10^{-3}. This study showed that a control of both the microstructure and interface properties considerably improves the mechanical properties of the recycled material, leading to high added-value applications. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 910–918, 2000

Key words: recycling; compatibilization; multilayer film; PP; PET; SiO$_x$

INTRODUCTION

Polymers are today commonly used for a single application and then considered as waste, even though, in most applications, these materials retain most of their properties after their first use. The reason for this lies in the problems often encountered during the recycling of polymer ma-

terials. Apart from potential problems related to recovery logistics, traditional limitations to polymer recycling range from the sensitivity of such materials to heat, that is, their readiness to degrade when subjected to high temperature and under mechanical loads, to their limited tolerance toward impurities. The latter factor is further accentuated by the number of polymer types currently available on the market, most of which are incompatible with each other. In many cases, the use of a single material for a given application is not possible, with the result that the combination of different material and polymer types renders recovery highly difficult. The present trend is to reduce, as far as possible, the number of materials used in a single application and to facilitate

the easy dismantling of a product into individual materials. However, this is not always possible, especially when good adhesion is needed between the different materials. Typical examples of products combining several polymers are found in multilayer films used to a considerable extent in the packaging industry.

The materials investigated in this study, that is, multilayer packaging film of polypropylene (PP) and silicon oxide-coated poly(ethylene terephthalate) (PET/SiO$_x$) were selected to study the recycling of incompatible polymer materials, which, in addition, contain a small fraction of an undesirable phase. Both polyolefins and PET are extensively used in packaging: Their mixed recycling is therefore an interesting field which has motivated numerous studies of polyolefins/PET blends, in general, and PP/PET blends, in particular. Blending different polymer types often creates materials with poor properties due to incompatibility between the polymers, principally induced by high surface energies which tend to create large domains of one phase within the other. To obtain a blend with good properties, a blend morphology of dispersed particles with a 0.1–5 μm diameter is usually required.[1] The benefits of blending derive from the formation and retention of the appropriate blend morphology. The formation of the finely dispersed domains is obtained by the flow and mixing of the blend during processing. Jabarin and Bhakkad[2] showed that higher shear rate induces smaller domains when processing in an extruder. However, the mobility of polymer molecules at higher temperature enables the gathering of domains, which increases their size. It is therefore still necessary to stabilize the morphology obtained after processing in order to obtain a performing blend. To this end, the compatibilization of polymers has been extensively studied through the diminution of the interfacial tension of the polymers present in the blend.[1,3–9] Compatibility of immiscible polymers may be improved by adding a copolymer (block or graft) with segments capable of specific interactions and/or chemical reactions with the blend constituents or by blending suitable functionalized polymers of specific enhanced interactions and/or chemical reactions.[3] This reduction of interfacial tension diminishes the driving force for a domain-size increase. Furthermore, increase in the chemical and/or physical interactions affects the adhesion between the phases, thereby inducing higher mechanical properties. In the case of PP/PET blends, the compatibilization of the polymers was obtained by the addition of PP
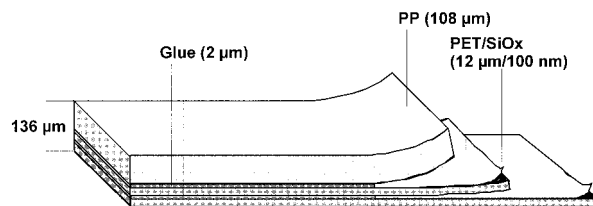

Figure 1   Schematic description of the PP/PET/SiO$_x$ film.

grafted with acrylic acid (PP-g-AA)[3,5] or with maleic anhydride (PP-g-MAH).[1,10]

The use of PET/SiO$_x$ as oxygen-barrier layers has seen a remarkable development in the past few years (see, for instance, the works in ref. 11) and are now used in combination with PP in layered films. The mechanical recycling of such a multiphase system into a reliable material raises the issue of the probable contamination of the polymer by dilute suspensions of foreign inclusions. These may dramatically affect the reliability of the recycled part,[12–14] and their analysis has received increasing attention in the past years. Recent work has, for instance, shown that, even at a volume fraction of the order of 1%, small oxide particles could significantly embrittle PET, which otherwise is very ductile.[15] Modeling efforts have been undertaken with the aim of predicting the properties of mixtures of virgin and reprocessed polymers (e.g., refs. 16,17). The study of the influence of impurities, both on engineering properties and relevant mechanisms on a local scale, appears to be a key element in promoting recycling of multiphase polymer systems. There is currently a strong need to develop novel methods of investigating the contamination of a polymer with an *a priori* undesirable dilute phase.[18–20] The objectives are therefore twofold: (i) to optimize the compatibilization of the PP/PET blend for reliable mechanical performance and (ii) to analyze the influence of SiO$_x$ fragments on the defect tolerance of the recycled blend.

