

# Reinforcement of the Interface in Drawn Polymer Blends PS/PA-12

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**ABSTRACT:** The origin of the reinforcement effect in uniaxially drawn films on the basis of immiscible blends composed of crystalline matrix of polyamide-12 (PA) and glassy polystyrene (PS) dispersed phase has been investigated. Other conditions being equal, the effect becomes the more pronounced the larger the draw ratio and the finer the PS dispersion. Since the latter factor is itself a strong function of phase viscosity ratio ( $\mu$ ), the following two techniques of adjusting the optimal value of  $\mu \approx 1$  have been adopted. According to the first one, a selective plasticizer, which is a good solvent for the PS minor phase and a nonsolvent for the PA matrix phase, was added to the more viscous PS. According to the second approach, the value of  $\mu$  was varied by the use of PS samples of different molecular

weights. It was shown that significant reinforcement effect appears on drawing regardless of the method of adjusting optimal phase viscosity ratio. These data as well as the results obtained with the help of IR-dichroism and transmission electron microscopy techniques evidence that the formation of a much more ordered crystalline morphology of the PA matrix located at the PS/PA interfaces and a large interface area are mainly responsible for the discussed reinforcement phenomenon. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1299–1305, 2007

**Key words:** reinforcement; polymer blends; drawn films; interface

## INTRODUCTION

In response to industrial demand, a vast variety of film polymeric materials have been designed. A large portion of these materials is prepared from immiscible polymer blends and used in aerospace,<sup>1</sup> medicine,<sup>2</sup> filters and membranes,<sup>3–7</sup> packaging,<sup>8</sup> and in many other conventional and special applications. Thorough tailoring of component properties, interfacial adhesion, phase morphology, and processing parameters can lead to designing novel heterogeneous film materials with unique characteristics unattainable with homopolymers.<sup>1–10</sup>

As far as heterophase binary polymer blends are concerned, the third component is always present in such systems. It is an interphase layer formed at the surface of contact of alternative phases. Depending on interfacial characteristics, the thickness of this layer can reach tens of nanometers; therefore, its total volume in a blend cannot be ignored.<sup>11–14</sup> Keeping in mind that characteristics of the interphase layer differ from those of the bulk components, one may expect a noticeable influence of its presence on final properties of compositions.<sup>3,6,7,9,10,12–14</sup>

Stretching of blend films resulting in molecular orientation of bulk polymers and the interface introduces

additional possibilities in development of novel materials with new qualities.<sup>1,3,5,6,15–18</sup>

In our previous paper,<sup>17</sup> the reinforcement of crystalline matrices with glassy particles of polystyrene (PS) has been detected. The effect became more pronounced when the PS phase was selectively plasticized to match its viscosity with that of the matrix, and the blend films were subjected to drawing.

The purpose of this work is to provide further insight into the mechanism of reinforcement of crystalline matrices by dispersions of glassy particles in drawn films.

## EXPERIMENTAL

### Materials

The materials used in the experiments include commercial grades of polyamide-12 (PA) with average molecular weight  $M_w = 2.4 \times 10^3$  g/mol and two bulk polymerized polystyrenes (PS) with  $M_w = 5.2 \times 10^5$  (PS0) and  $M_w = 7.8 \times 10^3$  g/mol (PS4). In all blends, PA was the matrix phase and PS was the dispersed (or minor) phase. Di-2-ethyl hexyl adipate (DEHA) has been chosen as a selective plasticizer for the PS dispersed phase. DEHA was shown to be a good solvent for PS and a nonsolvent for PA.

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TABLE I  
Some Properties of PS0 Containing DEHA, Samples of PS of Different Viscosity and Their Blends with PA

| Property                    | DEHA content in PS0 (wt %) |      |      |      |      | PA   | PS1  | PS2  | PS3  | PS4   |
|-----------------------------|----------------------------|------|------|------|------|------|------|------|------|-------|
|                             | 0                          | 5    | 10   | 20   | 30   |      |      |      |      |       |
| MFI (g/10 min)              | 2.8                        | 6.1  | 9.8  | 22.1 | 98.8 | 14.8 | 5.8  | 13.5 | 25.2 | 113   |
| $\eta$ (MPa s)              | 1.20                       | 0.51 | 0.32 | 0.14 | 0.04 | 0.20 | 0.63 | 0.23 | 0.11 | 0.033 |
| $\mu = \eta_{PS}/\eta_{PA}$ | 6.00                       | 2.55 | 1.60 | 0.70 | 0.20 | –    | 3.15 | 1.15 | 0.55 | 0.17  |
| $T_g$ (°C)                  | 95                         | 79   | 68   | 55   | 37   | 102  | 95   | 95   | 93   | 92    |

Data for PS0 are shown in the first column at 0 wt % of DEHA.

