

Melt Blending of Poly(ethylene terephthalate) with Polypropylene in the Presence of Silane Coupling Agent

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ABSTRACT: A silane coupling agent (SCA) was used as a compatibilizer for polypropylene–poly(ethylene terephthalate) (PP–PET) blends with 20, 40, 50, and 60% PET compositions by weight. PP–PET mixtures were blended with and without an SCA by a single-screw extruder. The effect of silane modification on the tensile and impact properties of the blends was investigated. The morphology and thermal behavior of the blends were examined with scanning electron microscopy (SEM) and differential scanning calorimetry (DSC), respectively. The presence of the SCA used in this work extensively improved the mechanical properties of the blends. Mechanical properties were found to be highly de-

pendent on the numbers of extrusions. SEM studies showed that substantially different morphology with better adhesion existed when SCA-treated blends were compared to non-treated PP–PET blends. The presence of individual melting temperatures of the polymers in all compositions with no significant T_m depression indicated that PET and PP were crystallized separately. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1039–1048, 2003

Key words: polypropylene; polyester; blend; compatibilization.

INTRODUCTION

This study covers the recycling of poly(ethylene terephthalate) (PET) bottles through melt blending with polypropylene (PP). There is no doubt that the main reason for blending is economy and creating new high-performance materials in terms of recycling processes.¹ Polyolefin mixing is preferred due to lower cost and also its resistance to high processing temperatures under suitable conditions. However, these PET–polyolefin blends are immiscible and incompatible and have extremely poor mechanical properties. This problem results from the low intermolecular forces between the components of the immiscible blends. As a result, most of the studies have been focused on the techniques to improve the compatibility and mechanical properties of these systems. A wide range of compatibilizers has been investigated to obtain compatible and high mechanical property blends.^{2–6}

Some reactive or nonreactive copolymers were used for the enhancement of the interaction, and, hence, compatibility between PET and PP was achieved. One

of the initial works of compatibilization, acrylic acid-functionalized PP by Xanthos et al., resulted in a fine dispersed phase morphology, improved processing, and the mechanical properties, and modified the crystallization behavior of the polyester component.² PET and PP at compositions of 20/80 and 80/20 were also modified with unfunctionalized SEBS and two functionalized grades containing either maleic anhydride (SEBS-*g*-MAH) or glycidyl methacrylate (SEBS-*g*-GMA) grafted to the midblock.³ The compatibilizing effect was far more pronounced with the functionalized copolymers, and GMA was found to be a more effective functionality than was MAH. Cheung and Chan⁴ studied the mechanical and rheological properties of PP/PET blends with the addition of Epolene E-43 (low molecular weight maleated PP) and found that the strength and stiffness of the blends were improved. The properties of the PET and PP blends and the PET/MAH-grafted PP (MAH-*g*-PP) reactive blends showed that the strength of the PET/MAH-*g*-PP blends produced good adhesion, compared with PET/PP physical blends.⁵ Reactive compatibilization of PP/PET blends was studied by PP-grafted GMA, which was an effective reactive compatibilizer for the PP–PET system.⁶ GMA provided a more ductile behavior without decreasing the material stiffness.

Silane coupling agents (SCAs) are generally used to change the interface between an organic polymer and an inorganic substrate.^{7–10} They are used in a variety of applications, including reinforced plastics, coatings, paints, inks, sealants, adhesives, and elastomers. Their use basically results in improved bonding and up-

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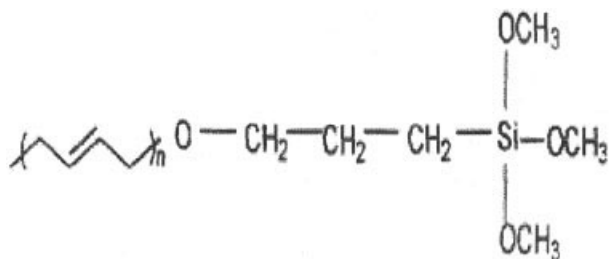


Figure 1 Chemical structure of POLYVEST 25, where $n = 10$ –12.

graded mechanical and electrical properties. SCAs have the structure of $R-Si-X_3$, where R represents an organofunctional group and X is generally alkoxy (methoxy or ethoxy). They are generally applied from water solutions or from organic solvent–water mixtures. In the presence of water, hydrolysis occurs stepwise to form alkoxy silanols and eventually silane triols were followed by condensation of the silanols to siloxanes. Under optimum conditions, hydrolysis is rapid and proceeds slower condensation reactions.

The main objective of this study was the recycling of waste PET bottles through blending with PP. The effect of an SCA as a compatibilizer in PET–PP polymer blend systems was never studied before. SCA was used to provide interfacial adhesion and increase interaction between PET and PP. It was expected that alkoxy groups of SCA might easily react with hydroxyl end groups of PET, and with this modification, PET could bind to PP by giving improved mechanical properties and a better morphology. In previous studies, our group showed that SCAs can be used to enhance the properties of not only inorganic fillers containing polymeric materials but also immiscible polymer blends.^{11–13}

EXPERIMENTAL

Materials

The granular PP [Petoplen MH-418, melt flow index ($g/10 \text{ min}$) = 5.0, density (g/cm^3) = 0.905, $M_w = 381\,951$, $M_n = 31\,098$] was supplied by the Turkish Petrochemical Industry (PETKM, Izmir, Turkey). PET was obtained from mostly waste soft-drink bottles, produced by the Sabanci Synthetic Fibre Co. (SASA, Adana, Turkey). The applied SCA is POLYVEST 25 (Fig. 1), which is a polybutadiene reactive site group product of the HÜLS-A VEBA Group Co. (provided by its representative in Turkey, Tükmay A. S., Istanbul).

Diethyl ether, supplied by Merck (Darmstadt, Germany) (>99.5% pure), was used as a solvent for silane treatment. Distilled water was used to increase the hydrolysis of SCA during application. Note that this SCA is insoluble in water.