EXPERIMENTAL

Materials

The multilayer film used in this study is depicted in Figure 1. It consists of one PP layer and two SiO$_x$-coated PET films, calendered together using an elastomeric polyurethane adhesive. The thickness of the various constituents is reported in Figure 1. The corresponding volume fractions of

Table I Extrusion and Injection-Molding Parameters

Extrusion	
Feed-zone temperature (°C)	200
Melting-zone temperature (°C)	245
Die temperature (°C)	235
Screw velocity (rpm)	50
Injection	
Feed-zone temperature (°C)	200
Melting-zone temperature (°C)	260
Injection pressure (MPa)	90
Injection time (s)	3.0
Hold pressure (MPa)	55
Hold time (s)	9.0
Mold temperature (°C)	30

PP, PET, the adhesive, and SiO_x are 76.8, 21.5, 1.5, and 0.2%, respectively.

The recycling of the film was performed in two steps: First, the film was fed into an extruder to obtain pellets; second, the pellets were injection-molded into tensile test specimens. An in-line drying system was built and directly connected to the extruder to prevent hydrolysis of the PET. The apparatus consists of a 1 m long metallic tube in which dry air is blown at 120°C, from the bottom to the top. The film was fed into the tube and directly into the extruder without further contact with ambient air, and its water content was measured to be within the limits reported in the literature.[15,21]

The extrusion was performed on a table-top corotating twin-screw extruder (PRISM TSE-16-TC), with a screw diameter equal to 16 mm and a length-to-diameter ratio equal to 16. The conditions used during extrusion are reported in Table I. The extrudate was cut into pellets, approximately 4 mm in length by 2 mm in diameter. The pellets were dried overnight in a vacuum oven at 80°C prior to injection molding into dog-bone tensile-testing specimens, of gauge length 12 mm and a rectangular cross section of 2×3 mm^2, using a Butler 10/90V mini-injection molder. The injection parameters are also listed in Table I.

Prior to reprocessing, the size of the SiO_x fragments was controlled by straining the film to 25% elongation. Studies have shown that, as a result of the stress transfer at the polymer/oxide interface, this process breaks up the oxide coating into small fragments, of average length equal to about 2.5 μm. The fragment-length distribution is very narrow, and the maximum fragment length is less than 4 μm. The recycled materials with a controlled particle size are referred to as "fragmented," while materials reprocessed without particle-size control are called "nonfragmented." In the latter instance, the average length of oxide platelets is of the order of several 10 μm, that is, an order of magnitude larger than the average length obtained after fragmentation.[15]

Compatibilization of the PP/PET blend was carried out using a grafted PP-g-MAH, in which the MAH fraction is equal to 6.4×10^{-4} (OR-EVAC CA100, Atochem). The compatibility of PP-g-MAH to PP is given by the PP main chain while the grafted MAH acts on the ester groups of the PET. The amount of PP-g-MAH added to the film was varied from 1 to 20% wt, corresponding to MAH fractions ranging from 6.4×10^{-6} to 1.28×10^{-4}. The processing parameters for the compatibilized materials are reported in Table I.

Characterization Techniques

The injection-molded specimens were tested at room temperature under uniaxial tension at a strain rate of 1.25×10^{-2} s^{-1}, on a screw-driven tensile-testing machine (Zwick) under displacement control and equipped with a 1-kN load cell. An extensometer was used to measure the deformation of the material in the gauge region. A differential scanning calorimeter (Perkin–Elmer DSC, Series 7) was used to characterize the physical state and the crystallization parameters of the film and of the reprocessed materials. Samples were loaded into the DSC cell, heated at 10 K/min under nitrogen from 50 to 300°C, and subsequently cooled to 50°C at the same rate. In the case of the films, the DSC samples were punched out of the film and set in 50-μL aluminum pans, which were then sealed and pierced to avoid pressure buildup, which would deform the pans and alter the heat transfer to the samples. The sample weight ranged from 6 to 8 mg. The DSC samples from recycled material were systematically cut from a whole section of the tensile specimens, within the gauge region. Fifty-microliter aluminum pans were used with the same sealing operation as for the films. The sample weight was approximately 15 mg. Melting temperature, crystallization temperature, and enthalpy were measured, and the crystallinity of PET and PP was then determined using the enthalpies of pure crystals, that is, 117.3 J/g for PET and 203.7 J/g for PP.[22]

