Studies on Miscibility of Uncompatibilized Nylon 66–Santoprene Blends

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ABSTRACT: This article investigates the miscibility of nylon 66 and santoprene blends. The nylon 66–santoprene was blended to give the following compositions: 100/0, 90/10, 75/25, 50/50, 25/75, and 0/100. No compatibilizer was used during blending of the two components. Thermal properties and morphology of the blends were checked by using differential scanning calorimetry and scanning electron microscopy (SEM). The effect of blend composition on the mechanical properties was checked through tensile and izod impact tests. Both components were immiscible, as confirmed by double melting temperature, corresponding to that of polypropylene component in santoprene and nylon 66. Also, the melting temperature of nylon was not significantly affected by blending it with santoprene. However, the crystallization temperature of nylon increased after blending. This was attributted to the ethylene–propylene–diene monomer content in santoprene, which acts as a nucleating agent. The effect of blend composition on mechanical properties occurred at the 50/50 composition and above. Evidence of immiscibility of both components was also confirmed by the presence of a two-phase structure, as revealed by SEM. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1285–1295, 1998

INTRODUCTION

High-performance polymers are now being made by blending two or more components. This system of creating new materials with unique mechanical and physical properties has been in existence for the past decades. Properties that can be improved as a result of blending include stiffness, thermal stability, processability, chemical resistance, and heat distortion temperature.[1–4] One of the major setbacks in blending is miscibility of the two components because most polymers are immiscible. However, immiscible blends can now be made partially miscible with the addition of a compatibilizer. The effect of compatibilization is to provide morphological stability, homogeneity, and specific interactions at the interface of the two components.[5–11]

Santoprene is the first brand vulcanizate thermoplastic elastomer resin developed by Monsanto in 1981. All grades of santoprene are polymerized polyolefin compounds (PP) with ethylene–propylene–diene monomer (EPDM) and they require no post-curing or annealing to attain their full range of performance and properties.[12] Other advantage of santoprene is that it can combine the processing characteristics of thermoplastics with the physical properties of vulcanized rubber. Blending of this type of thermoplastic elastomer resin with other thermoplastics hasn't been documented in the literature. Nylon 66 is one of the most prosperous engineering polymers that has been successfully used for various applications. Blending of nylon with other thermoplastics has been well accomplished.[13–17] Although, nylon is immiscible with many thermoplastics, with the addition of a compatibilizer, it has proven to be successful. Recent studies[18,19] on nylon with other thermoplastics have shown that compatibilization improves mechanical properties as well as heat distortion temperature.

The aim of this preliminary investigation is to blend nylon with santoprene (without a compatibilizer) and to check the miscibility and the effect of compositions on tensile and impact properties. The morphology of the two components at various compositions was also checked by using scanning electron microscopy (SEM).

EXPERIMENTAL PROCEDURE

Materials

Commercial-grade nylon 66 pellets were obtained from Toray plastics. It has an average molecular weight of 37,000 and a melting point of 265°C. The pellets were predried for 6 h at 80°C. The commercial-grade santoprene 101.73, having a specific gravity of 0.98 and a service temperature from −60 to 135°C, was purchased from Watas Holdings Ltd. Since the santoprene is for injection molding, predrying is not required as stipulated by the Monsanto Corporation.[12] The two components were mixed to give the following compositions of nylon to santoprene: 100/0, 90/10, 75/25, 50/50, 25/75, and 0/100.

The samples were fed into the extruder (Betol extruder), where mixing and blending occurred at 275°C. After blending, the samples were pelletized. The pellets were then injection-molded into a dumbbell shape. The molding conditions were as follows: injection pressure, 7 MPa; holding pressure, 5 MPa; clamping pressure, 9 MPa; injection temperature; 280°C and molding temperature 100°C.

Tensile Test

The dumbbell-shaped sample was 3 mm thick and 10 mm wide. The gauge length was 60 mm and the test was conducted at 10 mm/min using an Instron tensile testing machine. The experiment was carried out at room temperature on batches of five or more samples.

Fracture Toughness Test

A total of 2.5 mm single-edge v-notch was inserted at the center of the dumbbell samples (initially 2 mm and a further 0.5 mm was inserted) before testing on the Instron machine. The linear elastic fracture mechanics (LEFM) was adopted for evaluating the fracture toughness when the sample

shows a brittle behavior. The critical mode I stress intensity factor (K_{IC}) is given as[20]

$$K_{IC} = \sigma_C Y \sqrt{\pi a} \qquad (1)$$

where σ_C is fracture initiation stress (taken as the maximum stress), a is the crack length, and Y is the correction factor for single-edge notched tensile specimen given as.[21]

$$Y = 1.12 - 0.231\,(a/W) + 10.55(a/W)^2$$
$$- 21.72(a/W)^3 + 30.39(a/W)^4$$

where W is the specimen width. Within the frame work of LEFM, K_{IC} is converted to the critical energy release rate (G_{IC}) using the relationship

$$G_{IC} = K^2/E \qquad (2)$$

where E is the Young's modulus.

