



## Polypropylene + Polystyrene Blends with a Compatibilizer. Part 2. Tribological and Mechanical Properties

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**Abstract:** Styrene-ethylene/butylene-styrene (SEBS) block copolymer was used as the compatibilizer for PP + PS blends. We have investigated effects of the presence of SEBS on tribological and mechanical properties; dynamic mechanical analysis (DMA) was also performed. Since the copolymer causes formation of smaller particles of the dispersed PS phase in PP matrix blends, there is improved energy transmission and dissipation resulting in higher impact strength. The SEBS additive is relatively soft and causes a decrease in stress at break but an increase in elongation at break in tensile testing. In most cases the friction of the compatibilized blends is higher although in PS-rich blends we find a decrease. Scratch testing shows a change in wear mechanisms when SEBS is added to PP/PS. In uncompatibilized blends we observe adhesive wear, with crazes formed in the middle of the wear track. A compatibilized blend shows more ductile behavior and ploughing wear.

**Keywords:** polymer blends, compatibilization, polypropylene, polystyrene, polymer tribology, polymer mechanics

### 1. Introduction

As argued in the preceding paper [1], the use of polymer-based materials (PBMs) is rapidly increasing. The industries of today are more and more replacing metal parts with PBMs because of lower density, low maintenance and inexpensive prices [2]. Mechanics of PBMs is relatively well understood [3, 4]. However, perhaps even more needed is the tribology of PBMs, including the study of their wear resistance and friction [5]. Here the situation is different; tribology has been well developed for metals [6] but not for polymers. Metals may be coated with lubricants to provide sufficient wear resistance and low friction. In contrast, polymers often interact with such lubricants; they tend to swell, worsening the tribological properties. Thus,

methods of improvement of tribological properties of PBMs other than the use of lubricants have to be developed.

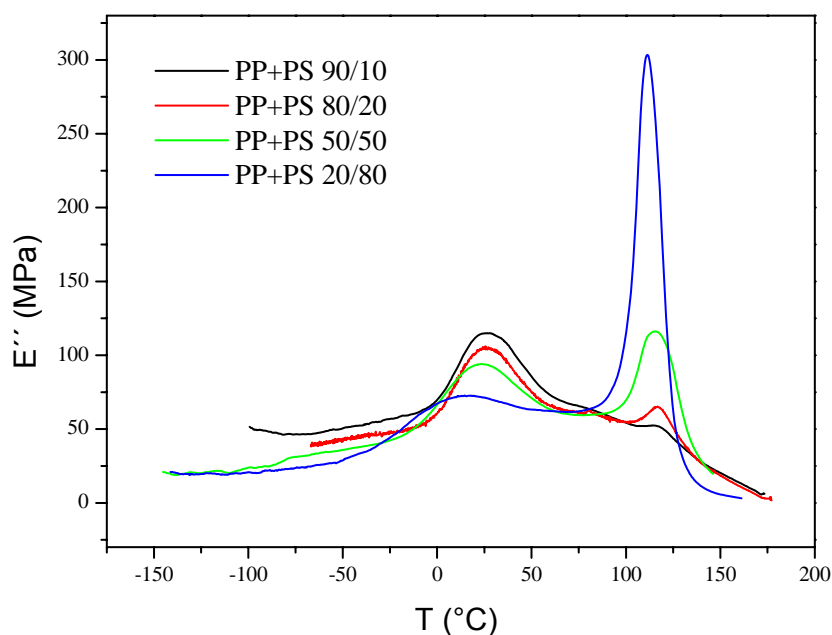
There are many kinds of PBMs available in the market with a wide range in properties and prices. Polypropylene (PP) and polystyrene (PS) as well as their blends belong to the most often used polymeric materials [7]. In particular, PP-based materials have important applications in medicine [8]. However, as already noted in [1], PP/PS blends exhibit relatively low impact strength, low wear resistance and high friction. In fact, PS is much more brittle than all other engineering polymers for which brittleness has been determined [9].

The disadvantageous characteristics of the PP/PS blends can easily be explained by poor compatibility of the components. Here lies the reason why compatibilizers are added to immiscible blends. Compatibilizers increase the miscibility of the components of the blend by reducing interfacial tension; that tension largely determines properties of multiphase systems [10 - 14]. In [1] we have demonstrated that the block copolymer styrene-ethylene/butylene-styrene block copolymer (SEBS) provides compatibility between PS and PP. In this paper we report how the compatibility affects tribological and mechanical properties.