The microstructure of the recycled materials was characterized from polished surfaces and rupture surfaces obtained by Charpy impact of

notched rectangular samples. Samples embedded into an acrylic resin were carefully polished using a sequence of polishing paper grades ranging from 200 to 4000 and subsequently observed on an Olympus SH-2 optical microscope. A Cambridge S100 scanning electron microscope was used for the observation of the rupture surfaces. A thin layer of gold was sputtered onto the sample to avoid electrostatic charging of the polymers during observation. The acceleration voltage was 15 kV and the working distance varied between 15 and 20 mm.

RESULTS AND DISCUSSION

Effect of a Dilute Fraction of Oxide Particles

During its residence time in the extruder, the molten PP/PET/SiO$_x$ material undergoes high shear rates that fragment the SiO$_x$ layer into flakelike platelets, which are dispersed in the polymer phase through the mixing effect of the corotating screws. As the temperature increases in the heated barrel, as a result of viscous dissipation, the two polymers melt and are mixed together under increasing pressure. After exiting from the die, the material solidifies prior to being cut into pellets. This operation does not further reduce the size of the SiO$_x$ platelets, as they already are considerably smaller than is the pellet size, neither does it alter the morphology of the polymer blend. During the subsequent injection molding, the extruded material is remolten and injected into a cold mold. Again, high shear rates are involved in the process, and the size of platelets might very well be further reduced, whereas their orientation along the flow direction is increased. A recent study devoted to reprocessing individual SiO$_x$-coated PET films showed that even though the oxide platelets are in a dilute concentration, the large platelets found in the injection-molded material considerably embrittled the PET.[15] By contrast, when the coating is fragmented prior to extrusion, the SiO$_x$ platelets found in the molded specimens are all smaller than is the critical stress transfer length, and these were found to have no influence on the high ductility of the PET. In the present case, the oxide particles are diluted in the polymer blend at much lower fractions, and one would expect that the behavior of the recycled material is dominated by the blend morphology, rather than by the size of the oxide platelets.
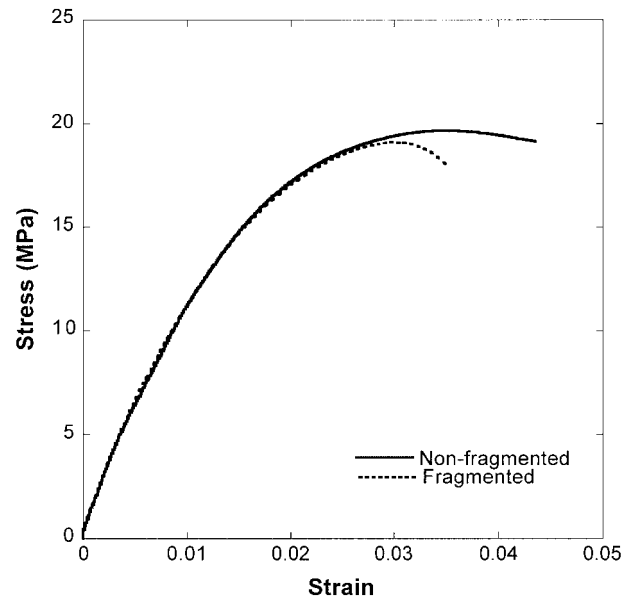

Figure 2 Tensile behavior of the fragmented and nonfragmented recycled PP/PET/SiO$_x$ materials.

The tensile behavior of the nonfragmented and fragmented PP/PET/ SiO$_x$ blends is presented in Figure 2. It is evident that the size of the oxide platelets, which differs by an order of magnitude in the two cases, has no significant influence on the mechanical behavior of the recycled materials. This result is contrary to what was observed in the case of the recycled PET/SiO$_x$, which indicates that the weak point in the present material is the interface between PP and PET and not between PET and SiO$_x$. The incompatibility between PET and PP is responsible for the large size of the PET nodules as well as for the lack of adhesion between the two polymers and is the main reason for the poor mechanical properties of the blend.