In the case where the sample is ductile, the J integral method is adopted. Thus, the critical value of the J integral (J_C) is obtained from load−displacement curves on the assumption that materials behave plastically at fracture initiation.

$$J_C = 2U_C/hb \qquad (3)$$

where U_C is the total work area under the load-displacement curve at fracture initiation, h is the specimen thickness, and b is the ligament length.

Impact Test

Izod impact test was carried out according to ASTM D256. The sample was $4 \times 10 \times 60$ mm. A 2.5 mm v-notch was inserted and the experiment was carried out on a standard pendulum tester at room temperature.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements of the samples were carried out by using Perkin−Elmer DSC, Model DSC 7 fitted with a thermal analysis data station. Each sample was heated to 300°C at a heating rate of 20°C/min (first scans). The sample was allowed to cool down at 20°C/min before being reheated at the same rate (second scans). The sample weight was 8 ± 0.025 mg. Thermal properties such as melting temperature (T_m), crystallization temperature

Table I Thermal Properties of Nylon 66–Santoprene Blends (First Scans)

Nylon 66–Santoprene (%)	Nylon 66			Santoprene		
	T_m (°C)	ΔH (J/g)	T_c (°C)	T_m (°C)	ΔH (J/g)	T_c (°C)
100/0	264	70.06	208	—	—	—
90/10	264	55.09	226	153	1.54	102
75/25	265	53.47	225	153	3.57	102
50/50	260	36.22	224	153	11.09	102
25/75	259	18.41	224	152	21.17	101
0/100	—	—	—	154	28.61	101

(T_c), and heat of fusion (ΔH) were all determined from the DSC thermograms.

The degree of crystallinity (χ_c) of nylon in the blend was evaluated from the following relationship:

$$\chi_c = \Delta H_{\exp}/\Delta H * W_f \qquad (4)$$

where $\Delta H_{\exp}$ is the experimental heat of fusion determined from DSC, ΔH^* is the heat of fusion of fully crystallined nylon 66 (188.37 J/g),[22] and W_f is the weight fraction of nylon in the blends.

Scanning Electron Microscopy

The morphology of the blends was examined by scanning electron microscopy (SEM) using Leica Cambridge, Model S-360, at 10 kV accelerating voltage. The fracture surface was coated with gold and examined at a magnification of 400×.

RESULTS AND DISCUSSION

Miscibility of the Blend

It is well documented in the literature that a miscible blend will show a single glass transition temperature (T_g) while immiscible blend will display dual T_gs. In this investigation, the results are based on DSC data on T_m and T_c. Tables I and II show the results obtained from DSC thermograms depicted in Figures 1 and 2. The melting points obtained after the second scans were lower (nylon 66 only) than those of the first scans due to the melting of imperfections or rearrangement of molecules.

In Figures 1 and 2, two peaks are observed in the thermograms. Santoprene, as had been mentioned earlier, is a thermoplastic elastomer containing EPDM and polypropylene. The first peak around 153°C corresponds to the melting temperature of polypropylene while the second peak around 264°C is that of nylon 66. The presence of double T_ms indicates that both components were immiscible. If both systems are miscible, one phase is likely to dissolve completely in the other phase, thereby leading to a single T_m. Recently, Lee et al.[23] reported a T_m depression of nylon as an evidence of miscibility when blended with a copolymer that acts as a compatibilizer. In this case, a compatibilizer was not used but we expect the EPDM component in santoprene to have a compatibilizing effect. However, slight depression of T_m of nylon is due to good mixing, hence the plasticizing effect of EPDM on nylon. Another important parameter taken into consideration is the degree of crystallinity of nylon. The degree of crystallinity of nylon as measured from the heat of fusion (ΔH) obtained from the DSC results is

Table II Thermal Properties of Nylon 66–Santoprene Blends (Second Scans)

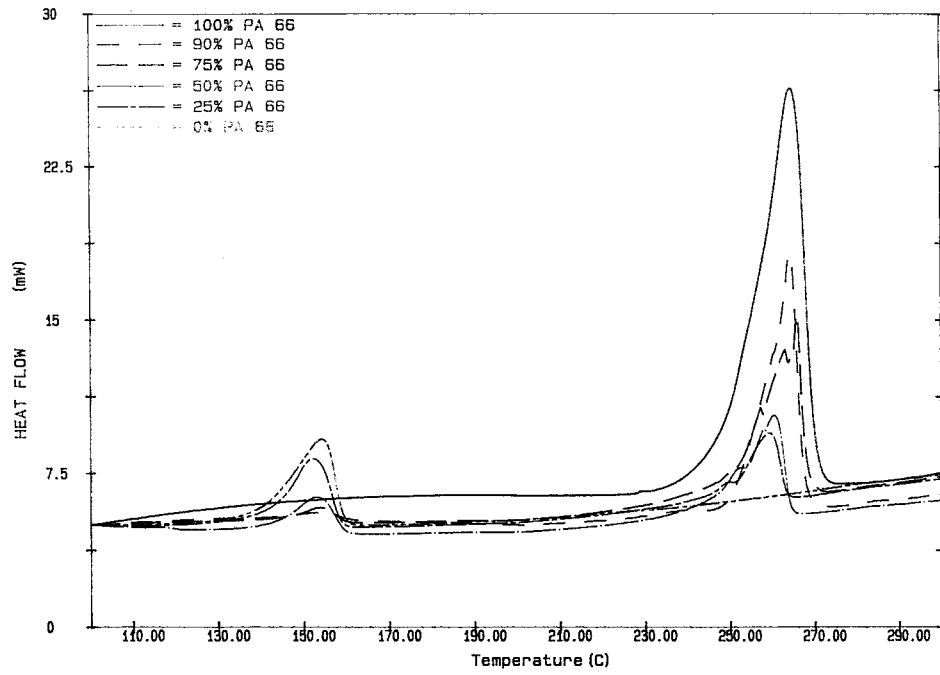| Nylon 66–Santoprene (%)	Nylon			Santoprene		
	T_m (°C)	ΔH (J/g)	T_c (°C)	T_m (°C)	ΔH (J/g)	T_c (°C)
100/0	261	51.43	208	—	—	—
90/10	260	61.85	226	152	1.30	102
75/25	261	53.11	225	153	4.33	102
50/50	258	34.39	225	153	12.48	102
25/75	257	17.80	225	152	21.17	102
0/100	—	—	—	153	28.61	101

