IMPACT BEHAVIOR OF POLYPROPYLENE/STYRENE-BUTADIENE-STYRENE BLOCK COPOLYMER BLENDS

Hernández, M.[1]*, Ichazo, M.N.[1], González, J.[1], Albano, C.[2], Santana, O.[3]

[1]Universidad Simón Bolívar, Departamento de Mecánica, Grupo de Polímeros II
[2]Universidad Central de Venezuela, Facultad de Ingeniería, Caracas, Venezuela.
[3]Centre Catalá del Plástic, Terrassa, Spain.

*corresponding author: marherna@usb.ve

Received: October 26th, 2007. Accepted: March 10th, 2008

ABSTRACT

The objective of this work was to study the impact properties of Polypropylene /Styrene-Butadiene-Styrene Block Copolymer (PP/SBS) Blends. Concentrations of SBS were 15, 30 and 40 %wt. Special reference was made to the influence of the blend ratio and the vulcanization method (dynamic and static). Impact measurements exhibited that pure PP has extremely low impact strength. Improved impact strength can be achieved by blending PP with SBS via dynamic vulcanization. However, static vulcanization proved to be not as efficient as dynamic vulcanization for improving impact resistance. SEM analysis corroborates these results.

Keywords: impact behavior, polypropylene, elastomer, dynamic vulcanization, static vulcanization

RESUMEN

El objetivo de este trabajo fue estudiar las propiedades de impacto de mezclas de Polipropileno/Estireno-Butadieno-Estireno (PP/SBS). Las concentraciones empleadas de SBS fueron 15, 30 y 40% en peso. Se hizo énfasis en la influencia de la relación de mezcla así como del método de vulcanización (dinámica y estática). Los resultados obtenidos indican que el PP puro posee una extremadamente baja resistencia al impacto. Se puede mejorar dicha resistencia al mezclar PP con SBS vía vulcanización dinámica. Sin embargo, la vulcanización estática de la mezcla es ineficiente para mejorar tal propiedad. Los análisis via SEM corroboran estos resultados.

INTRODUCTION

Polypropylene (PP) is a versatile commodity plastic with one of the largest global consumption per annum because of its low cost and other attractive properties. However, its application as a structural material is somewhat limited because of its relatively moderate fracture performance, especially at sub ambient temperatures. Nonetheless, the impact toughness of PP can be improved by the addition of elastomers such as ethylene-propylene rubber (EPR), ethylene-propylene diene monomer, and styrene-butadiene-styrene (SBS) block copolymer. This toughness upgrade is achieved at the cost of stiffness and strength characteristics, since the incorporation of elastomers into PP leads to a reduction in the modulus and yield stress. Therefore, issues concerned with the simultaneous reinforcing and toughening of PP have attracted considerable attention. One way is to vulcanize the rubbery phase. This vulcanization can be either dynamic or static [1-4]. Dynamically vulcanized blends consist typically of a finely dispersed chemically crosslinked elastomer phase in a melt processable thermoplastic matrix. Improvements in properties from dynamic vulcanization include higher tensile strength, better elastic recovery, improved properties retention at high temperatures, greater resistance to attack and swell by fluids, greater stability of morphology and more consistent processability. While in statically vulcanized blends, the rubbery phase is previously cured by means of pressure and temperature and then grounded and mixed with the thermoplastic matrix. Other interest of the statically cured blends is the possibility of reusing scrap rubber when blending it with a virgin thermoplastic material.

In this paper, effort has been undertaken to study in detail the impact behavior of thermoplastic/elastomer (PP/SBS) blends by varying the blend ratio and the vulcanization method (static or dynamic).

MATERIALS AND METHODS

Isotactic Polypropylene (PP) J-300 having a melt-flow index (MFI) of 7 dg/min (230 °C/2160 g) was supplied by Propilven S.A. Styrene-Butadiene-Styrene copolymer (SBS) SOLPRENE with a density of 0.94 g/cm3 , a melt flow index of 6.4 dg/min (200 °C/5000 g) and a styrene content of 30 % was supplied by INSA.

PP/SBS blends dynamically and statically vulcanized were prepared with concentrations of SBS of 15, 30 and 40 %wt. For the dynamically cured blends (DV), compounding was performed using a Berstorff ECS 2E25 co-rotating twin-screw extruder at a temperature profile of 210 °C and a screw speed of 50 rpm. While for the statically cured blends (SV), vulcanization of the rubbery phase took place in a Carver Hydraulic press at 200 ºC. Vulcanized rubber sheets were then cut and granulated with the intention of obtaining an appropriate particle size in order to be fed into the extruder when preparing the blend with PP. Pure PP was also subjected to the same extrusion process in order to get the same thermal and mechanical histories of all blends.