PP/PET Blend Compatibilization

During reprocessing of the PP/PET/SiO$_x$ film, the melting and compounding of PP and PET creates a blend consisting of a continuous PP matrix in which PET nodules are present. The high shear and cooling rates involved in injection molding induce an elongated morphology of the PET nodules. An optical micrograph of a polished section parallel to the flow direction is shown in Figure 3. PET nodules of sizes ranging from less than 1 μm to over 50 μm are visible. This is in good agreement with the findings of Dharmarajan et al.,[1] who stated that polymer blends obtained by conventional mixing of incompatible polymers have a morphology on the scale of 0.1–50 μm.
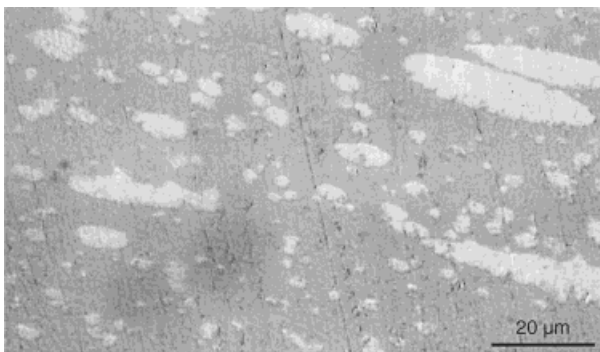
Figure 3 Microstructure of the recycled PP/PET/SiO$_x$ material: The white nodules are PET.

A DSC thermogram of the recycled material is shown in Figure 4. The endothermic melting peak temperatures of the PP and the PET are equal to 150 and 250°C, respectively. These temperatures correspond to the melting points of the film constituents.[15] This result indicates that no miscibility has developed between the two polymers, as the melting temperature of miscible polymers in a blend tend to be shifted toward each other, eventually displaying only one melting peak corresponding to the miscible blend. Just before the onset of the melting peak of PP, one notices an exothermic peak corresponding to the cold crystallization of PET. It is clear that these two peaks overlap, which hinders the determination of their respective areas and, therefore, the crystallinity of the two phases in the blend.
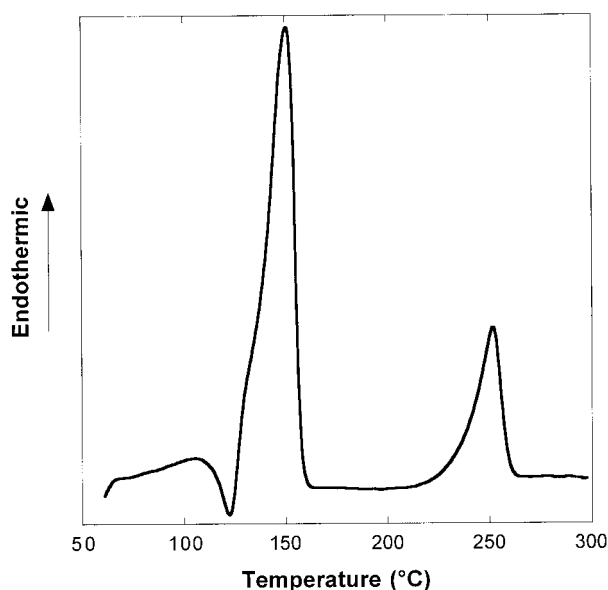

Figure 4 DSC thermogram of the recycled PP/PET/SiO$_x$ material.
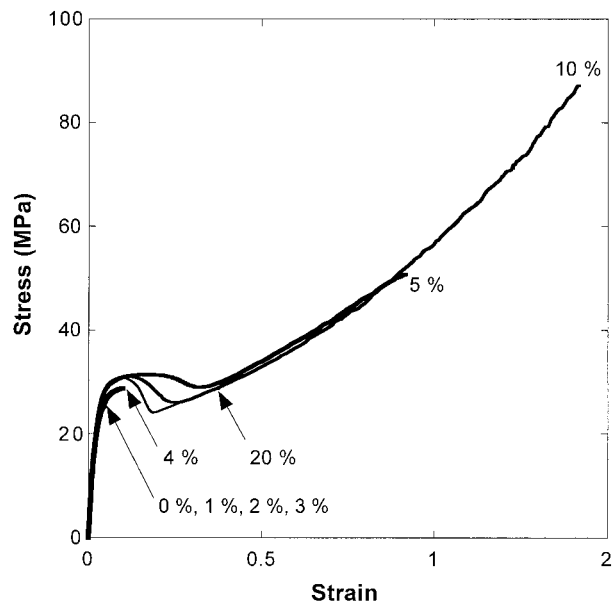

Figure 5 Stress–strain behavior of the recycled PP/PET/SiO$_x$ materials, with different amounts of the PP-g-MAH compatibilizer, as indicated on the curves.