Figure 1 DSC thermograms (melting) of neat nylon 66, neat santoprene, and their blends (first scans).
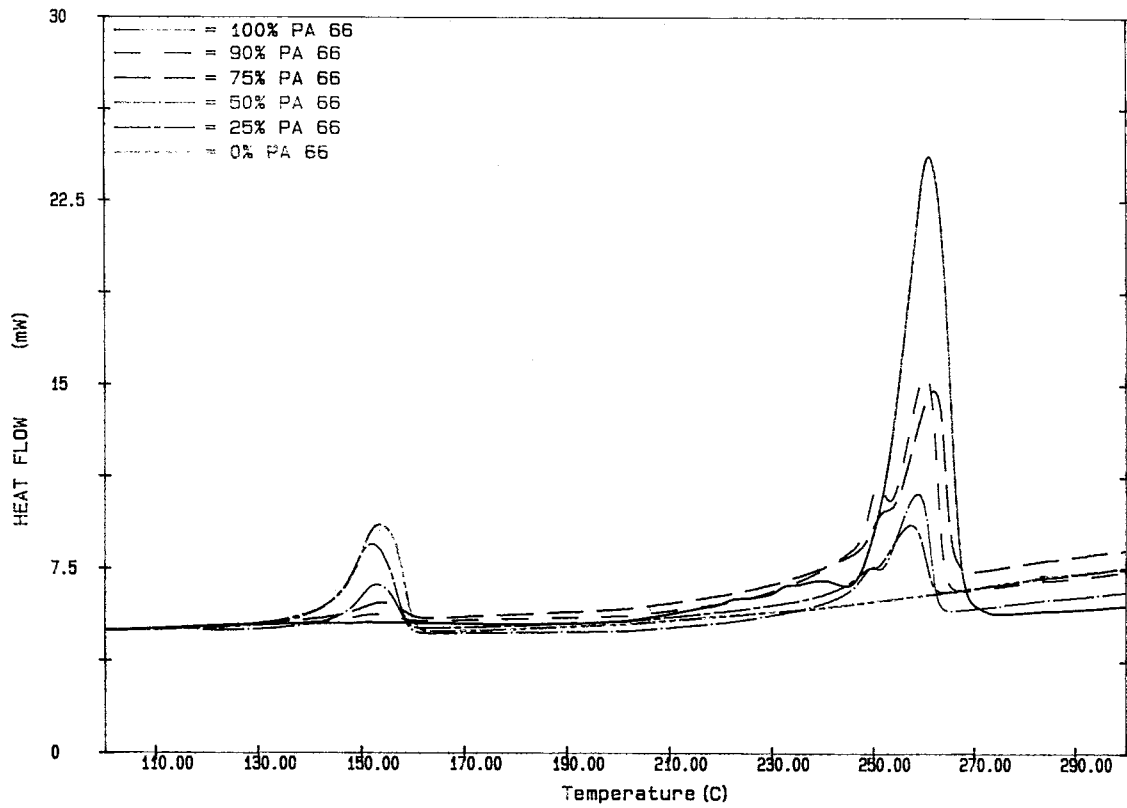