### Blend preparation and procedures

Two techniques of varying component viscosity ratio  $\mu = \eta_{PS}/\eta_{PA}$  (where  $\eta_{PS}$  and  $\eta_{PA}$  are the apparent viscosities of the PS and PA phases) have been employed. The first one is the addition of different amounts of DEHA into the PS0 dispersed phase. The second one implies the use of unplasticized PS samples with different melt viscosities. To prepare PS samples with intermediate viscosities, the PS0 and PS4 grades were melt mixed at component ratios of PS0/PS4 75/25, 50/50, and 25/75 and designated as PS1, PS2, and PS3, respectively. Some viscous characteristics of polymer samples measured at shear rate of  $10 \text{ s}^{-1}$  are presented in Table I.

All polymers were vacuum-dried at  $80^\circ\text{C}$  overnight before use. Preliminary mixing PS0 with DEHA was carried out on a heated two-roll mill at  $150^\circ\text{C}$  for 10 min. Blends of PA with plasticized PS0 (PSpl) or unplasticized PS0–PS4 polystyrenes with component ratios PS/PA 5/95, 10/90, 20/80, and 70/30 were prepared on a heated two-roll mill at  $190^\circ\text{C}$  for 20 min. After cooling, these blends were pelletized in a laboratory grinder.

Grinded blends were processed through a laboratory single screw extruder ARP-20-150 (screw diameter is 20 mm, rotational speed is 14 rpm, barrel temperature is  $190^\circ\text{C}$ ) equipped with the slot die 80 mm wide and  $300 \mu\text{m}$  thick. Melt films on their way to the take-up rollers were cooled by air fan.

Uniaxial drawing of extruded films was carried out in a laboratory drawing machine at deformation rate of  $1000\% \text{ min}^{-1}$  and drawing temperature of  $120^\circ\text{C}$ . The film samples with gauge section 95 mm long and 45 mm wide were stretched in the direction of extrusion. Grids were marked on the specimens for measuring the draw ratio. After drawing, the films were rapidly cooled to ambience temperature. It was shown in preliminary experiments that these drawing conditions were optimal and ensured maximum mechanical properties of the films.

The two-capillary technique<sup>19</sup> and weight capillary rheometer MV-2 were used to characterize rheological properties of polymers at  $190^\circ\text{C}$ . The values of apparent viscosity and component viscosity ratio were calculated from the flow curves at a shear rate of  $10 \text{ s}^{-1}$ .

Morphologies of films were analyzed by transmission electron microscopy (TEM) with the use of Tesla BS 513 microscope and conventional carbon replicas technique described elsewhere.<sup>20</sup>

Instron TM-1122 tensiometer was employed to measure tensile properties of blends in draw direction at room temperature and a strain rate of  $100 \text{ mm min}^{-1}$ .

Molecular orientation parameters of the PA phase were measured by birefringence and IR-dichroism techniques.

Glass transition temperatures ( $T_g$ ) of the virgin and plasticized polymers were measured on a thermomechanical analyzer UIP-70 under a periodic loading regime with the accuracy of about  $\pm 2^\circ\text{C}$ .

### RESULTS AND DISCUSSION

On the basis of swelling behavior presented in Figure 1, a selective plasticizer for the blends has been chosen. Obviously, DEHA is a thermodynamically good sol-