The tensile behavior of blends containing different weight fractions of PP-g-MAH is shown in Figure 5. The amount of the compatibilizer added to the blend on the tensile behavior obviously has a considerable effect on the tensile behavior. Up to 3 wt % of PP-g-MAH, the polymer is brittle and fails at a strain close to 4%. At 4 wt % of PP-g-MAH, some degree of yielding is evident, with a strain at failure equal to about 12%. At 5 wt % of the compatibilizer, a remarkable increase in ductility is achieved, which further increases at a fraction of 10 wt %. At this stage, the strain at failure reaches about 1.4 and the tensile strength is equal to 87 MPa. Interestingly, as the PP-g-MAH fraction is increased to 20 wt %, these values decrease to less than 0.5 and 30 MPa, respectively.

These observations are summarized in Figure 6, where the Young's modulus, strain at rupture, and strength of the reprocessed multiphase polymers are reproduced as a function of compatibilizer weight fraction. The modulus of the blend is, within experimental scatter, close to 1250 MPa at low PP-g-MAH fractions and increases to about 1400 MPa above 5 wt % PP-g-MAH. Below 5 wt % PP-g-MAH, the strain at failure and tensile strength increase only slightly. Conversely, above this limit, both values increase drastically, showing a maximum at 10 wt % of the compatibilizer. The addition of a higher fraction of PP-g-MAH decreases the properties of the blend to a level close to that observed for the low concentrations.
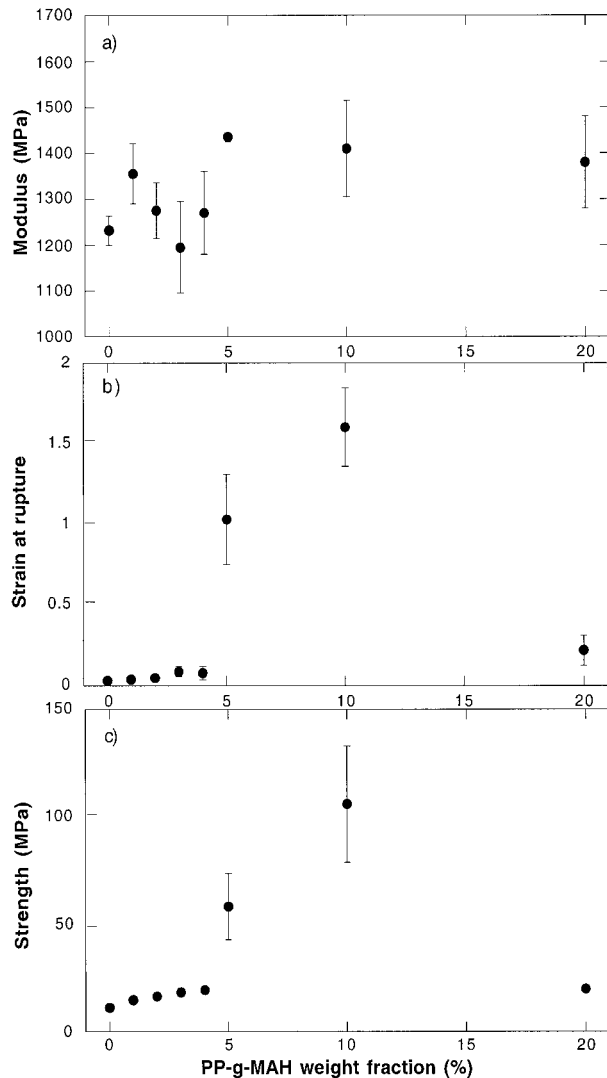
Figure 6 Mechanical properties of the recycled PP/PET/SiO$_x$ as a function of the compatibilizer content: (a) modulus; (b) strain at rupture; (c) strength.

This type of behavior was observed by many authors (e.g., ref. 2) and is explained by the microstructural changes induced by the compatibilizer, which are described below.