## 2. Dynamic mechanical properties

The temperature dependence of dynamic loss modulus  $E''$  of uncompatibilized PP + PS blends is shown in Figure 1. Several techniques are in use for determination of glass transition temperatures  $T_g$  [16]. In our experience,  $T_g$  values determined by DMA are more accurate than those obtained by other techniques. We see in Figure 1 that the blends exhibit two glass transitions  $T_g$  corresponding to pure components but varying with composition. Thus, we have  $T_g$  values for a PP-rich phase and for a PS-rich phase. Numerical values are summarized in Table 1; needless to say, since we are dealing with peak maxima, tenth of a degree values reported should not be taken literally.

Effects of addition of the SEBS block copolymer on glass transition temperatures are seen in Figure 2; see also Table 1. SEBS increases the glass transition temperature of the relatively rigid PP-rich phase.

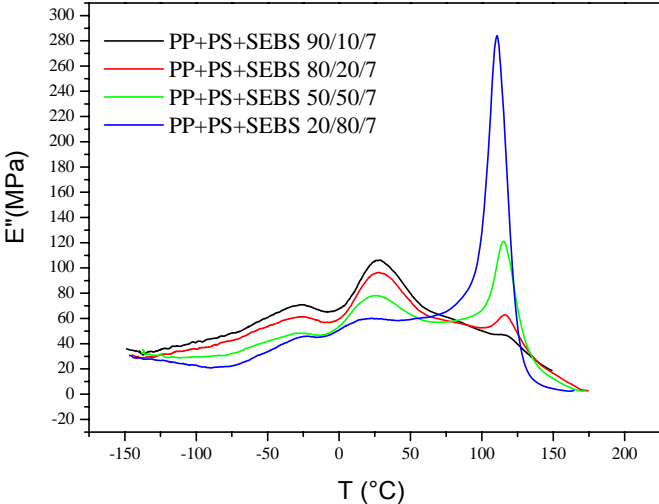


**Fig. 1.** Loss modulus  $E''$  of uncompatibilized PP + PS blends.

**Tab. 1.** Glass transition temperatures  $T_g$  and storage modulus  $E'$  of the blends.

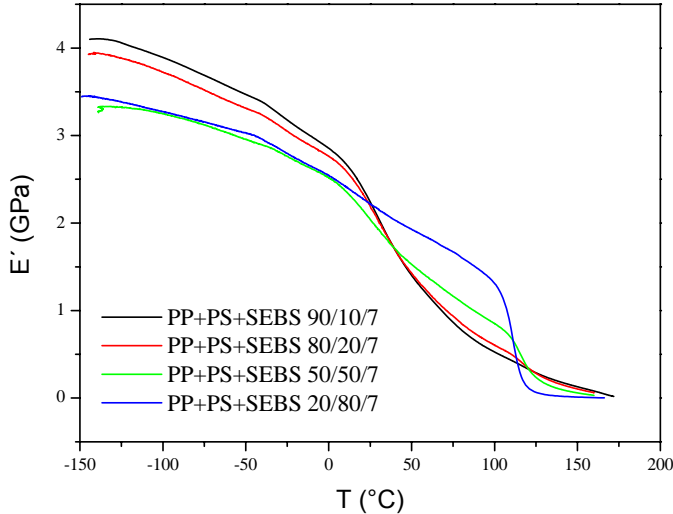
SAMPLE	$T_g$ EB °C	$T_g$ PP °C	$T_g$ PS °C	$E'$ GPa 25 °C
PP/PS 90/10	/	25.6	117.2	2.480
PP/SEBS/PS 90/5/10	- 26.3	27.6	117.7	2.467
PP/SEBS/PS 90/7/10	- 26.4	28.1	115.2	2.264
PP/PS 80/20	/	25.5	117.2	2.389
PP/SEBS/PS 80/5/20	-25.5	29.5	117.0	2.341
PP/SEBS/PS 80/7/20	-25.4	28.1	115.6	2.193
PP/PS 50/50	/	22.0	115.7	2.280
PP/SEBS/PS 50/5/50	- 25.3	27.4	117.9	2.132
PP/SEBS/PS 50/7/50	- 28.9	25.7	115.7	2.056
PP/PS 20/80	/	17.1	112.0	2.513
PP/SEBS/PS 20/5/80	- 17.1	24.7	117.1	2.100
PP/SEBS/PS 20/7/80	- 23.6	22.5	111.0	2.219