Preparation of blends

Waste soft-drink bottles were cleaned with tap water and dried at room temperature. They were cut into small square ($5 \times 5 \text{ mm}$)-shaped flakes. PET flakes were treated with SCAs. The SCAs used were 2% by weight with respect to PET in a slurry mixture where the solvent was diethyl ether (50 mL) and 10 mL of distilled water was later sprayed over this mixture. This mixture was continuously mixed until most of the solvent, ether, was evaporated at room temperature. Final drying was carried out in an oven overnight at 60°C and also carried out in the same way at a higher temperature, 110°C . The effect of the temperature on the SCA in the surface treatment of PET was found to be very sensitive against oxidative degradation, especially at 110°C , because of the presence of the butadiene reactive side. PET, 60°C -treated, 110°C -treated, and nontreated, was mixed with PP in 20, 40, 50, and 60% compositions by weight of PET.

Volume fraction

Volume fractions (ϕ) of PET blends are given in Table I. Densities of PP and PET were taken as $PP = 0.905 \text{ g/cm}^3$ and $PET = 1.350 \text{ g/cm}^3$, respectively.

Processing

Blends were prepared using a single-screw extruder (Model CS-194) attached to a Brabender PlasticCorder torque rheometer, PLV-151 (Germany), in which the zone temperatures were adjusted to 230, 250, 265, and 275°C . To increase the homogeneity of the blends, second and third extrusions were applied after the first extrusion. The PP–PET blend films of 250–850- μm thickness were obtained on an adjustable speed conveyer belt. Every blend film of the extrusions was cut into small squared-shaped flakes and reextruded (second and third extrusions).

Finally, PP–PET blend films were prepared for tensile and impact tests, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The specimens for impact testing were obtained by compression molding of the extruded films at 275°C in specially prepared steel molds.

TABLE I
Weight and Volume Fraction (ϕ) Values of PET and PP

Weight composition	ϕ_{PET} (%)	ϕ_{PP} (%)
20% PET + 80% PP	14.35	85.65
40% PET + 60% PP	30.89	69.11
50% PET + 50% PP	40.13	59.87
60% PET + 40% PP	50.14	49.86

Tensile testing

Tensile tests were carried out in an Instron tensile testing machine (TM102) with standard dumbbell-shaped films, which were cut from extruded blend films along the extrusion direction. The draw rate and gauge length in measurements were 5.0 cm/min and 3.5 cm, respectively. All measurements were performed at room temperature and the average of at least five dumbbell-shaped extruded blend films was reported.

Impact testing

For impact testing, first extrudates were compression-molded at 275°C, which, considering the thermal history, corresponded to the mechanical testing of the second extrudates. Hence, the compression molding of the second extrudates corresponded to the third extrusion process in terms of the thermal history. A pendulum impact testing machine, a Coesfeld PSW 4J, was used for the Charpy impact measurements with standard notched and unnotched samples (nearly 0.3 × 0.7 × 6.0 cm) at room temperature. In the notched samples, the V-shaped notch depth was 1.3 mm and the notch tip radius angle was 22.5°.

SEM

SEM analyses were carried out on tensile fractured surfaces of PP–PET blend films with protective coatings for their morphological properties by using a JEOL JSM-840A.

DSC

The thermal behavior of extruded PP–PET blends was carried out using a Perkin–Elmer DSC-4. The measurements were done under a N₂ atmosphere from 50 to 270°C with a 15°C/min heating rate. Heating, cooling, and reheating cycles were carried out under the same conditions; the melting and crystallization peaks of the blend polymers followed.

RESULTS AND DISCUSSION

Measurements during blending and extrusion process

During the extrusion process, several measurements were performed for the preparation of 20, 40, 50, and 60% PET nontreated and 60 and 110°C silane-treated blend films. The average output of the blend films was measured in gram per minute (g/min) for the first, second, and third extrusions. The variation of the viscosity of blends in terms of torque was recorded.

In general, the aim of the first extrusion was the initial homogenization of PP and PET and also the

compatibilization of the system when silane was applied. The reason for performing second and third extrusions was to improve the homogeneity of the blends. While we were achieving homogeneity, PP and PET were most likely to start to degrade and oxidation and chain scission and also crosslinking to a certain extent occurred, especially after the third extrusion. Due to this degradation, the ultimate property changes became inevitable.

The average output and torque (hence, viscosity) reading data of nontreated and silane-treated PET–PP blends at 60 and 110°C after multiprocessing are shown in Figures 2 and 3, respectively. The average output of nontreated blends and 60°C silane-treated blends clearly showed a decreasing trend with successive extrusions (Fig. 2). Despite the observed relative decrease in the output amount in nontreated and 60°C silane-treated blends, there was no big significant change in the average output in 110°C silane-treated blends with the number of extrusions. In both silane applications, the viscosity of the blends, as given by the torque measured, increased compared with the nontreated blends, particularly for the second and third extrusions. When the PET composition increased, the viscosity of the system occasionally decreased. The fast decrease in the torque reading in the second and third extrusions in nontreated PET–PP blends indicates the thermal degradation, but when lowering the viscosity, the average output did not show a clear increase. The possible explanation of the decrease both in average output and the viscosity can be the counteracting effects of homogenization of PET with PP accompanied by an extensive thermal degradation of both polymers, especially PET. Furthermore, PET in the blend became more dominant and the viscosity decreased after the second and third extrusions, and the average output of the blends decreased as a result of an increasing interaction between PET and PP.

However, the viscosity of the blends apparently increased with the presence of the SCA. Surface-treated PET, at different temperatures, also affected the average output and viscosity of the blends. At high temperatures, the butadiene group of the SCA was found to be very sensitive against oxidative degradation. The color of the PET–PP blends after the second and third extrusions in 110°C SCA treatment turned from light to dark yellow. The yellowing effect directly indicated the degradation of the blends. The butadiene group in the SCA seems to be affected greatly by air oxidation during the initial drying step at 110°C. This deterioration resulted in a yellowish brown color in the third extrusions of the high-content PET blends, especially with 50 and 60% of PET in case of 110°C silane-treated blends. Furthermore, this also caused lower mechanical properties.