It was previously pointed out that the role of a compatibilization in blends is to reduce the size of the domains of the dispersed phase and to increase the adhesion between these domains and the matrix, through the formation of an interphase presenting high interactions with both polymer types. The effect of the compatibilizer on the microstructure of the blend is observed on micrographs of the rupture surfaces. Figure 7 shows the rupture surfaces of Charpy-impacted specimens containing weight fractions of PP-*g*-MAH ranging from 0 to 20%. Four different types of morphology are observed:

(i) As described earlier in Figure 3, the material with no compatibilizer contains large PET domains elongated up to 50 μm, presenting smooth surfaces. This suggests that little interaction takes place between PET and PP and that the interface is the weak point of the blend. This lack of adhesion explains the brittle behavior of the blend observed above.

(ii) The main effect of the addition of 1 and 2 wt % of PP-*g*-MAH is the reduction of the size of the PET domains, to approximately 10 μm for the largest ones. However, the interaction between PP and PET does not seem to be significantly affected, as the rupture still obviously passes along the interface, leaving a number of cavities in the PP surface, previously occupied by PET domains. The slight increase of strain at rupture and the strength of the blends containing small amounts of the compatibilizer reported in Figure 6 is due to the decrease of the size of the PET domains.

(iii) The morphology observed at higher concentrations, 5 and 10 wt % of PP-*g*-MAH, is completely different. In both cases, the size of the domains is further decreased, showing a maximum size of approximately 7 μm. The PET domains present a rough surface which strongly adheres to the PP matrix, forcing the crack to pass across the particles, rather than around them. This clearly indicates that the interface between PET and PP no longer represents a weak point of the blend. The increase observed in the modulus of the blend at this compatibilizer concentration (Fig. 6) is fully consistent with these observations, as the reinforcing mechanism of any multiphase material is the ability of stress to be transferred from the matrix to the reinforcing phase, through the interface, which must be capable of withstanding these stresses. Further, the brittle-to-ductile transition observed at 5 wt % PP-*g*-MAH in Figures 5 and 6 is also explained by strong adhesion at the interface between the nodules and the matrix, which does not, therefore, initiate premature rupture. It is, moreover, observed that the internal structure of the PET domains is rather complex. The nature of this internal structure, already observed by other
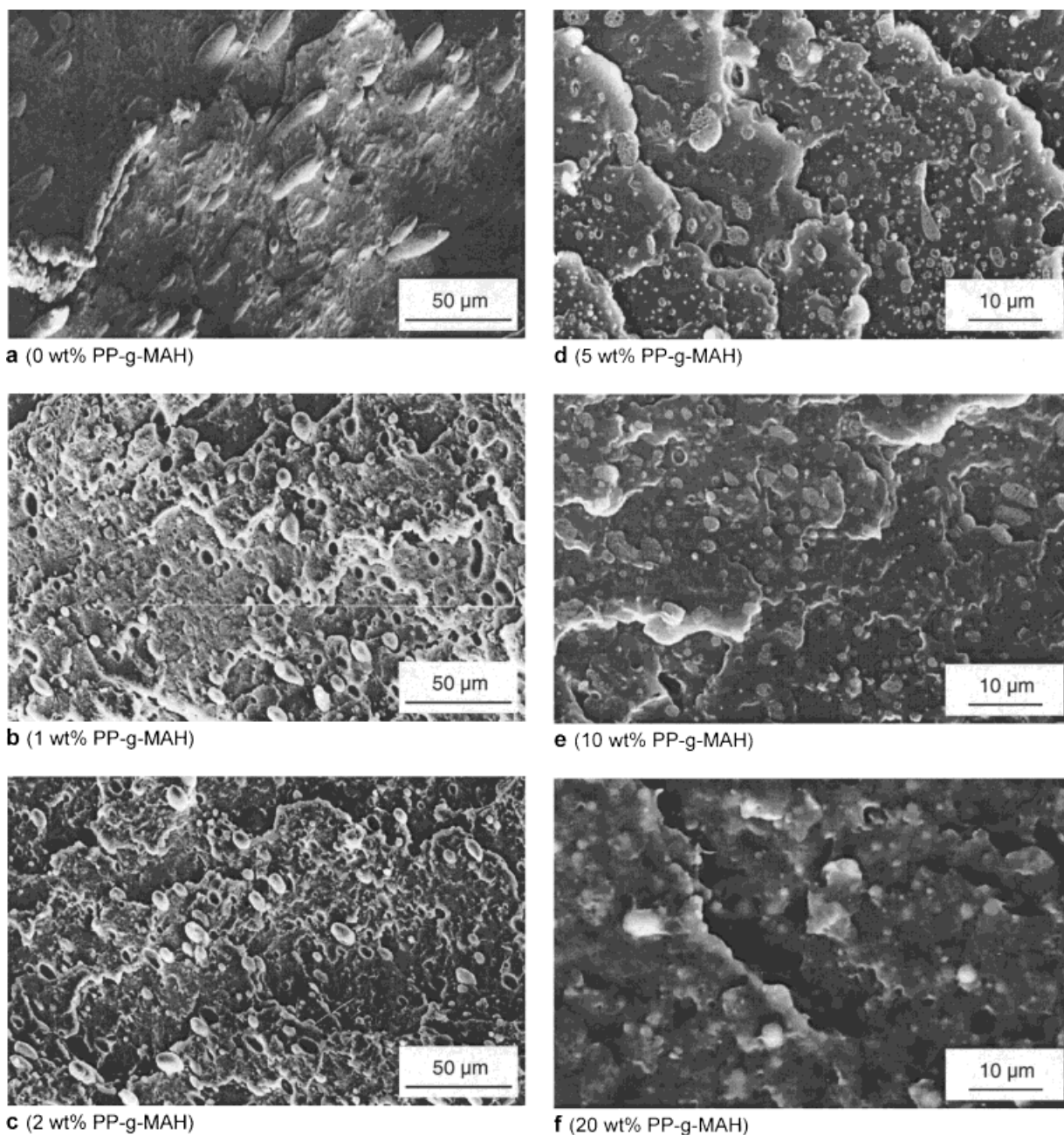
Figure 7   Morphology of the rupture surface of the reprocessed PP/PET/SiO$_x$ material at various compatibilizer weight fractions: (a) 0%; (b) 1%; (c) 2%; (d) 5%; (e) 10%; (f) 20%.