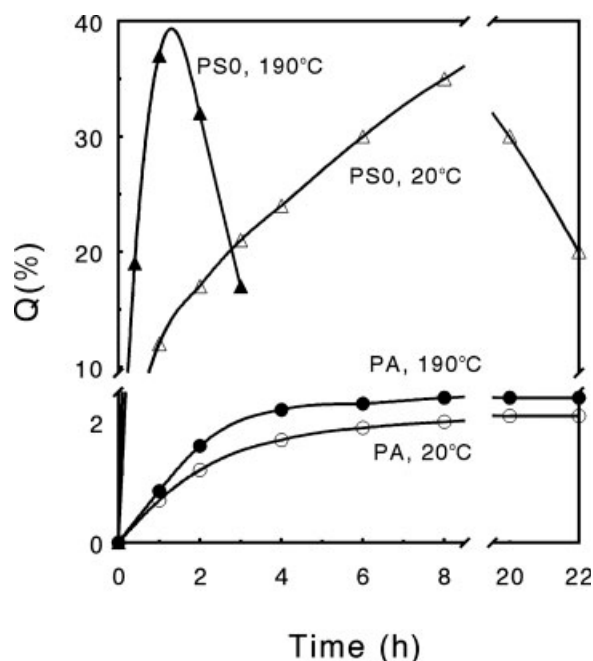
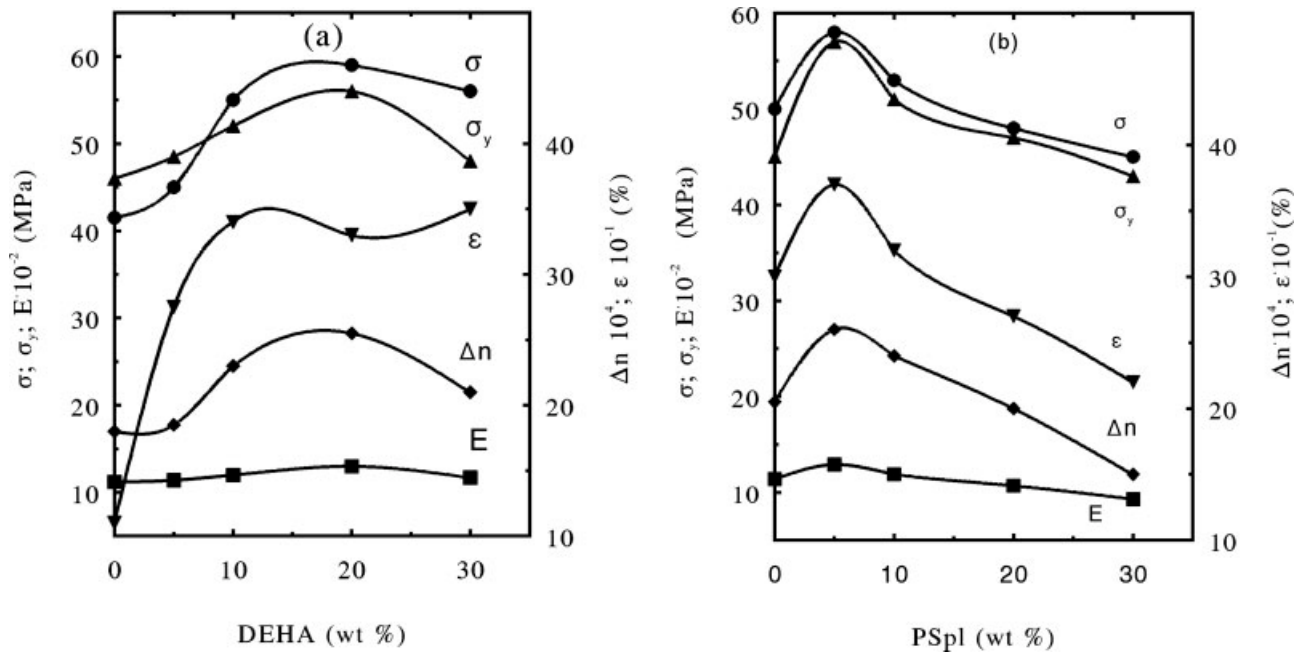


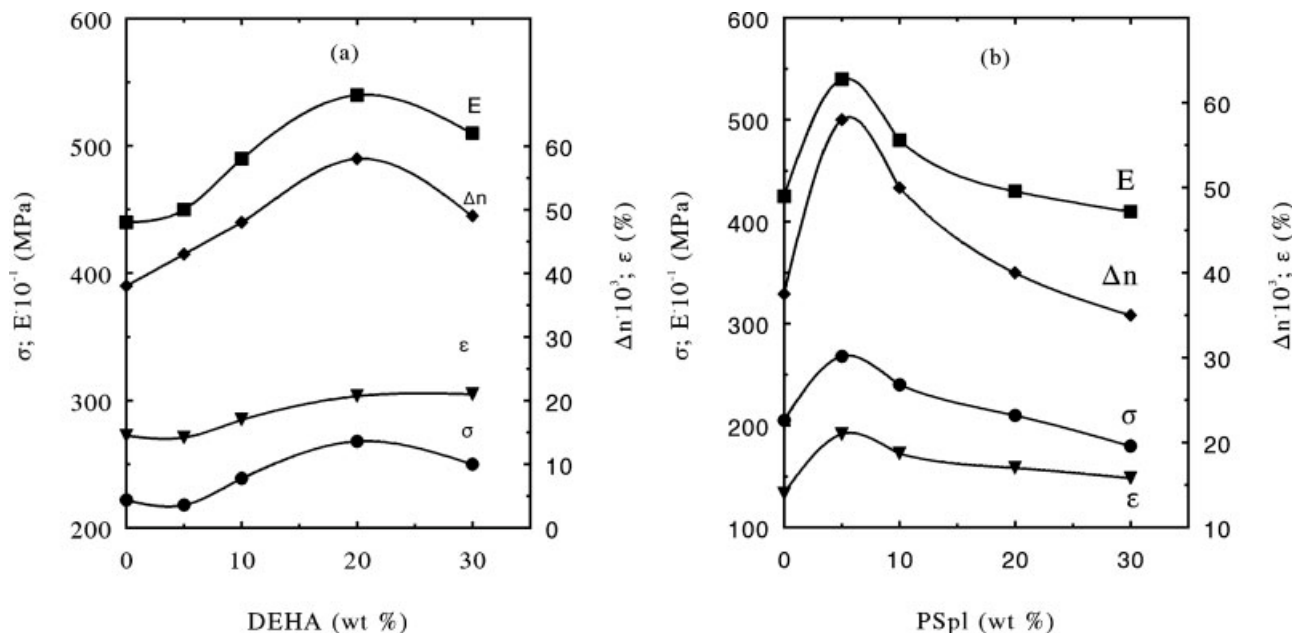
Figure 1 Kinetics of swelling of PA and PS0 in DEHA at 20 and  $190^\circ\text{C}$ .