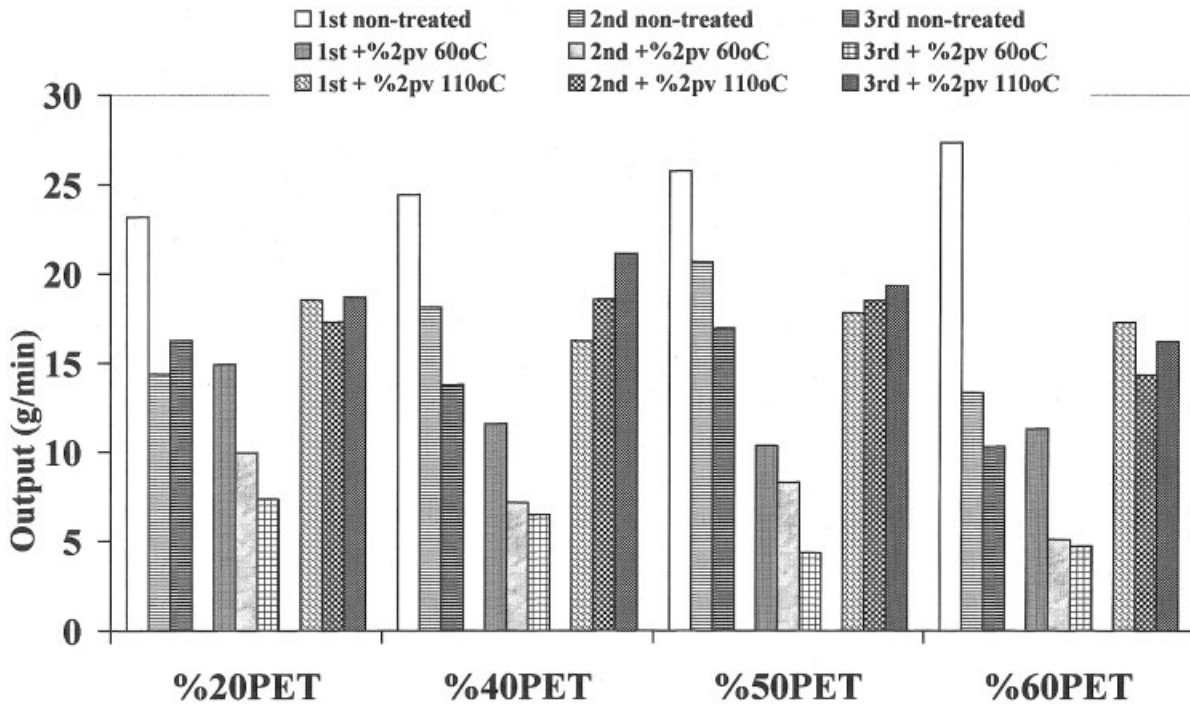


Figure 2 Average output after extrusion process for nontreated and 60 and 110°C silane-treated PET-PP blends with different compositions (pv stands for POLYVEST 25 SCA).

In all cases of second extrusions, the torque readings were found to be lower than that of the third extrusions. This appears to be very difficult to explain, considering the order observed in the output results. It is more likely that the effectiveness of the SCA with its butadiene group was strongly involved in the homogenization process, particularly at the second extrusion.

Tensile testing

Ultimate tensile strength and percent elongation-at-break bar graphs of nontreated and 60°C and 110°C silane-treated blends are shown in Figures 4 and 5. In general, as the PET content of the blends increased, the tensile strength and percent elongation at break de-

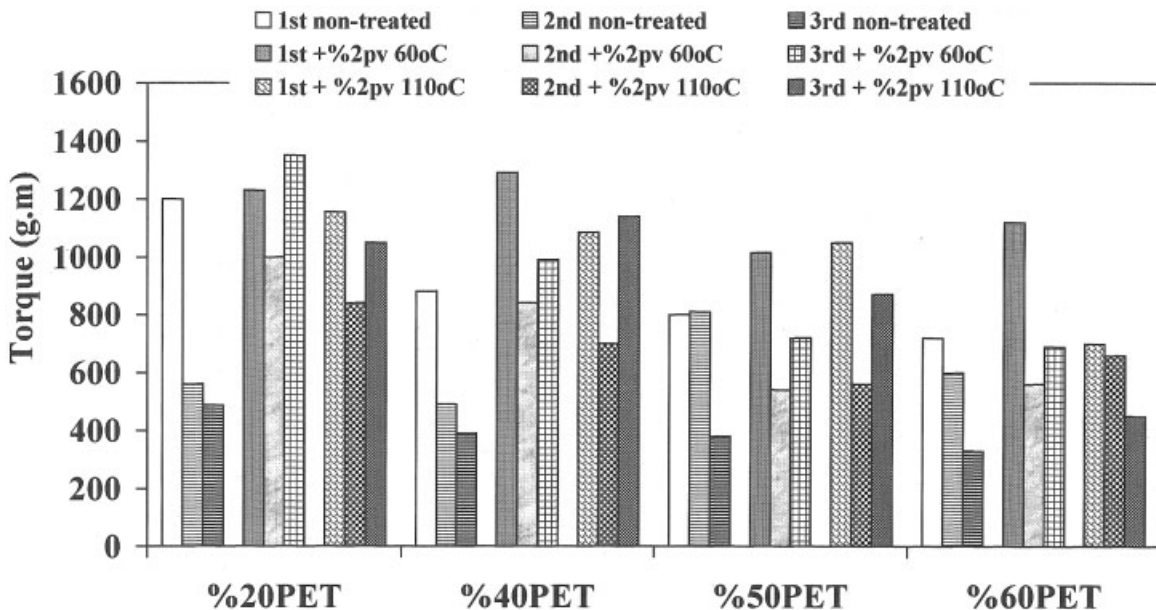


Figure 3 Torque reading graph of nontreated and 60 and 110°C silane-treated PET-PP blends with different compositions.