One  $T_g$  of the PS-rich phase is seen - due to good affinity of PS blocks of SEBS and the PS homopolymer.  $T_g$  of the PS-rich phase is unchanged by the addition of SEBS in the PP matrix blend. Concentration of the compatibilizer does not influence  $T_g$  of the soft ethylene/butylene (EB) phase in blends with PP matrix. This is not the case for the blends 50/50 and 20/80 where higher content of SEBS causes a reduction in  $T_g$  of the EB phase; a consequence of a faster macromolecular conformation changes of the soft phase.



**Fig. 2.** Loss modulus  $E''$  of PP + PS blends compatibilized with 7 wt. % SEBS block copolymer.

Figures 1 and 2 both show that the presence of PS lowers the loss modulus at room temperature; we shall return to this observation in Section 7.

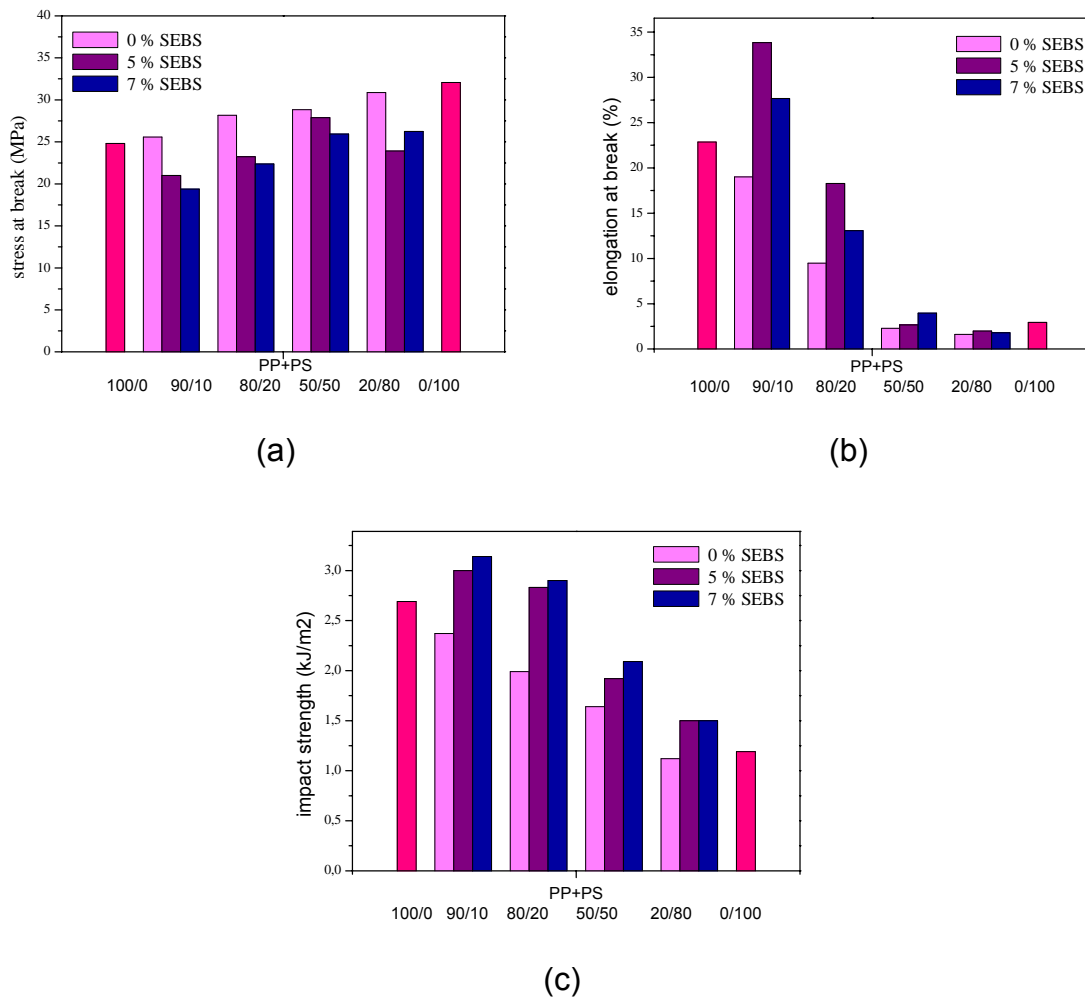


**Fig. 3.** Storage modulus  $E'$  of compatibilized PP + PS blends as a function of PS content.

In Figure 3 we look at the storage modulus  $E'$ . Similarly as differential scanning calorimetry results reported in [1], now DMA results show a compatibilizing effect of SEBS in the PP + PS blends. We infer there is strengthening of the interactions between PP and PS components - especially so in PP matrix blends. At low temperatures the more PP is present, the higher the modulus. As expected, this situation changes above the glass transition of the PP-rich phase (see again Table 1); now blends with high PP concentrations have low moduli. The situation changes again above  $T_g$  of the PS-rich phase; thus, the situation above all glass transitions is similar to that at temperatures below all glass transitions.

### 3. Mechanical Properties

Results of mechanical tests are reported in Figure 4. As expected, uncompatibilized blends show poor mechanical properties. This is a consequence of incompatibility of the components and also of the already noted brittleness of PS [9].