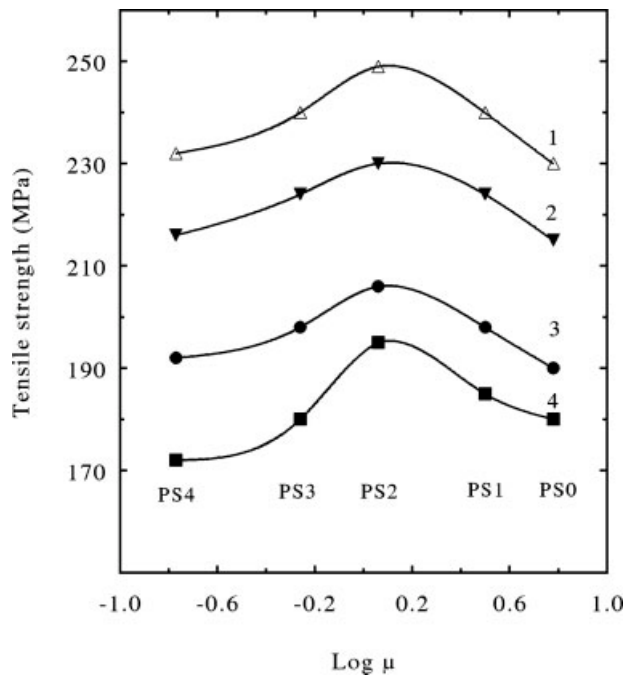
**Figure 2** Dependences of tensile strength,  $\sigma$ , yield stress,  $\sigma_y$ , elastic modulus,  $E$ , elongation at break,  $\epsilon$ , and birefringence,  $\Delta n$ , on DEHA concentration in PS0 (PSpl/PA 5/95) (a) and on the content of PSpl (20 wt % of DEHA) in blends with PA (b). Extruded films.

vent for PS0, because it dissolves this polymer even at room temperature. The curves, which are going through the maxima, indicate the loss of sample weight due to dissolution of PS0. In contrast, the equilibrium swelling of PA in DEHA at 20°C and at 190°C was only 1.7 and 2.3%, respectively. These data prove that DEHA demonstrates selective action towards the PS minor phase.

Figure 2 illustrates the influence of DEHA concentration in the PS0 phase (plasticized PS0 is abbreviated as PSpl) in blends 5/95 PSpl/PA (a) and the content of the PSpl dispersed phase (concentration of DEHA in PS0 is 20 wt %) (b) on yield stress ( $\sigma_y$ ), tensile strength ( $\sigma_b$ ), elastic modulus ( $E$ ), birefringence ( $\Delta n$ ), and elongation at break ( $\epsilon$ ) for the extruded films. It may be observed that the molecular orientation and tensile