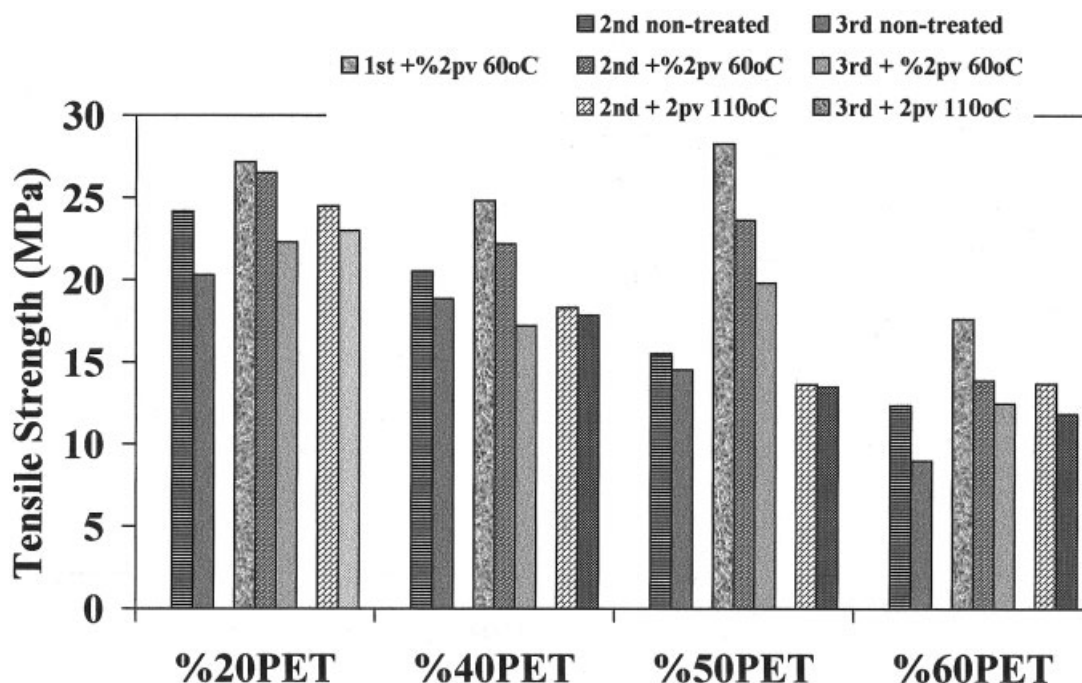


Figure 4 Tensile strength versus percent composition graph of nontreated and 60 and 110°C silane-treated PET-PP blends. 1st, 2nd, and 3rd stand for the number of extrusions.

creased from about 25 to 15 MPa for second extrudates. Silane treatment, especially 60°C, undoubtedly appeared to improve the tensile strength of the blends. Here, the mechanical testings of the first extrusion, although the initial mixing was expected to be not enough for complete incorporation of these two polymers, was found to be better than were the results of second and third extrusions. The lowest tensile

strength, at 60% of the PET nontreated blend in the third extrusion, was the most brittle one, showing the highest phase separation between PP and PET. Although the tensile strength of the blends decreased as the PET content increased, it was observed that the 60°C silane-treated 50% of PET blend gave the most substantial increase in the ultimate tensile strength compared to the others. The optimum and the best

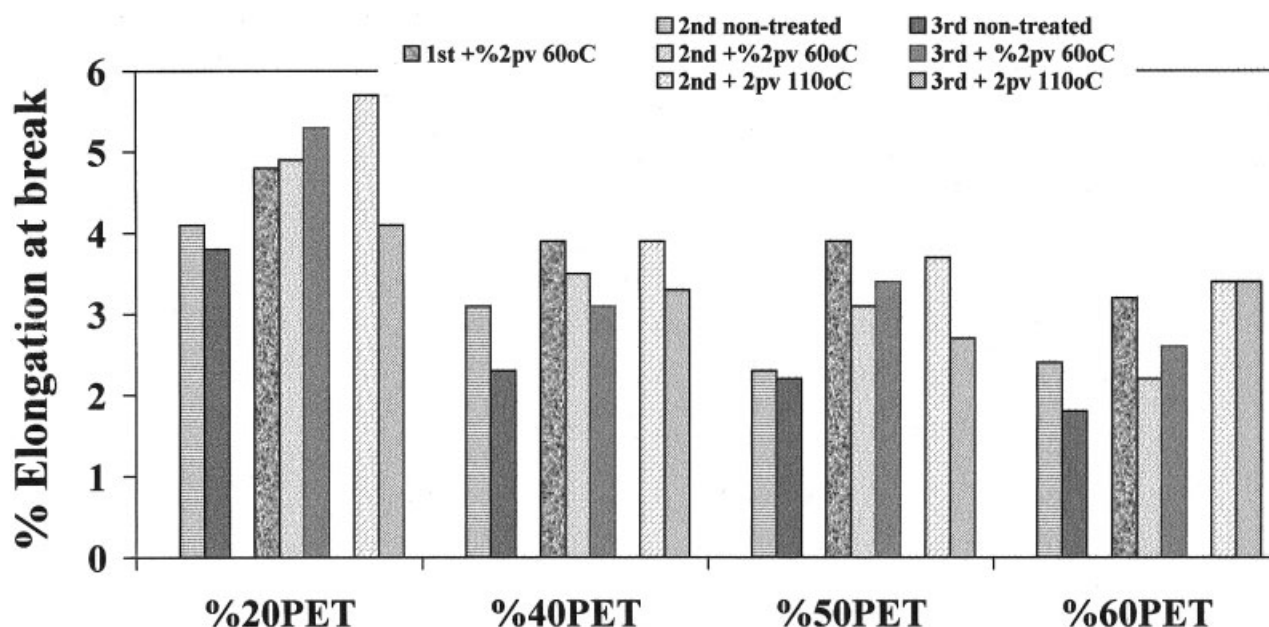


Figure 5 Elongation at break versus percent composition graph of nontreated and 60 and 110°C silane-treated PET-PP blends. 1st, 2nd, and 3rd stand for the number of extrusions.