A Fractovise drop-weight system was used to conduct instrumented impact tests at 0 ºC. The mass of the tup was 8.920 kg. The tests were conducted at an impact velocity range of 2-15 m s-1. The sensor attached to the tup measured the force generated within the impact specimens during the test, and the signal was fed into a computerized data acquisition system. The load-time curves were recorded. To investigate the morphological aspects associated with the fracture process, the fracture surfaces were examined by scanning electron microscopy (SEM), using a Hitachi S2400 system, after coating the samples with a thin platinum/palladium layer.

RESULTS AND DISCUSSION

Fig. 1 shows typical impact force vs. time curves for dynamically and statically vulcanized compounds.

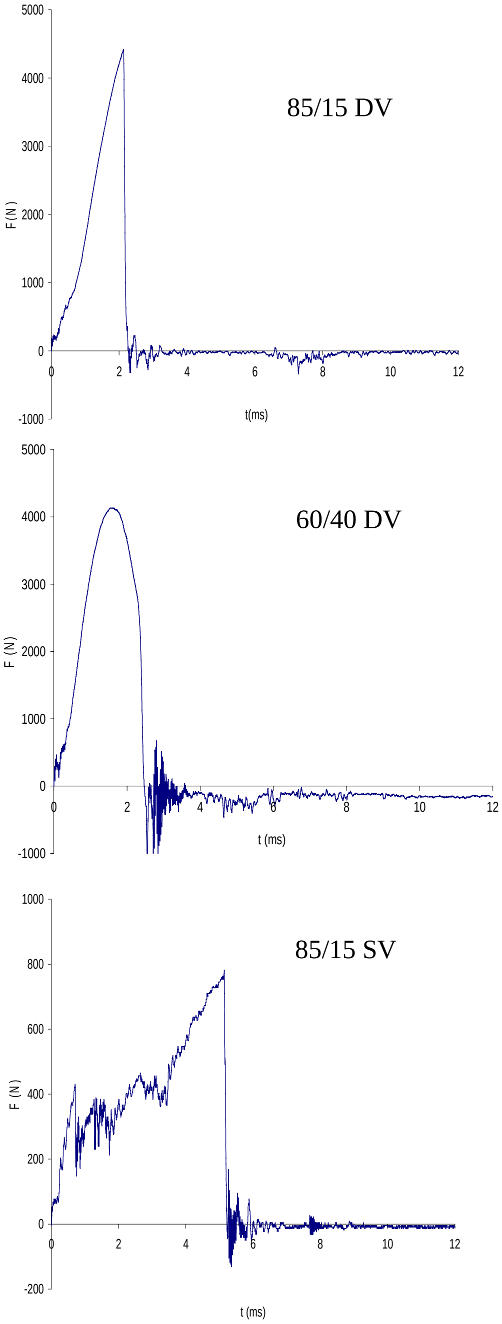

Fig. 1. Impact force vs. time curves for PP/SBS blends: (a) 85/15 DV; (b) 60/40 DV; (c) 85/15 SV.

The maximum point in the curves is a transition from the crack-initiation stage to the crack-propagation stage. The load decreased steeply from the maximum force for the

85/15 DV compound. This implies that the specimen consumed very little energy during the crack-propagation process. This transition is less pronounced in compound 60/40 DV where the rubber content increases up to 40% [5]. In contrast, when the blend is statically vulcanized, the shape of the curve is less smooth compound 85/15 SV, although there is also a sharp peak. The energy absorbed on impact is the sum of the energy to fracture the glassy matrix and the work to break the rubber particles.

The drop-weight-impact energy of PP and PP/SBS blends was also measured, as observed in Table I. Pure PP exhibited extremely low impact strength, as expected.

Table I. Impact strength of PP and PP/SBS dynamically (DV) and statically (SV) vulcanized blends.

BLEND	**ENERGY (J)**
Pure PP	0.74 ± 0.01
PP/SBS 85/15 DV	5.56 ± 0.16
PP/SBS 70/30 DV	8.20 ± 0.03
PP/SBS 60/40 DV	11.22 ± 0.09
PP/SBS 85/15 SV	1.90 ± 0.01
PP/SBS 70/30 SV	1.93 ± 0.02

The impact resistance of PP was increased by the addition of SBS, irrespectively of the vulcanization method. It is also apparent that the energy tended to increase with increasing rubber content. The presence of soft and flexible particles allows the absorption of more energy during fracture, so the material impact strength rises. Nonetheless, when the compound was dynamically vulcanized, the increase in impact energy was more significant, because of the toughening effect of elastomers [5].