Figure 2 DSC thermograms (melting) of neat nylon 66, neat santoprene, and their blends (second scans).
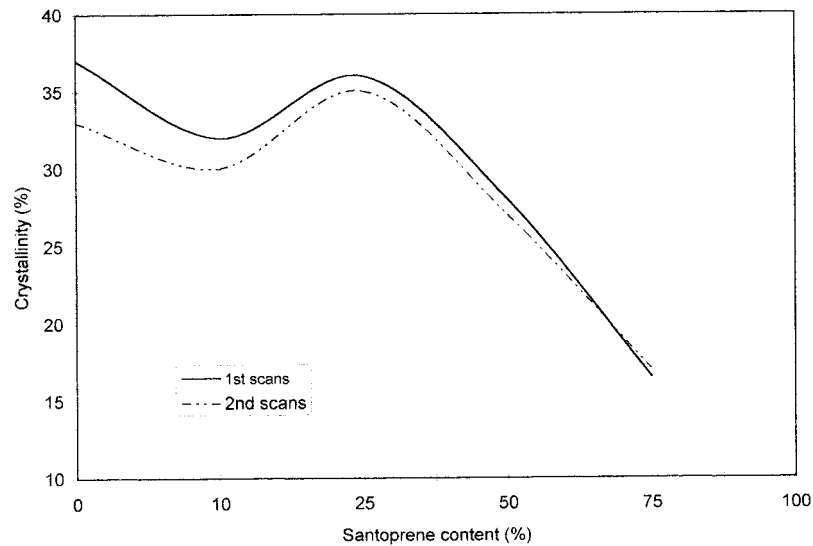
Figure 3 Degree of crystallinity of nylon 66 as a function of santoprene content.

shown in Figure 3 for first and second scans. The crystallinity in the first scan was slightly higher than the second scan as a result of rearrangement of molecules mentioned above. The degree of crys-

tallinity of nylon, which was reduced after blending with santoprene, attests that little interaction occurred during blending. The crystallization from the melt affects the degree of crystallinity of
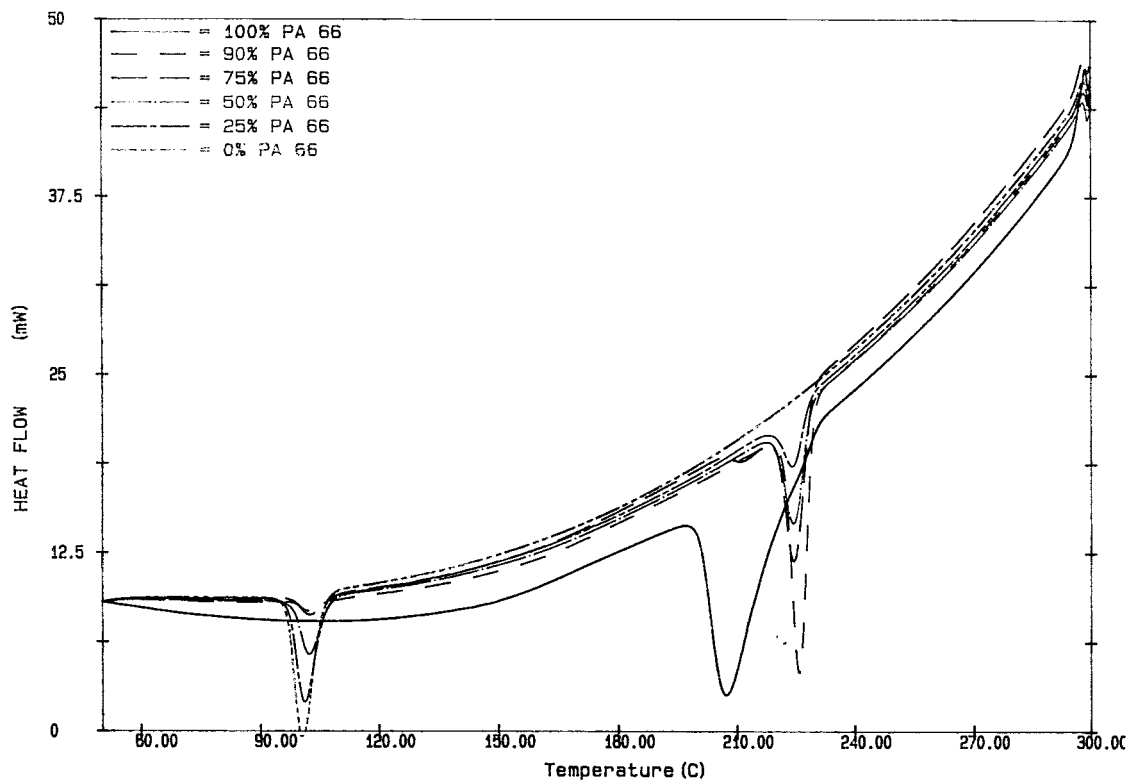