compatibility between PET and PP in 50% of PET with 60°C silane treatment were apparently achieved. In addition, after each successive extrusion, the tensile strength of the blends decreased as a result of the incorporated degradation in the PP and PET blends. Extrusions of pure PP under the same conditions specified in the Experimental section showed no distinct changes in the mechanical properties. Therefore, it eventually is very possible that the loss in the tensile strength after successive extrusions is directly due to the presence of the heat-sensitive polymer PET rather than of PP. Regarding the 60°C SCA-treated 60% PET-PP blends, they were still better than those of nontreated PET-PP and 110°C SCA-treated PET-PP blends. SCA treatment of 110°C was found to be rather unsuccessful in improving the tensile strength, except at 60% PET.

Figure 5 shows the percent elongation at break of nontreated and silane-treated blends. The 60°C silane treatment seemed to improve the elongation at break of the blends slightly but not as much compared with the nontreated blends. The 110°C silane-treated PET-PP blends, in which the reactive butadiene group in the SCA was oxidatively degraded, showed the highest strain-at-break values in the second-extrusion samples compared to the others, but these samples had lower strength. The results of the elongation at break were not very conclusive as was observed by the tensile strength, in which most of the ultimate elongations generally ranged from 2 to about 5.5.

Impact testing

Impact strengths of the PET-PP blends with and without silane treatment after each successive extrusion are shown in Figure 6(A,B). As mentioned in the Experimental section, the films obtained from extrusion processes were compression-molded. Therefore, in all compression-molding processes, an additional thermal history at 275°C should be considered for the blends.

Silane treatment abruptly improved the impact strength of the blends. The most significant improvement was observed in the unnotched 40% PET blend after the first extrusion. In addition, the highest impact strength was obtained in the unnotched 20% PET blend [Fig. 6(A)]. Obviously, the impact strengths decreased as the PET content increased. The general behavior of the silane-treated blends in regard to the impact strength is a decreasing trend with the compression-molding process. Note that, again, each compression molding caused thermal degradation in the blends. This became very evident in the third-extrusion samples in the silane-treated blends since a fourth thermal process was carried out. The highest impact strengths were observed in first extrusion (plus compression-molding process) of the silane-treated samples, yet the 20% silane-treated PET-PP composition

had almost the same impact strength with the first-extrudate specimens. The variation in the impact strength in nontreated PET-PP blends appeared to be not greatly changed with the number of extrusions and the compression-molding process. All the nontreated PET-PP blends were found to have impact values less than 10 kJ/m² and decreased well below 5 kJ/m² with an increased PET content. In comparison, the impact strength of pure PP measured 30 kJ/m²; none of the blends including those silane-treated reached this value. A closer look may show that the PET-PP blends would never reach the high impact property of virgin PP. Yet, silane treatment gave a substantial improvement in the impact strength, especially in 20 and 40% blending.

A further study on the impact strength was carried out in notched samples of selected PET-PP blends. Upon notching, the impact energy is localized around the notched area; hence, it causes a better visualization of the improvement in the impact strength. The big difference in the 40% PET-containing blends upon silane treatment [Fig. 6(B)] well coincides with the unnotched samples. In addition to this, the difference in impact strengths of notched 50 and 60% PET-PP blends shows that the SCA as a compatibilizer is very effective in improving the impact properties. No attempt was carried out for 110°C silane-treated blends because their tensile properties were found not to be efficient enough.

SEM

A morphological study of 20, 40, 50, and 60% PET tensile fractured surfaces of blends with and without silane treatment is given in Figures 7-10. In general, silane treatment at both 60 and 110°C changed the morphology of the PET blends totally and surprisingly. The main difference came from the existence of fibrillar and tubular extension morphology in both 60 and 110°C silane-treated blends. It became difficult to distinguish PP and PET separately in the fractured surfaces after silane treatment. However, phase separation was clearly observed in all nontreated blends where PP and PET could be easily differentiated in Figures 7(A), 8(A), 9(A), and 10(A). The spherically shaped beads belonged to PET where the main matrix is PP in the nontreated blends, as was observed in many previous studies.^{2-6,14-16} Spherical voids and holes were clearly observed in nontreated blends due to the pullout of these weakly interacted polymers from the main matrix (PP) after tensile testing.

There was no observation of the PP matrix orientation in the tensile testing of nontreated blends of any composition [see Figs. 7(A), 8(A), 9(A), and 10(A)]. These nontreated samples broke at lower strength and elongation. When the SCA was involved in the blend preparation, the morphology was altered completely. At lower PET