authors[3,8] in the case of PP–PET blends compatibilized with PP-g-AA, is unknown.

(iv) Further increasing the fraction of PP-g-MAH to 20% again changes the rupture mode of the blend. As in the case of low compatibilizer fractions, the rupture goes around the particles and not across them. However, the appearance of the PET domains is now completely different, as the PET is embedded in PP-g-MAH. As it is

based on very low molecular weight PP, PP-g-MAH is a brittle material. The presence of this thick layer around the PET particles therefore represents a weak point through which the crack propagates easily, which explains the embrittlement observed during tensile testing.

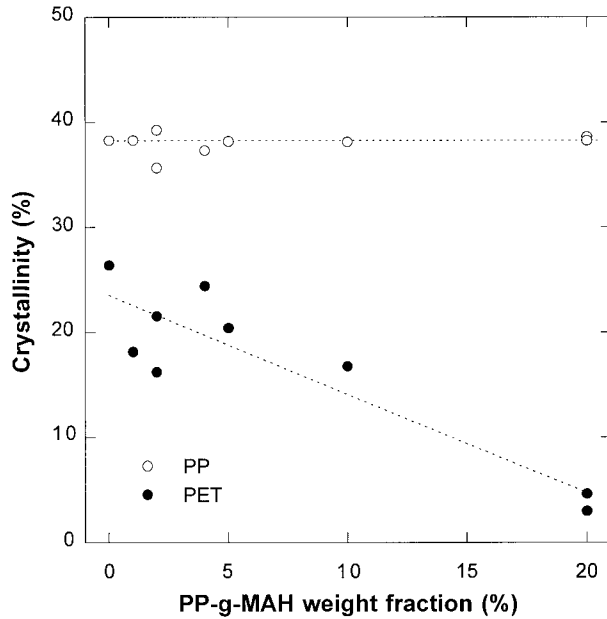As seen in Figure 4, the determination of the crystallinity present in the injected materials is

Figure 8 Degree of crystallinity of PP and PET in the recycled PP/PET/SiO$_x$ materials induced during cooling from the melt at a rate of 10 K/min.

hindered by the overlapping of the cold crystallization of PET and the melting of PP. An insight into the crystallization behavior of the different blends is, however, obtained during the cooling of the blends from the melt. Figure 8 shows the crystallinity of PP and PET in the blends cooled from the melt in the DSC at a rate of 10 K/min. It is evident that the crystallinity of PP is not affected by the increasing amount of compatibilizer and is approximately equal to 38%. Conversely, a considerable decrease in the crystallinity of PET is observed, from about 25% at no compatibilizer fraction down to less than 5% at the highest compatibilizer fraction. This result contradicts the observations of Jabarin et al. on the crystallization behavior of blends composed of PET and MAH-grafted polyethylene. These authors showed that a greater concentration of the grafted material increased the crystallization of PET.[2] However, in these studies, PET was the matrix phase, contrary to the present case. The complex internal structure of the PET domains observed in Figure 7(d,e) might indicate that the observed nodules are themselves blends of PET and the glue and/or PP, which would hinder their crystallization. Further investigations are necessary to examine this behavior.