**Fig. 4.** Mechanical properties of selected blends; a) stress at break, b) elongation at break, c) impact strength.

Consider first results of tensile testing. Stress at break  $\sigma_b$  decreases when adding SEBS for all investigated compositions (Figure 4a). This can be explained by relative softness of elastomeric SEBS. SEBS block copolymer increases elongation at break  $\varepsilon_b$  in all investigated blends; the effect of the compatibilizer is much more pronounced in the blends with PP as the matrix (Figure 4b). Elongation at break  $\varepsilon_b$  is higher in PP matrix blends, 90/10 and 80/20, compatibilized with 5 % of SEBS block copolymer than in those with 7 % SEBS. At equal weight concentrations of PP and PS, 7% SEBS provides a higher elongation at break than 5% does. We note that, other things being equal, higher  $\varepsilon_b$  values cause lower brittleness  $B$  [9]. We have  $10^{10}B/(\% \cdot \text{Pa}) = 8.783$  for PS and in the same units only 0.056 for PP [9].

All samples tested show an improvement in impact strength with increased concentration of SEBS block copolymer (Figure 4c). Neat PP has a much higher impact strength than the PS matrix, again a consequence of much higher brittleness of PS. 7 wt. % SEBS enhances the impact strength more than 5 %. This is when we have just seen that 7 % SEBS lowers the elongation at break  $\varepsilon_b$ . These results can be explained in terms of the time scales of the experiments. Izod impact testing causes a very fast response of the 'attacked' material. More SEBS provides better transmission in the specimen of the energy coming from outside. Tensile testing is significantly slower, 50 mm/minute, and apparently 5 % SEBS provides optimum compatibility of the major PP-rich and PS-rich phases at 90 and 80 % PP.

We infer that the SEBS concentration of 5 % is sufficient to achieve good compatibilization, resulting in formation of smaller particles of the minority component seen in SEM [1]. Since SEBS is a more expensive polymer than polypropylene or polystyrene, it was important to determine if its 5 wt. % instead of 7 % would dramatically alter the results of impact testing. We find that this is not the case.