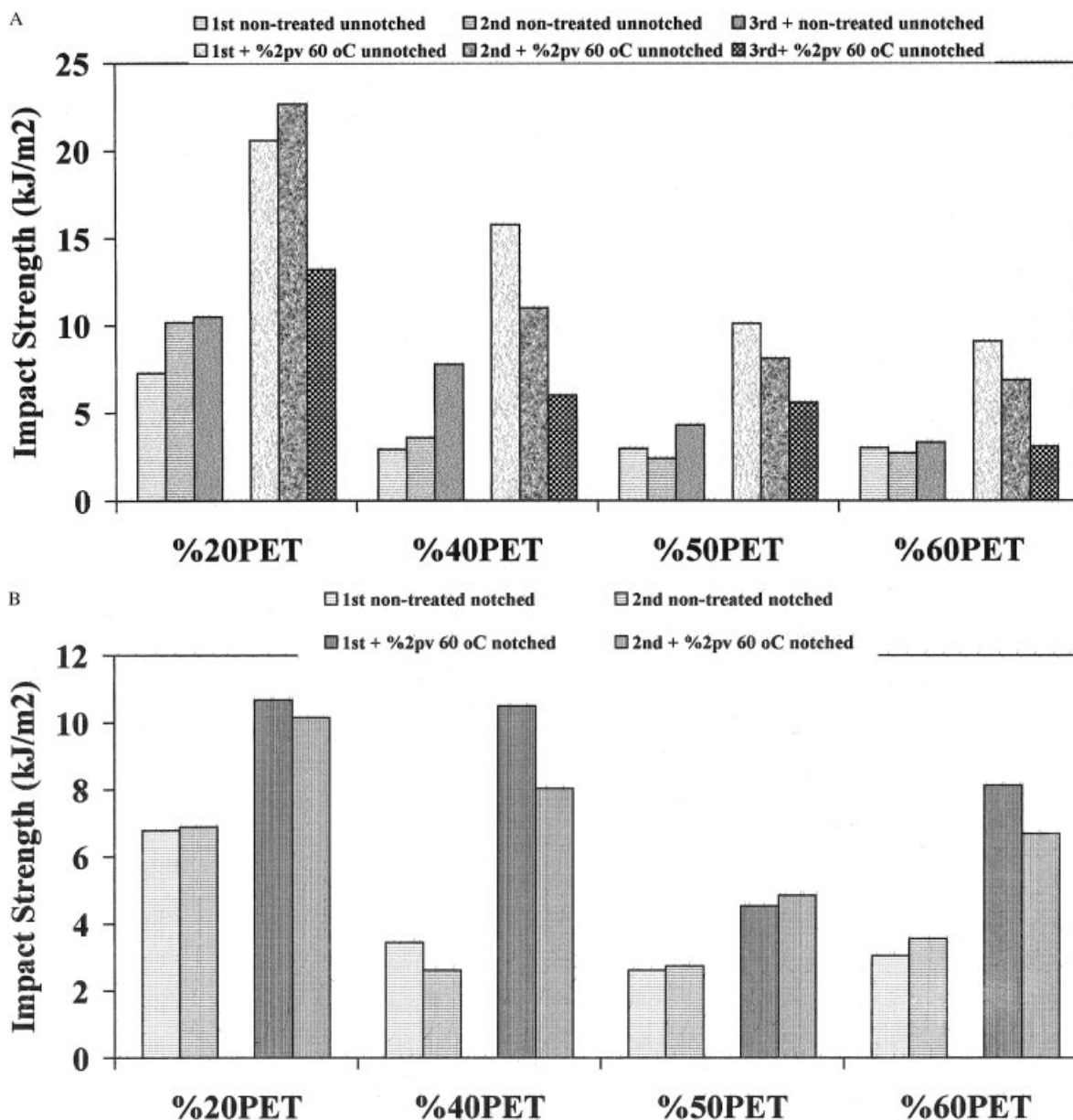


Figure 6 Impact strength versus percent composition graph of (A) unnotched for the 1st, 2nd, and 3rd extrusions and (B) notched nontreated and 60°C silane-treated PET-PP blends for the 1st and 2nd extrusions.

compositions, 20 and 40% PET by weight, the main matrix [Figs. 7 and 8 (B,C)] (regardless of the temperature of the silane treatment) PP showed orientation upon drawing. Furthermore, as seen in Figure 8(B,C), the fibrillar and also tubular extensions from bead structures became predominant in the 40% silane-treated PET blends. This morphology continued to exist for higher PET-containing blends [Figs. 10 and 11 (B,C)]. No voids exist in silane-treated blends when nontreated and silane-treated morphologies are compared, although we observed almost the same morphology of nontreated and 110°C silane-treated blends [Fig. 9(A,C)]. In Figure 9, with almost the same magnification, the beads of PET were not free, as seen clearly, and were strongly held in

the matrix and few fibrillar and tubular extensions were still present.

DSC study

In general, DSC thermograms showed the melting point peaks (T_m) of PP and PET at about 160 and 249°C, respectively. The T_m values of PET and PP in the blends were found to be not greatly changed. For each composition of the blends, even after each successive extrusion, the T_m of PP decreased very slightly as a result of multiprocessing. Furthermore, as the PET content increased in the blends, the intensity of the