Figure 4 DSC thermograms (crystallization) of neat nylon 66, neat santoprene, and their blends.
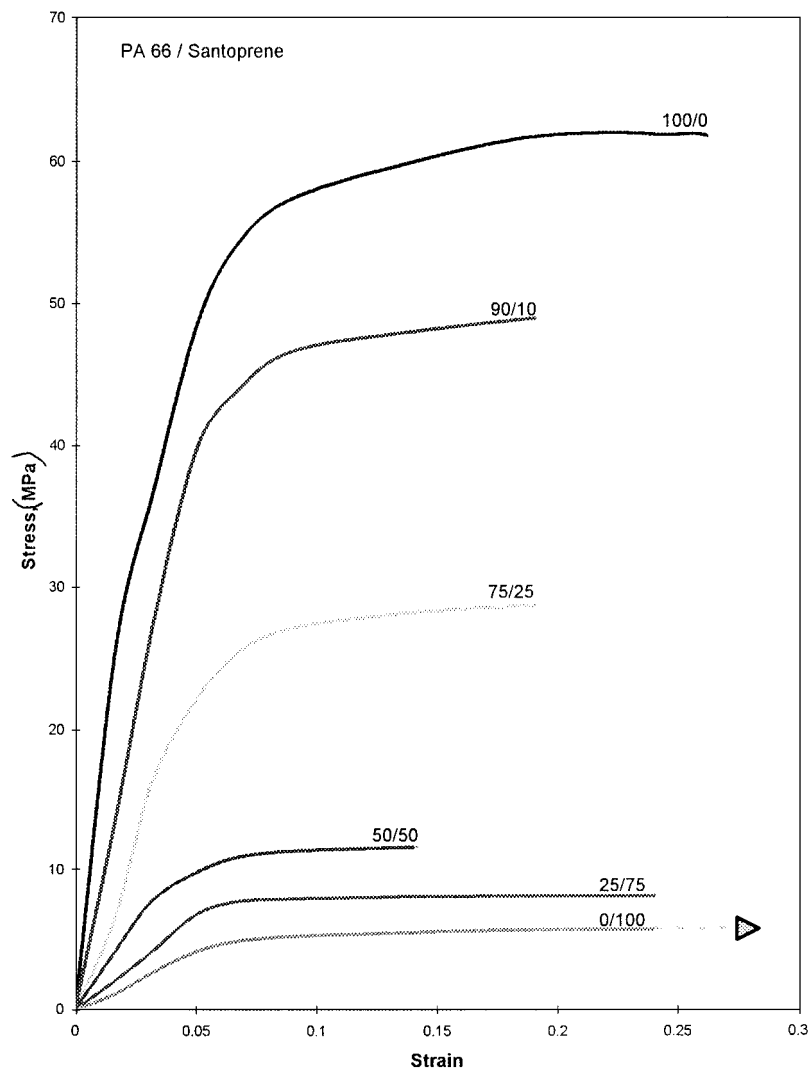
Figure 5   Stress–strain curves of nylon 66–santoprene blends.

nylon in the blend. Crystallization of the blends, which occurred below the melting point of nylon, generates an ordered structure in both the crystalline and amorphous phases of the blends. The temperatures (T_c) in Table I were extracted from the DSC thermograms shown in Figure 4. Neat nylon crystallized at 208°C while the crystallization temperatures of the blends lie between 224 and 226°C. The crystallization temperature of santoprene was not affected as a result of blending it with nylon. The effect of santoprene on nylon should not be confused with blend miscibility. It simply elucidates that despite the fact that they are immiscible, good mixing of both components did occur during blending. The most likely explanation to the increase in crystallization temperature of nylon is due to the EPDM component in

the blend. Two things may have occurred in the blend when cooling from the melt: (1) The EPDM may contain a component that is slightly soluble in nylon, thereby plasticizing it; and (2) the santoprene via the EPDM component may have acted as a nucleating agent.

Both effects lead to an early crystallization of the blend. The EPDM component that provides a nuclei for heterogeneous crystallization accelerates the formation of crystallized region at high temperature. The increase in crystallization temperature did allow the degree of crystallinity of the blend to be lower than that of the neat nylon 66 resin.

Tensile Properties

Stress–strain curves of neat nylon 66, neat santoprene, and their blends, as obtained from the
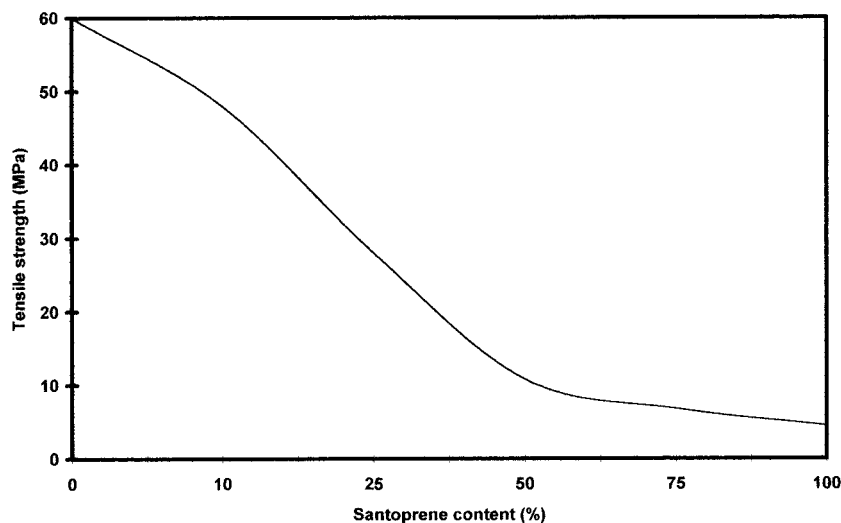
Figure 6 Tensile strength of nylon 66–santoprene blends versus santoprene content.