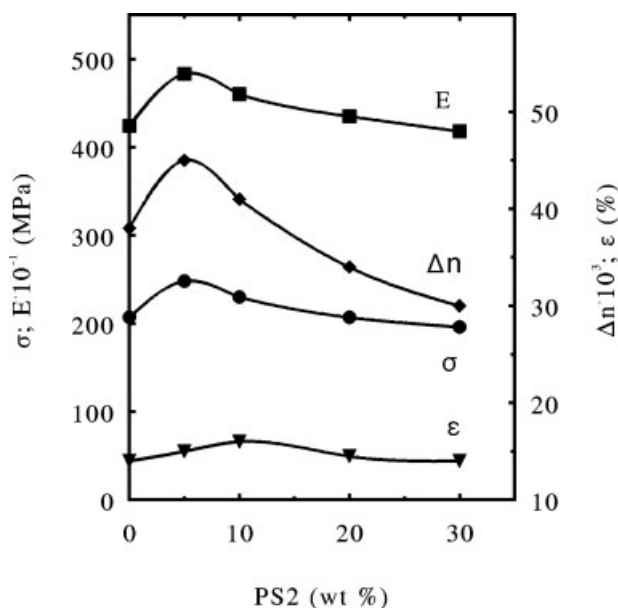
**Figure 3** Dependences of  $\sigma$ ,  $E$ ,  $\Delta n$ , and  $\epsilon$  on DEHA concentration in PS0 (PSpl/PA 5/95) (a) and on PSpl (20 wt % of DEHA) content in its blends with PA (b). Uniaxially drawn films;  $K = 4$ .



**Figure 4** Tensile strength versus phase viscosity ratio for unplasticized films with the composition ratios (PS/PA): 5/95 (curve 1), 10/90 (2), 20/80 (3) and 30/70 (4). Polystyrene samples PS0–PS4 (shown under the curves) were used to prepare blends with corresponding  $\mu$  values. Uniaxially drawn films;  $K = 4$ .

properties reach slight maxima at 20 wt % of DEHA in PS0 and at 5 wt % of PSpl in blends with PA.

The reinforcement effect grows noticeably when the blends are subjected to drawing. Figure 3 shows that, at draw ratio  $K = 4$ , the tensile strength and elastic

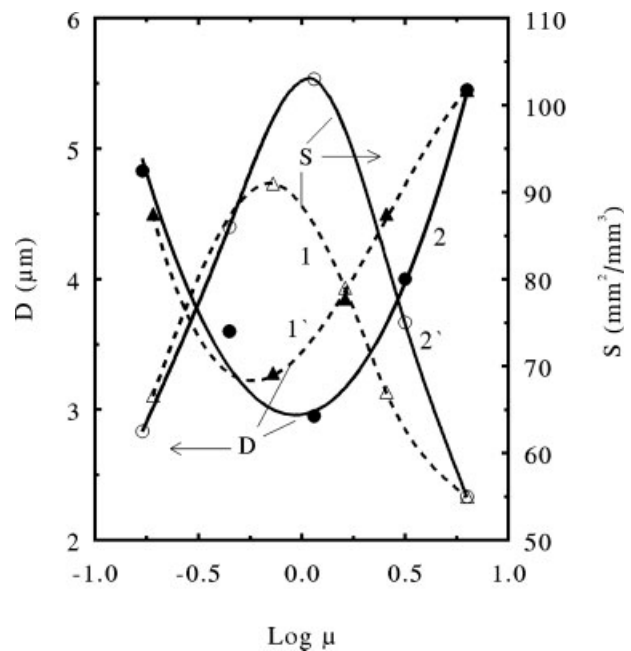


**Figure 5** Dependences of  $\sigma$ ,  $E$ ,  $\Delta n$ , and  $\varepsilon$  of unplasticized PS2/PA blends on PS2 content. Uniaxially drawn films;  $K = 4$ .

modulus of blends with the optimal compositions increase from 59 and 1300 MPa to 268 and 5400 MPa, respectively. Moreover, the presence of the PSpl domains enlarges the drawability of the films from  $K = 4$  for the virgin PA to  $K = 5$ –6 for the blends.

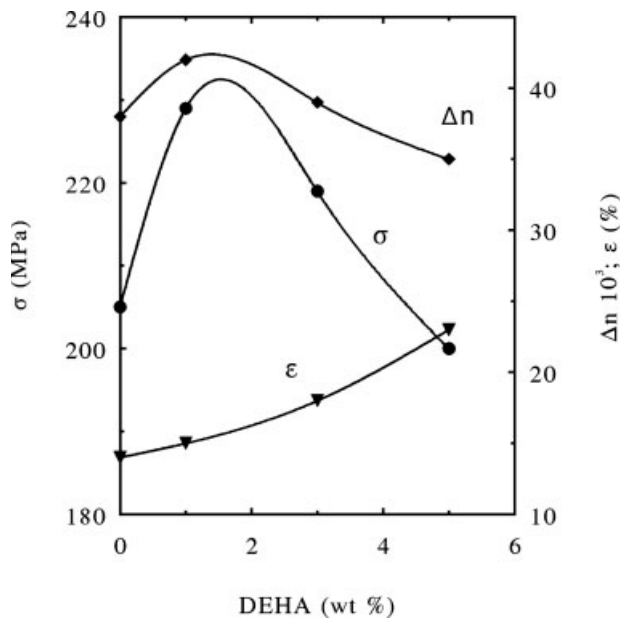
The role of DEHA in plasticized polystyrene can be understood from the data in Table I. It is clear that the increase of DEHA content decreases  $T_g$  and makes PS0 less viscous, so that at 20 wt % of DEHA the viscosity of the PSpl phase becomes close to that of PA ( $\mu = 0.70$ ). This value of phase viscosity ratio, as it was shown elsewhere,<sup>12</sup> favors the formation of fine dispersion of the PSpl domains in the matrix of PA upon melt blending. This morphology is further optimized by the proper blend composition PSpl/PA 5/95 [Fig. 3(b)], at which the smallest particles of the PSpl dispersed phase are formed. Thus, the results presented seem to indicate the dependence of the reinforcement effect upon the scale of dispersion of the blends.