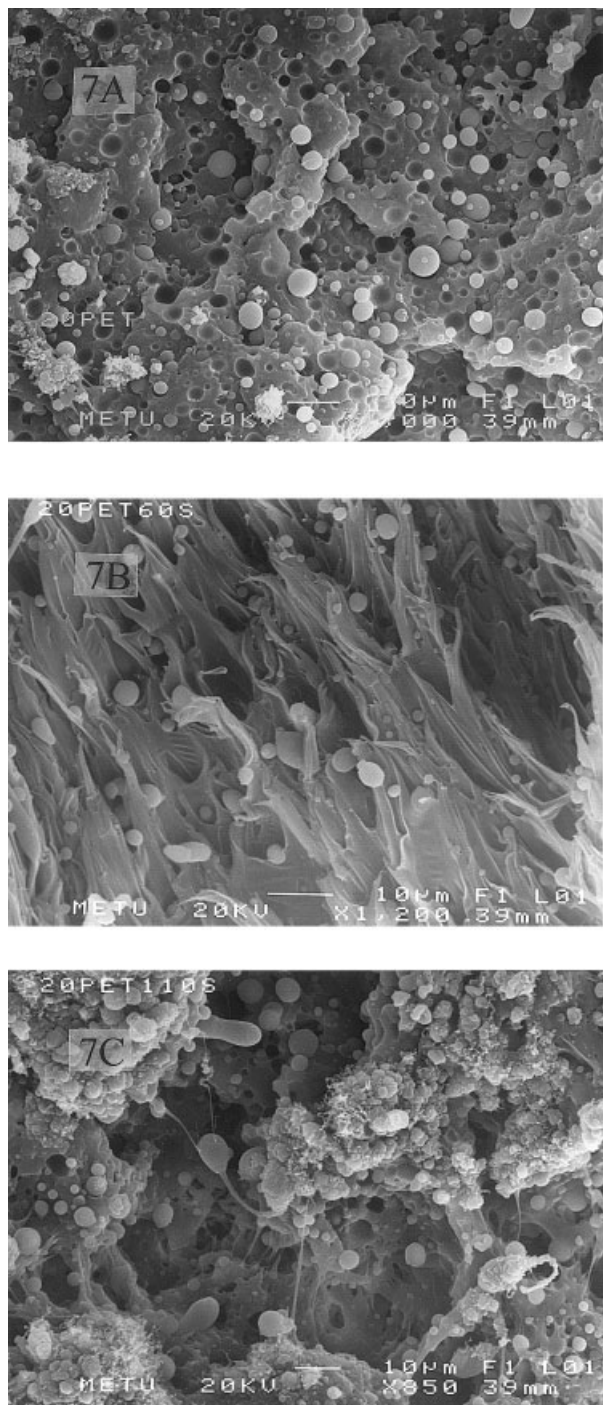


Figure 7 Tensile fractured surface SEM photograph of (A) nontreated, (B) 60°C SCA treatment, and (C) 110°C SCA treatment of 20% PET-PP blends for second extrusion

melting peaks that belong to PET increased and, obviously, the melting peak intensity of PP decreased.

The crystallization peaks (T_c) that appeared at about 130°C in the first run of heating of 60- and 110°C-treated blends belonged to PET. It was interesting that these T_c peaks did not appear in the nontreated blends, which proved that silane treatment changed the thermal history of the system, in which, in the

absence of the SCA, PET is mostly crystallized in the blend. In the second run after cooling, exothermic crystallization peaks disappeared in all cases. Moreover, we also noticed that in the second run, particularly in all 40, 50, and 60% PET blends, single endotherm peaks of PET at about 249°C turned into a doublet. There is no evidence of cocrystallization of PET and PP together. In addition, they crystallized

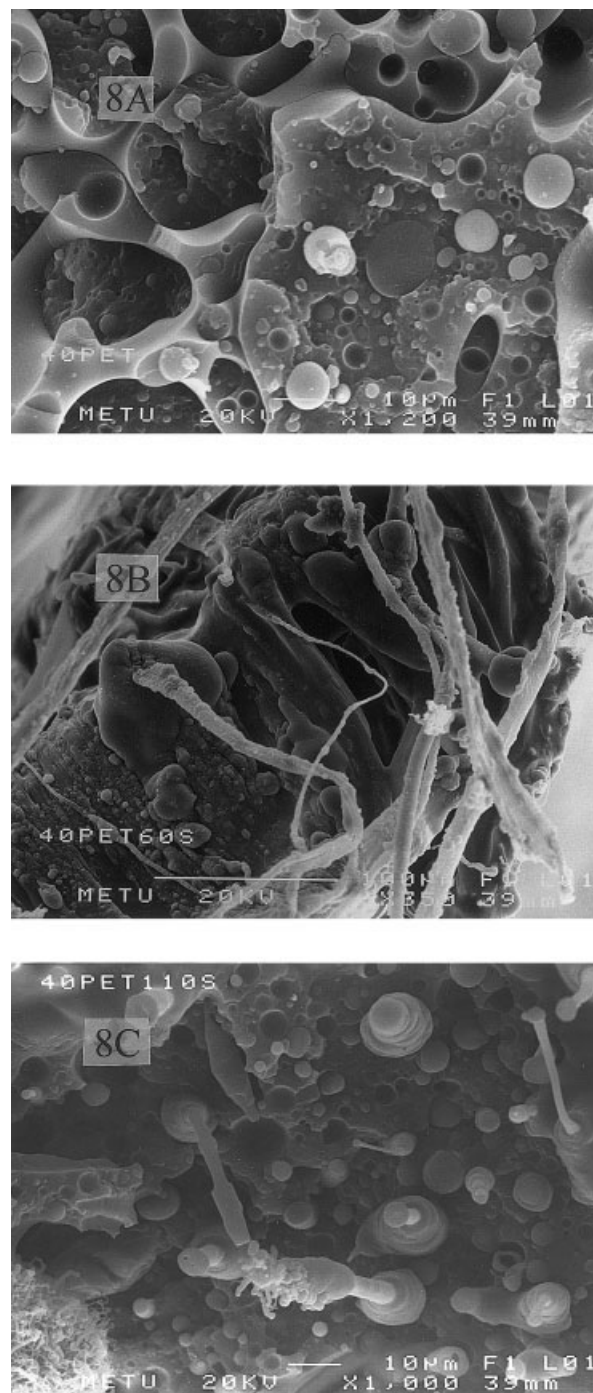


Figure 8 Tensile fractured surface SEM photograph of (A) nontreated, (B) 60°C SCA treatment, and (C) 110°C SCA treatment of 40% PET-PP blends for second extrusion.