load–elongation curves, are shown in Figure 5. All samples showed ductile behavior before failure. However, neat santoprene did not break due to its elastomeric nature. The highest stress value was recorded for nylon while the value for the neat santoprene was the lowest. As can be seen in Figure 5, the stress value of nylon reduces with increasing santoprene content. The critical stress level, that is, the tensile strength as a function of santoprene content, is shown in Figure 6. It is clear from the figure that blending of santoprene with nylon reduces the tensile strength of nylon as the concentration of santoprene increases. The reduction of tensile strength of nylon with increasing santoprene content occurred only in a nylon-rich region. No further reduction can be observed in the santoprene-rich region. This observation indicates that the influence of nylon in increasing the tensile strength of santoprene occurred above the 50/50 composition. The results for tensile modulus against santoprene content (Fig. 7) also show a similar trend except for linear reduction with increasing santoprene content. The tensile modulus of neat santoprene was about 0.18 GPa, which is about nine times lower than that of neat nylon (about 1.6 GPa). The tensile test results indicate that, although both components are immiscible at a micro level, they mixed well due to alteration of properties. This means that part of santoprene did dissolve in nylon.

The fracture toughness (energy approach) of the samples are tabulated in Table III. Fracture toughness is the resistance of a material to propagation of an existing crack. In this case, depending on compositions, the single-edge notched samples showed both brittle and ductile failure modes. It is seen in Table III that 100% nylon was brittle while 100% santoprene was highly ductile. The values quoted in Table III were obtained from average of six specimens using eqs. (2) and (3), respectively. In the nylon-rich region, where the fracture mode was brittle, eq. (2) was used while eq. (3) was adopted in the santoprene-rich region where ductile failure ensues. G_{IC} of neat nylon reduces with increasing santoprene content but suddenly enhanced in the 50/50 sample. This behavior is unanticipated because the presence of EPDM in santoprene is expected to enhance the toughness of nylon. A drop of about 10% between 100/0 and 75/25 may be due to the polypropylene content in santoprene. Polypropylene is known to have low toughness, and a significant interaction with nylon might have occurred during blending. The increased fracture toughness in 50/50 sample demonstrates the region where the interaction of the two components is highest. This is in agreement with the result of tensile test (Fig. 6), where the improvement in tensile strength of santoprene commenced in the 50/50 region. It is evident from the above results that in immiscible blends (without compatibilizer), the two components can generate a significant improvement in properties. Although, at a micro level, phase separation may occur, but careful

Table III   Fracture Toughness

Composition	G_{IC} (kJ/m^2)	J_C (kJ/m^2)	Fracture Behavior
100/0	82	—	Brittle
90/10	75	—	Brittle
75/25	73	—	Brittle
50/50	89	—	Brittle
25/75	—	57	Ductile
0/100	—	351	Ductile

blending may show evidence of good mixing, where part of one component partially dissolved in the other.

Impact Strength

Izod impact testing of the two components with their blends were carried out. Neat nylon 66 had a very low impact strength while the impact strength of neat santoprene was about six times higher. The impact strength of nylon was not affected in the nylon-rich region. However, with the 50/50 blend composition, the impact strength of nylon was slightly improved and it increased in the santoprene-rich region. However, if the two components are miscible, with the addition of as low as 10% elastomer,[24] one would expect an improvement in impact strength of nylon in the nylon-rich region. Poor impact strength in nylon-rich re-

gion may simply be due to lack of adhesion at the interface of the two components resulting from the large size of the dispersed phase. Santoprene, being a flexible polymer, has a very high impact strength, which was lowered after blending with nylon. It is seen in Figure 8 that a dramatic reduction of impact strength of santoprene occurred as a result of blending with nylon. However, at the 50/50 composition, no further reduction can be seen. The same trend can be observed in impact energy as a function of the santoprene content shown in Figure 9. Once again, the low impact energy of nylon remains unchanged until 50/50 composition. The EPDM in santoprene is expected to enhance the impact energy of nylon but this effect did not occur until around 50/50 composition. As mentioned earlier, the presence of low toughness polypropylene in the santoprene may be responsible for inactivity of santoprene in the nylon-rich region.

Morphology

The morphologies of the neat nylon 66, neat santoprene, and their blends are shown in Figure 10. Neat nylon 66, shown in Figure 10(a), contains a spherical aggregate of spherulites, which is a typical characteristic of semicrystalline polymers. The EPDM and polypropylene, which are the two main santoprene components, show one phase that is an evidence of miscibility of the two components [Fig. 10(b)]. The morphology displays a
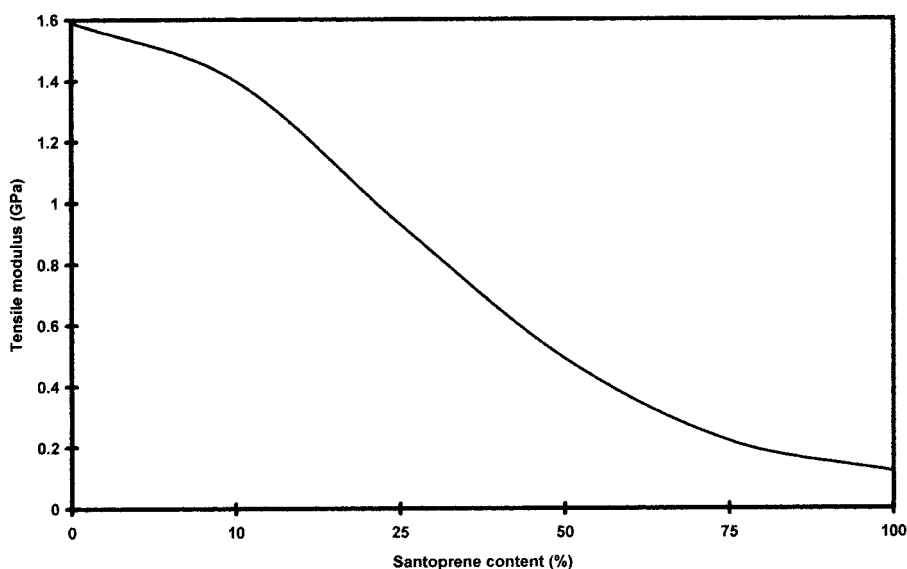