It was interesting to clarify the role of DEHA in the reinforcement phenomenon. With this in mind, the second series of oriented blends was prepared under similar conditions in which phase viscosity ratio was varied by changing the viscosity of the PS phase in absence of a plasticizer (Table I). The dependences of  $\sigma$ ,  $E$ , and  $\Delta n$  on phase viscosity ratio go through the maxima at  $\mu = 1.15$  when PS2 is used as the dispersed phase. As an example, Figure 4 illustrates the influence of phase viscosity ratio, which is varied by using polystyrene grades PS0–PS4, on the tensile strength of



**Figure 6** Average diameter ( $D$ ) of PS domains (solid lines) and specific interface area ( $S$ ) (dashed lines) versus phase viscosity ratio ( $\mu$ ) of blends. The value of  $\mu$  was varied by changing DEHA content in PS0 (curves 1, 1') or by variation of viscosity of the PS samples (curves 2, 2'). Extruded films.





**Figure 7** Influence of the content of DEHA on the tensile strength,  $\sigma_b$ , elongation at break,  $\epsilon$ , and birefringence,  $\Delta n$ , of the drawn PA films;  $K = 4$ .

drawn blend films. These data proves that the properties of stretched films are optimized provided PS2 with the melt viscosity close to that of the PA matrix is used. Figure 5 shows that similarly to previous case concerning plasticized systems the measured properties reach maximum values at composition ratio PS2/PA 5/95.

Analysis of Figures 2–5 leads to the following conclusions. The properties of both plasticized and unplasticized blends are optimized at composition ratio PS/PA 5/95 and at phase viscosity ratio  $\mu \sim 1$  when maximum scale of dispersion of the blends is achieved.

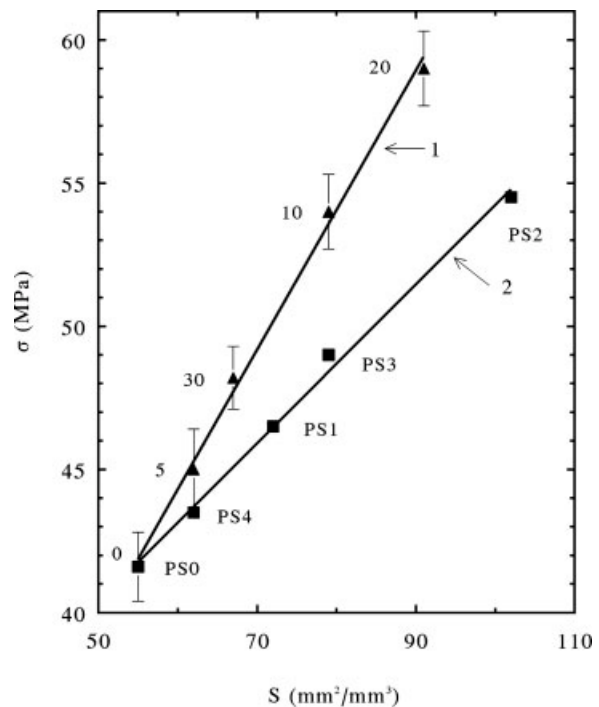
Figure 6, representing the dependence of the average domain diameter of the PS minor phase (solid lines) and the specific interface area,  $S$  (dashed lines) for both types of extruded blends on phase viscosity ratio,  $\mu$ , proves this conclusion. Curves 1 and 2 describe the blends obtained with plasticized and unplasticized polystyrenes, respectively. Regardless of the manner of changing  $\mu$ , the domain sizes of PS go through the minima and  $S$  goes through the maxima when the viscosities of the phases are properly matched. These data strongly support the idea that the total interfacial area of blends plays an important role in the reinforcement phenomena discussed herein.