Another example of the good adhesion between PET and PP in the blends containing PP-*g*-MAH fractions above 5 wt % is found in Figure 9, which

reproduces the DSC thermogram of the blend containing 5 wt % of the compatibilizer, before and after tensile testing. The main differences between the two curves are the larger melting peak of PP and the disappearance of the cold crystallization peak of PET. Both materials are known to crystallize when strained to a certain level. The reason for the strain-induced crystallization of PP is clear. However, for the PET to crystallize, it has to be strained during the test, implying that the strain applied to the PP is transferred to the PET, which requires good adhesion between the two phases.

This study shows that the control of both microstructure and interface properties considerably improves the mechanical properties of the recycled multiphase material. It is therefore expected that the conclusions drawn from the analysis of the particular multilayer film should be of a broad interest for recycling polymer products into high added-value applications.

CONCLUSIONS

Mechanical recycling of multilayer packaging films consisting of oxygen-barrier SiO$_x$-coated PET and PP films was studied with particular attention paid to the effects of dilute SiO$_x$ platelet contamination and to compatibilization of the PP/
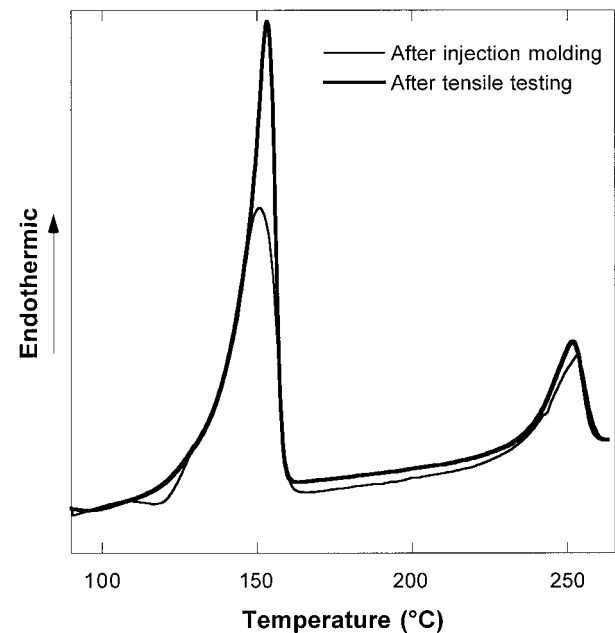

Figure 9 DSC thermograms of recycled materials containing 5 wt % PP-*g*-MAH after injection molding and after straining.

PET blend. It was shown that SiO_x particles, whatever their size, have no detectable influence on the tensile performance of the recycled material, their volume fraction being as low as 0.2%. This result is in contrast to previous analyses of recycling of individual PET/SiO_x films, where the size of the oxide fragments was found to control to a considerable extent the ductility of the polymer.

The effect of a compatibilizer on the crystallization behavior differs considerably between PP and PET. The crystallinity of PP in the blend was found to be equal to about 38%, independent of the amount of the compatibilizer. On the contrary, the crystallinity of PET in the blend decreases from 25% at no compatibilizer fraction down to less than 5% at a compatibilizer fraction of 20 wt %.

The unmodified recycled PP/PET/SiO_x blend exhibits a coarse morphology and is brittle, due to a lack of adhesion between the two polymer phases. The addition of a PP-*g*-MAH compatibilizer reduces the size of the PET domains; however, at concentrations of less than 4 wt%, no significant improvement in tensile behavior of the blend is achieved. Compatibilizer concentrations of 5 and 10 wt % induce a fine blend morphology, with PET domains smaller than 7 μm. The blend shows high ductility, thanks to an efficient interfacial stress transfer, as revealed by a strain-induced crystallization phenomena of the PET domains. Beyond 10 wt % of PP-*g*-MAH, a brittle interphase forms between the PP and the PET, with a corresponding drop in the ductility of the blend.

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