Figure 7   Tensile modulus of nylon 66–santoprene blends as a function of santoprene content.
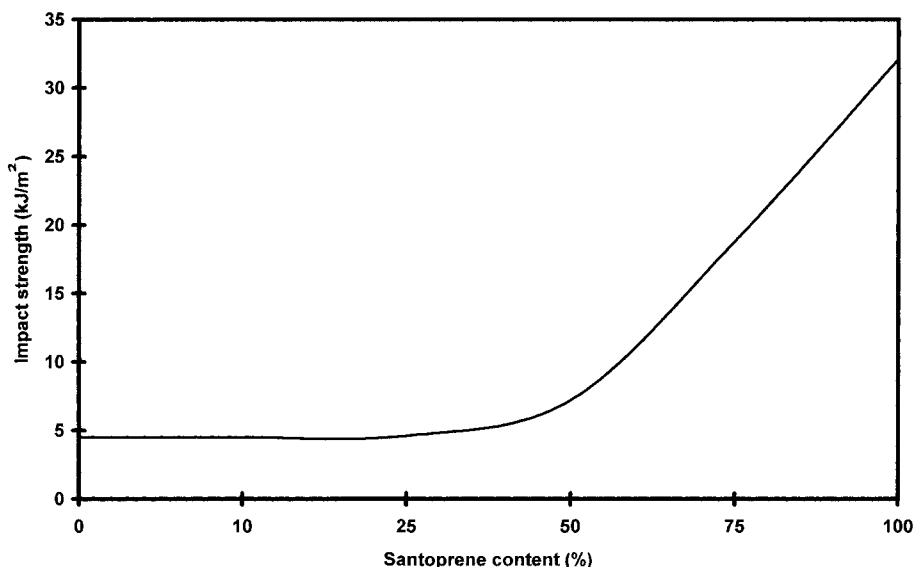
Figure 8 Izod impact strength of nylon 66–santoprene blends versus santoprene content.

typical ductile failure without any phase separation. However, at 90/10 Fig. 10(c), with as little as 10% santoprene added to nylon, a significant phase change occurred. Thus, the occurrence of double phase between the components is an evidence of immiscibility. In this case, the morphology of the 90/10 blend contains large dimples embedded in the nylon matrix. The dimples of irregular shape, which are loosely placed, indicate poor adhesion at the interface of the two components. In the 75/25 blend, the dimples are now extended,

indicating ductility of the blend. The 50/50 blend, as well as the 25/75 blends, on the other hand, displayed a different character; that is, the two components mixed well, with good interaction between the components. The size of the dimples is now smaller than in either the 90/10 or 75/25 blends. This is a sign of little cohesion between the components. The phase change as a result of various blend compositions is reflected in the mechanical properties shown above. Significant changes occurred in both tensile properties and impact properties in the
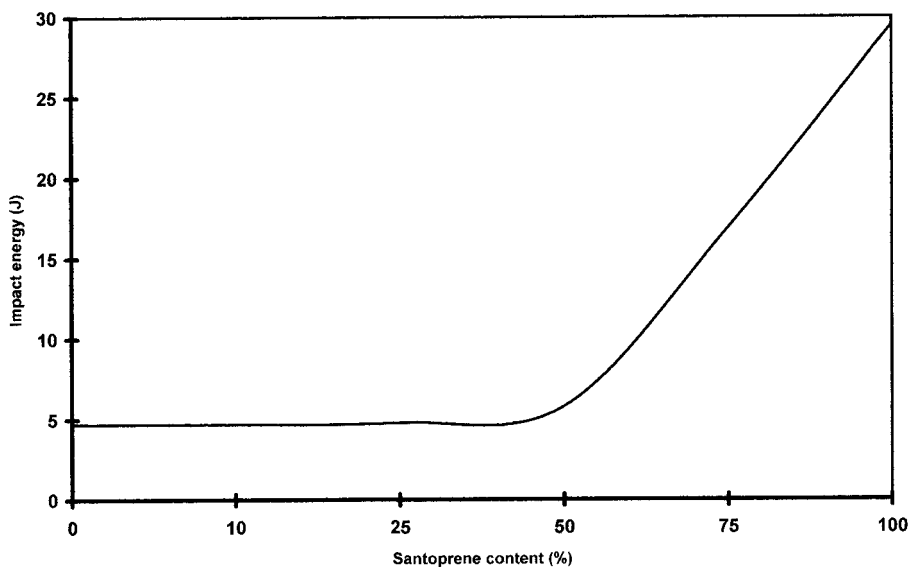