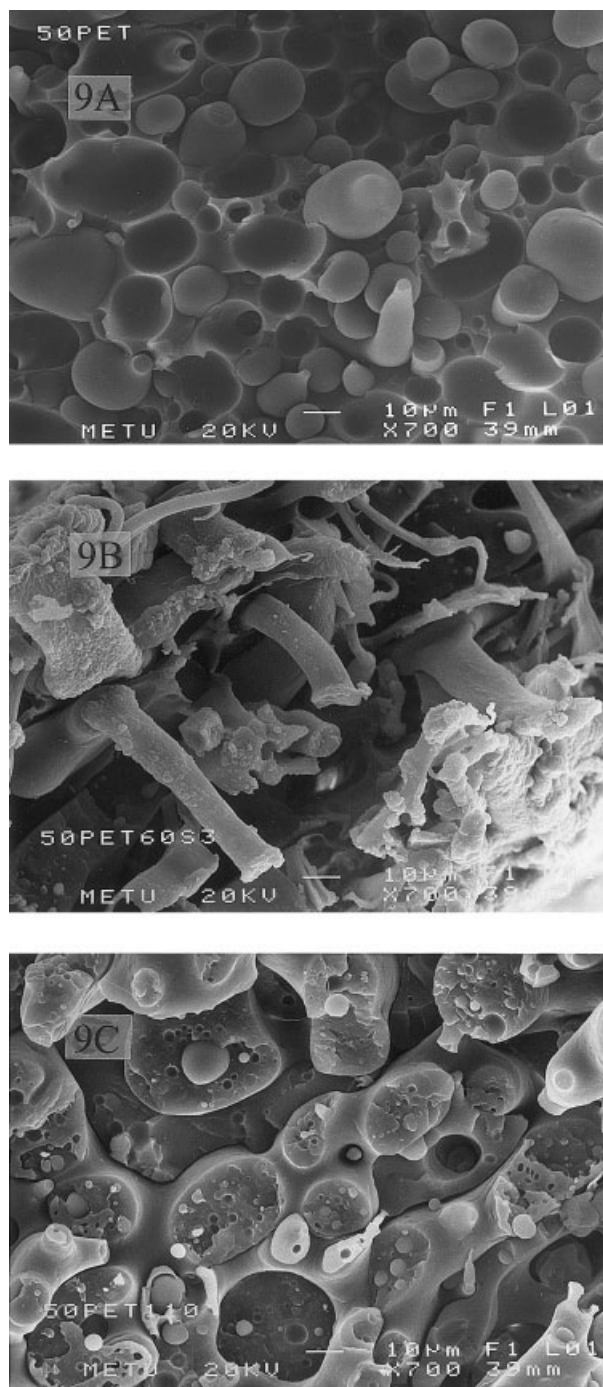


Figure 9 Tensile fractured surface SEM photograph of (A) nontreated, (B) 60°C SCA treatment, and (C) 110°C SCA treatment of 50% PET-PP blends for second extrusion.

separately without a significant change in the T_m values.

CONCLUSIONS

The SCA used in this work undoubtedly improved the mechanical properties of the PET-PP blends. The 60°C

silane-treated 50% PET blend gave the most substantial improvement in the ultimate tensile strength and percent elongation at break compared to other nontreated blends. On the other hand, the silane treatment of PET at 110°C was found to be not as efficient as compared with the 60°C SCA-treated blends.

The most significant improvement in the impact strength up to 500% was in the unnotched 40% PET

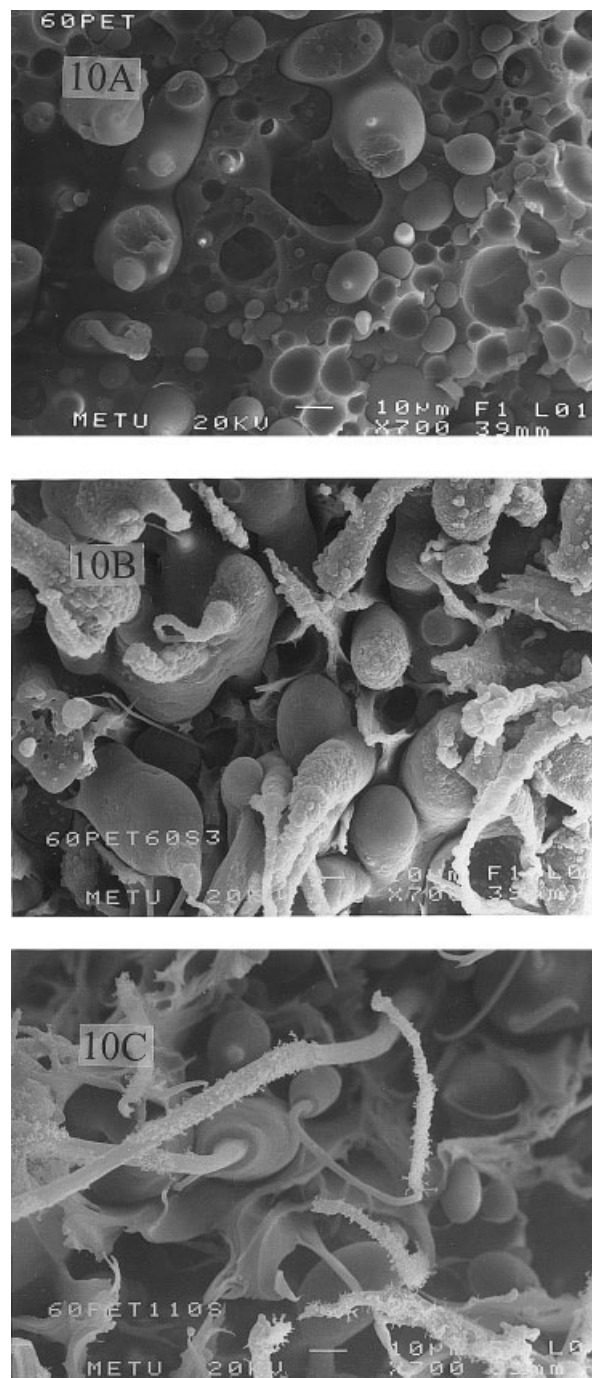


Figure 10 Tensile fractured surface SEM photograph of (A) nontreated, (B) 60°C SCA treatment, and (C) 110°C SCA treatment of 60% PET-PP blends for second extrusion.

blend after the first extrusion compared to the non-treated blends. The improvement in the ultimate mechanical and impact properties of blends also proved that there was a strong interaction between PET and PP in the presence of the SCA, which strongly induced the interaction between PET and PP.

The presence of individual melting temperatures and no significant melting point changes indicated that PET and PP crystallized separately. Furthermore, the crystallization peak of PET in the SCA-treated blends showed that PET in these blends mostly remained in the amorphous phase rather than as a crystalline state.

SEM studies also showed a remarkably different morphology when compared with the existing literature in silane-treated blends. The tubular-type fibrillar extensions, without any voids in the SCA-treated blends, were particularly very interesting. This morphology, on the other hand, explains the enhancement in the mechanical properties. In conclusion, the SCA used in this work appeared to be a very suitable and useful candidate in the compatibilization with a very obvious improvement in the mechanical properties of the PP and PET blend.

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