On the other hand, the level of properties of drawn films attained with unplasticized PS of different viscosities is lower compared with that of the plasticized ones. Therefore, one can assume that DEHA not only helps to match the viscosities of the phases but also affects properties of the matrix as well. To verify this assumption, a series of blends of virgin PA with varying contents of

DEHA were prepared and studied under conditions similar to those in previous experiments.

It was shown that the large amounts of DEHA in PA generally produce negative effects on tensile properties of extruded films. In contrast, as Figure 7 illustrates, small amounts of DEHA (about 2.0 wt %) result in some reinforcement of PA from 205 to 230 MPa in drawn films. This is assumed to be a well known effect of reinforcement action triggered by small portions of plasticizer of poor thermodynamic quality, which (at optimum doses) favor the processes of orientation and crystallization of polymers.<sup>12</sup>

The data presented earlier can be summarized in the following way. Generally, incompatible glassy domains in a crystalline matrix act like mechanical defects reducing mechanical properties of the blends. The reinforcement appears only in the drawn films (note that the extruded films are slightly oriented) provided a small content of the inner phase and its smallest domain sizes are in place. The second requirement is met when the viscosities of phases are matched properly upon blending. The best properties of the films are achieved when a selective plasticizer for the dispersed phase is used to equalize the viscosities of polymers. In this case, the plasticizer itself additionally reinforces the matrix upon drawing.



**Figure 8** Tensile strength versus specific interface area for extruded 5/95 PS/PA blends containing PS0 loaded with different amounts of DEHA (curve 1) or unplasticized PS samples of different molecular weight (curve 2). Concentration of DEHA (in wt %) and PS samples are shown next to corresponding experimental points.

**TABLE II**  
Orientation Parameters for the PSpl/PA Blends/Virgin PA  
at Different Draw Ratios

| $K$ | $R$         | $\Phi$    | $F_y$     |
|-----|-------------|-----------|-----------|
| 1   | 2.02/1.56   | 45.8/49.0 | 0.25/0.14 |
| 2   | 4.17/3.46   | 34.4/36.9 | 0.52/0.46 |
| 3   | 8.99/7.49   | 24.8/28.6 | 0.73/0.68 |
| 4   | 16.48/11.79 | 18.7/21.9 | 0.85/0.79 |
| 5   | 22.82/-     | 15.47/-   | 0.907/-   |

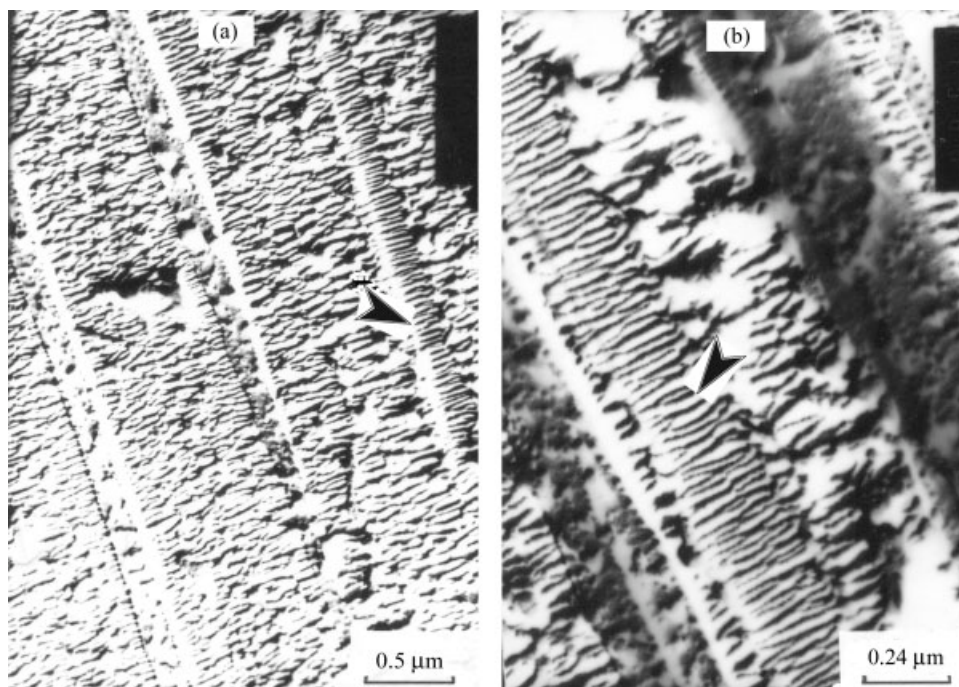
Dichroic ratio ( $R$ ); average segment orientation angle ( $\Phi$ ), and Hermans function ( $F_y$ ).