Figure 9 Impact energy as a function of santoprene content.
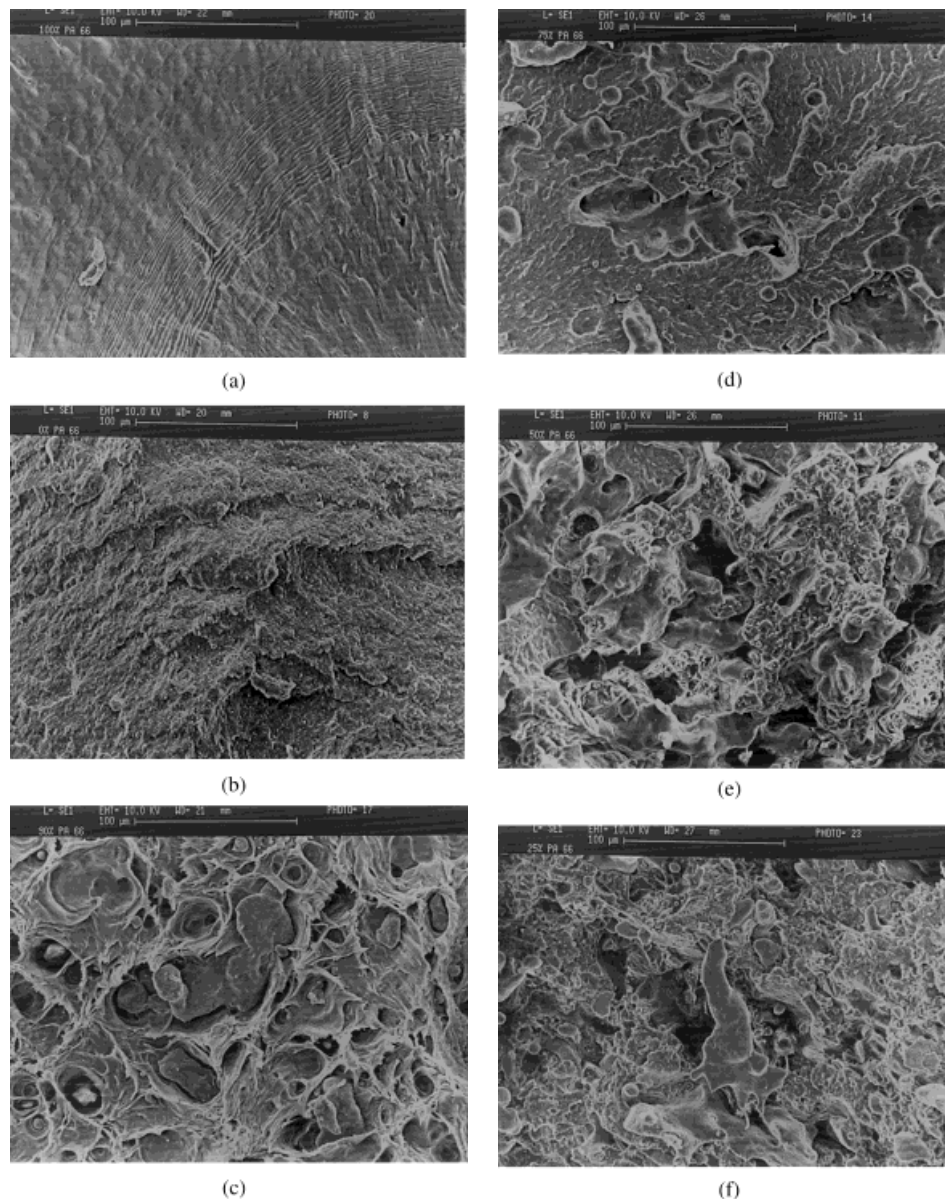
Figure 10   Morphology of nylon 66–santoprene blends: (a) 100/0, (b) 0/100, (c) 90/10, (d) 75/25, (e) 50/50, and (f) 25/75.

50/50 blend compositions. It may be postulated that for both blends to be active in modifying each other's properties without compatibization, the blend composition must be around 50/50.

CONCLUSIONS

The work had revealed that nylon 66 and santoprene are immiscible, but a good interaction did occur during blending. This was based on the results of thermal and mechanical properties. The blends irrespective of compositions showed double melting temperatures corresponding to that of the polypropylene component in satoprene and nylon 66. The increase in crystallization temperature of nylon was attributed to the EPDM component, which acts as a nucleating agent. A significant effect of the blend composition on mechanical properties occurred at around 50/50 composition. The SEM micrographs of the blends revealed a two-phase structure confirming phase segregation of the two components, especially in the nylon-rich region.

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