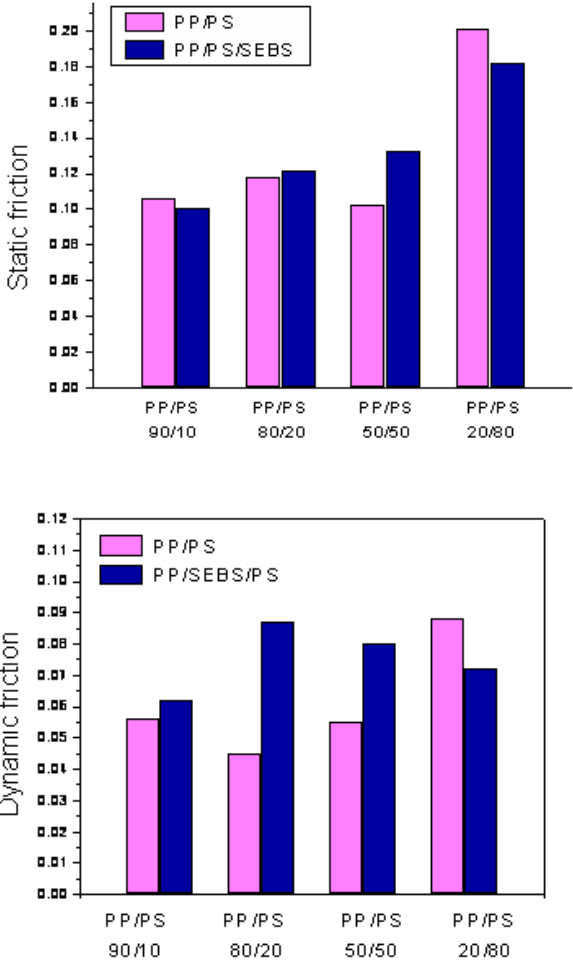
Possibly cracks that eventually lead to fracture in an impact event begin at the protruding points on the surface. We have an idea from molecular dynamics simulations how cracks propagate in polymers in tension [21, 22]; the crack propagation in impact might be similar. The finer morphology of the compatibilized blends results in a more even surface, which lends the material a larger surface area at which the initial stress is applied. Effectively, this reduces the maximum force applied to any one point on the exterior of the system and increases the total amount of energy from outside that it can withstand.

The compatibilizer increases impact strength internally as well. In an immiscible blend, the component that forms the matrix takes on the majority of the force of the impact. The high degree of phase separation does not allow the energy to travel easily between the components within the system. The presence of the compatibilizer on the interface allows a better stress transfer across the phase boundary, allowing better dispersion of the impact energy - in the bulk as well as on the surface. When both compatibilized and non-compatibilized received the same amount of energy in an impact event, the compatibilized ones were able to diffuse more efficiently that energy throughout its entirety.

#### 4. Friction

The thermoplastic SEBS is an elastomer with characteristically high friction. Thus, it may be expected that its addition to any polymeric system would increase the friction. We see in Figure 5 that effects of the presence of 5 % SEBS on static friction of PP-

rich materials (90 or 80 % PP) are small. At 50 % of each major component there is a clear increase of the friction caused by the presence of SEBS. However, the material with 20 % PP has a very high friction to begin with; the presence of SEBS lowers the friction.