Still it seems that the major role in the reinforcement of the drawn films belongs to the interfacial area. One can speculate that in the oriented films the PS domains continue to act like defects, but the positive effect of the reinforcement of the matrix overrides this negative contribution and leads to overall positive response. Figure 8 shows a practically linear growth of the tensile strength of the blends upon increasing specific interface area. These data are obtained for the extruded films with low level of molecular orientation of the PA matrix. Unfortunately, very long fiber-like PS domains in drawn blend films fall outside the microscopic images making impossible the accurate measurement of their volumetric sizes.

Figures 2–4 show that the birefringence,  $\Delta n$ , varies symbotically with mechanical responses. It means that

the maximum level of mechanical properties is owed to the highest degree of molecular orientation of the matrix. To get more information about this matter, a method of IR-dichroism had been employed. Thin ( $\sim 80 \mu\text{m}$ ) films of virgin PA and different blends containing plasticized PS were analyzed on the computerized IR-spectrometer UR-20 at wavenumbers 425 and  $537 \text{ cm}^{-1}$ . The data listed in Table II illustrate the growth of the dichroic ratio ( $R$ ), average segment orientation angle ( $\Phi$ ), and Hermans function ( $F_y$ ) with the draw ratio ( $K$ ) of the films and prove the results obtained with the birefringence technique. It should be emphasized here that the level of orientation of the PA matrix in the blends is 10–20% higher than that in virgin PA at the same draw ratios. It may be due to the presence of dissimilar PS particles increasing the local degree of orientation of the matrix. The results obtained support the orientational origin of reinforcement effect, which develops in the crystalline matrix. But the key point of the subject is that this effect is enhanced substantially when highly developed interface is formed.

To further clarify the role of the interface in the reinforcement mechanism, TEM studies of drawn films have been undertaken using the carbon replicas technique. Owing to weak adhesion between phases in studied blends, the drawn films were delaminated along the draw direction and exposed to vapor carbon deposition.



**Figure 9** Transmission electron micrographs of carbon replicas made from fracture surfaces of 5/95 PSpl/PA drawn films,  $K = 4$ . DEHA concentration in PS0 is 5 wt %. (a) General picture illustrating the morphology of a blend with thread-like PSpl domains embedded into a crystalline matrix of PA. One of the threads is absent baring the interface (pointed by arrow); (b) a closer view of the previous image showing the PSpl/PA interface (pointed by arrow). Notice the difference between crystalline textures on the interface and in the bulk PA.

The carbon replicas obtained from both fracture surfaces were contrasted by aslant deposition of Al and analyzed by TEM at magnifications of up to 100,000. The micrographs shown in Figure 9 illustrate two-phase morphology of films represented by structureless amorphous highly elongated thread-like domains of plasticized PS embedded into the crystalline matrix of PA.

The principal feature of the employed technique of sample preparation is that because of weak interfacial adhesion some part of the PSpl threads are eliminated from their places upon film splitting leaving naked interfaces (indicated by arrows). The bulk matrix material is represented by the lamellae oriented normally to the draw direction. It can be seen that interlamellar distances on the interface are much smaller than those in the bulky PA. In other words, in contrast to the bulk portions of PA, the crystalline structure on the interface looks annealed and better organized.

It can be assumed from these data that chain segments of PA on the interface are more mobile when compared with those in the bulk material. They form a more ordered and strong crystalline morphology, which, keeping in mind a large interfacial area, makes a substantial contribution to mechanical response of the blends. This effect grows significantly upon drawing because both molecular orientation and interfacial area are progressively increased with draw ratio.

Because the reinforcement effect pertains to both selectively plasticized and unplasticized PS/PA blends, it is clear that the plasticizer itself does not produce this effect, but enhances it according to the mechanism mentioned earlier. Considering very weak interfacial adhesion in studied blends, it can be assumed that the formation of highly developed interface and proper orientation are the main conditions, which can produce similar reinforcement phenomena in other crystalline matrices irrespectively of chemical nature of the dispersed phase.

## CONCLUSIONS

The mechanism of reinforcement of crystalline matrix of PA-12 by dispersions of glassy particles of PS in drawn films has been proposed and discussed. The highest reinforcement effect is observed in drawn films provided composition ratio and phase viscosities

(i.e.,  $\mu \sim 0.7$ ) are matched properly to ensure the highest interfacial area possible. The presence of a selective plasticizer in the PS phase enhances the effect.

The main features of the mechanism proposed are as follows. Chain segments of PA at the interface seem to have higher mobility compared with those in the bulk matrix, especially in the presence of a selective plasticizer in the alternative phase. This favors the formation of a more ordered and strong crystalline regions in PA at the interfaces. The effect is enhanced noticeably by drawing and increasing the interface area.

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