**Fig. 5.** Static and dynamic friction of selected blends.

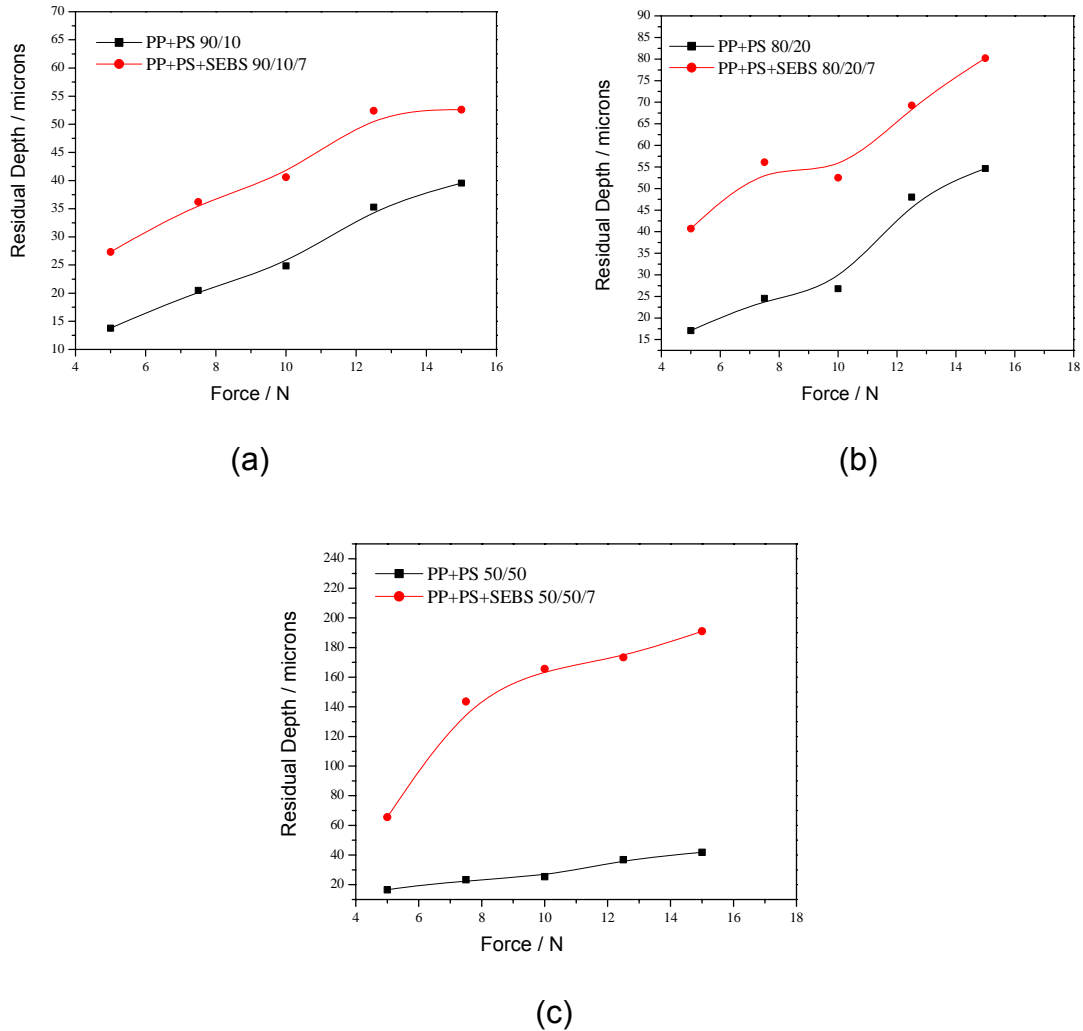
As for dynamic friction, the presence of SEBS increases it – with the sample containing 20 % PP again as an exception. Thus, only at high PS concentrations the presence of SEBS has a beneficial effect.

**5. Scratch resistance**

The importance of scratch resistance has been argued before [9, 17 - 20]. Since SEBS is a relatively soft material, it is expected that its addition to PP + PS blends will increase the scratch depth; this is confirmed by single scratch results, see Figures 6a) - 6c). Penetration depth as well as residual depth increase with SEBS addition and with the applied load to the sample in all investigated blend compositions. Since the final result of scratch testing is the residual depth, we do not include penetration depths for brevity.

Residual depth is higher in blends with higher content of polystyrene due to lower recovery of polystyrene and its lower degree of viscoelasticity. See again the loss

modulus  $E''$  values for the room temperature in Figure 1; the material with the highest PS concentration of 80 % has the lowest  $E''$  value. Thus, while the time scale of scratch testing (5 mm/minute) is much larger than in the DMA (1 Hz). PS does not relax significantly since it is inherently incapable to do so. We recall the brittleness values for PP and PS [9] quoted above.



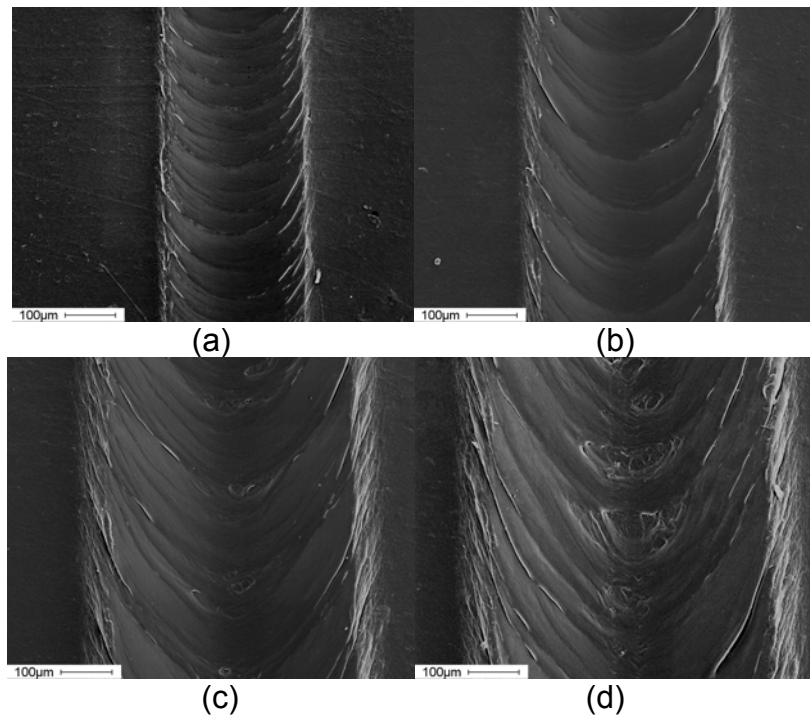
**Fig. 6.** The residual depths of uncompatibilized and compatibilized PP + PS blends: a soft SEBS component effect.

For 10 % PS blend we recall the result reported in [1]: SEBS affects the PS particles in the PP-rich phase, namely those particles become smaller. The finer morphology of the compatibilized blend results in a material with higher scratch resistance in comparison to the other compatibilized blends; compare Figure 6a with Figures 6b and 6c.

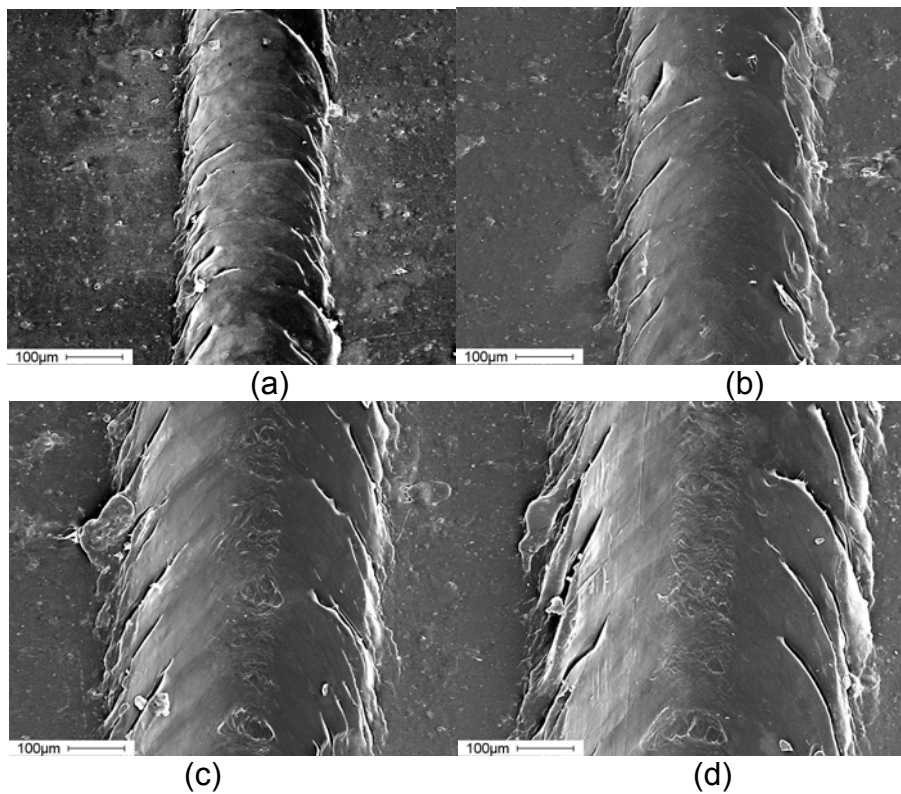
SEM images in Figures 7 and 8 show respectively the damage surfaces of uncompatibilized and compatibilized PP + PS 90/10 blend as a function of applied load after a single scratch experiment. We see an increase in plastic deformation and wider wear tracks for higher applied loads. In the case of uncompatibilized blends, adhesive wear mechanism is observed, with crazes formed in the middle of the wear



track. As discussed by Donald [23], craze formation is a defensive mechanism of the material. Compatibilized 90/10 blend shows more ductile behavior and ploughing wear mechanisms.



**Fig. 7.** SEM images for uncompatibilized PP + PS blend 90/10 after single scratch testing. Results for a) 5.0 N, b) 10.0 N, c) 15.0 N, d) 20.0 N.



**Fig. 8.** SEM images for PP + PS blend 90/10 compatibilized with 7 wt. % SEBS after single scratch experiments; a) 5.0 N, b) 10.0 N, c) 15.0 N, d) 20.0 N.

## 6. General discussion

PP + PS blends with and without block copolymer SEBS as compatibilizer have been prepared and studied. SEM imaging shows that there is a compatibilization action of SEBS on PP + PS blends by improving the interaction between the two polymers. This results in a finer structure with smaller particles of the minor component. The glass transition temperatures of the PP-rich phase and the PS-rich phase in uncompatibilized blends change when SEBS is added. This change is provoked by a modification of molecular interactions induced by SEBS at the interphase between PS and PP. Impact strength and elongation at break are two mechanical properties that increase in the blends when SEBS is added. On the other hand, the stress at break is lowered by the compatibilizer.

The addition of SEBS to PP + PS blends generally increases the friction values because of the rubbery nature of the compatibilizer. However, in the case of PS matrix blends, the addition of SEBS decreases the friction of the blends. This change is attributed to lowering the brittleness of PS. The compatibilized blends present higher penetration and residual depths in the scratch tests caused by the soft rubbery nature of the compatibilizer. The wear mechanisms also are changed; mainly plastic deformation and adhesive wear for uncompatibilized blends while plastic deformation and ploughing are the main mechanisms in the compatibilized blends.

## 7. Experimental

### *Materials and processing*

The materials used were the same as in the preceding paper [1]. The processing procedure was also the same.

### *Dynamic-mechanical analysis*

Dynamic-mechanical analysis (DMA) was performed to obtain primary viscoelastic functions: storage modulus  $E'$ , loss modulus  $E''$ , and loss tangent  $\tan \delta = E''/E'$ . The experiments were performed at the fixed frequency of 1.0 Hz, over the temperature range from -100 °C to 150 °C, at the heating rate of 5 K/minute. DMA and the significance of the information it provides has been described in some detail by Menard [15, 16].

### *Mechanical Testing*

Tensile measurements were determined using an Instron machine Model 1185 at room temperature and the crosshead speed of 50 mm/min, according to ISO 527-1 and ISO 527-2 standards.

The Izod test is one of the popular impact testing methods. The device consists of a loading device that holds the bottom half of the sample and a pendulum hammer that is released from a set height. The pendulum hammer then breaks the sample and swings up to a second lower height, which is measured. The height difference corresponds to the energy necessary to break the sample and provides us with the Izod impact strength. A Franck – ISO 180 impact tester was used.

### Scanning electron microscope

SEM experiments were performed as described in the preceding paper [1].

### Scratch resistance

Scratch resistance was determined using a CSEM micro scratch tester from Neuchatel, Switzerland, at room temperature (23 °C). When the diamond indenter scratched the surface, we obtained the initial or penetration depth  $R_p$ ; 5 minutes later we measured the residual or healing depth  $R_h$  [17]. The machine provided also the capability of multiple scratches along the same groove for sliding wear determination [18 – 20, 9]. The scratches were made at the speed of 5 mm/minute for 1 minute at the constant forces of 5.0, 7.5, 10.0, 12.5, 15.0, 17.5 and 20.0 Newtons. After single scratching some samples were analyzed by SEM to examine the wear mechanisms.

### Friction

An MTS QTest 5 machine in the friction test mode was used to obtain static and dynamic friction values. The machine has a 4.5 kg load cell and a 700 gram sled. The tests were run at the test speed of 150 mm/minute on a polytetrafluoroethylene (Teflon) surface. The machine measures the resistance to initial and continuous movement across the surface and then quantifies these, respectively, as the static and dynamic friction on that surface.

### Morphology

A detailed study of the PS + PP blends morphology has been reported in our previous paper [1]. We recall that the presence of SEBS reduces sizes of dispersed PS particles in PP-rich blends. In Section 7 we consider SEMicrographs of surfaces after passage of an indenter in scratch testing.

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