For PP toughened with elastomers massive crazing and shear banding are known to be the main fracture mechanisms. It is generally accepted that the mechanical properties of thermoplastic/elastomer blends depend on the morphology and interfacial adhesion between the matrix and elastomer. An optimum particle size and good interfacial bonding are required for effective toughening. Interfacial adhesion is associated with an energy absorbing mechanism in addition to the increasing strength of the composites. This interface may undergo debonding cavitation to relieve the triaxial stress imposed by the plane strain constraint at the crack tip. The relaxation of the interface can prevent the matrix from premature brittle fracture during impact loading [6].

Similar results were obtained by Saroop et al for PP/SBS dynamically cured blends. They found that the impact strength increased gradually with increasing SBS content until 30 wt%, attributing this behavior to a higher interfacial adhesion explained on the basis of a smaller size of the dispersed rubber particles [7].

For the statically cured systems, the increase in impact energy is less notorious, probably owed to the tendency the elastomeric material has to form agglomerates of big size when vulcanized by this method, which induces the formation of catastrophic cracks [2]. Poor adhesion between phases could also be one of the causes why impact strength is low for the statically vulcanized blends.

It should be highlighted that increasing rubber content from 15% to 30% in DV blends, originates a rise in impact energy of 47%, while the same increase in SV blends does not produce changes in impact energy. In DV blends, more rubber content implies more energy absorption by the rubber particles during fracture; while in SV blends, even though there are more rubber particles, there are no rubber-matrix interactions. This fact can be corroborated when comparing Figs. 2 and 4 and 3 and 5, respectively.

SEM examination of the fracture surfaces of impact specimens provides valuable information on the deformation mechanisms.

Direct inspection of the impact fracture surface of PP/SBS blends is shown in Figs. 2 to 5.

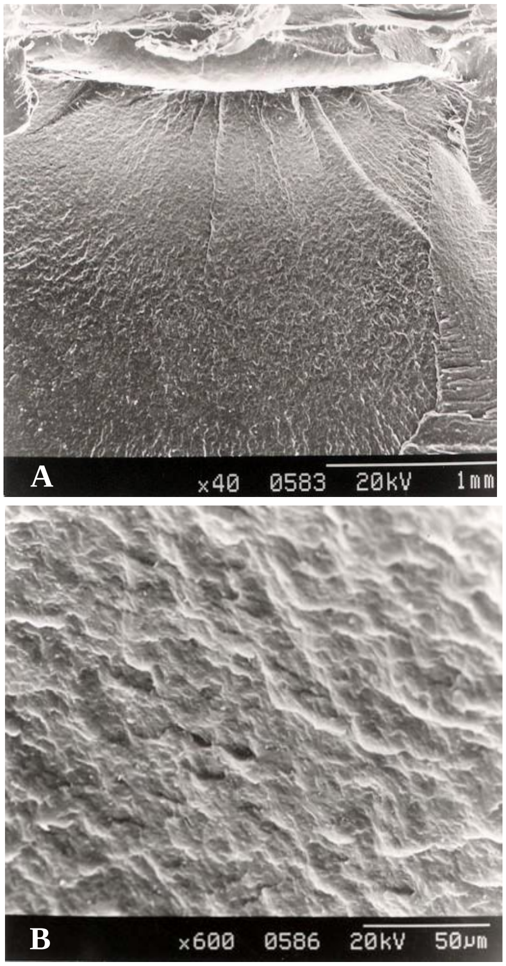

Fig. 2. SEM micrographs taken from the impact fracture surface of PP/SBS 85/15 DV blends. A. 40x, B. 600x

It can be seen that for the dynamically vulcanized specimen PP/SBS 85/15 DV, craze-like bands appear to initiate from the notch tip and from rubber particles, and propagate in different directions (Figures 2A and 2B). In contrast, rougher surface appearance with micro voids and poor interfacial bonding can be observed in the micrograph of the PP/SBS 85/15 SV blend (Figures 4 and 5). In this case, it can be seen that rubber particles are rather large and that the rubber/matrix adhesion is also quite limited and the result is that the cavitated particles have an inadequate stabilizing action on the growing craze-like bands [8]. As a consequence, these bands tend to be extremely localized and tend to degenerate prematurely into cracks.

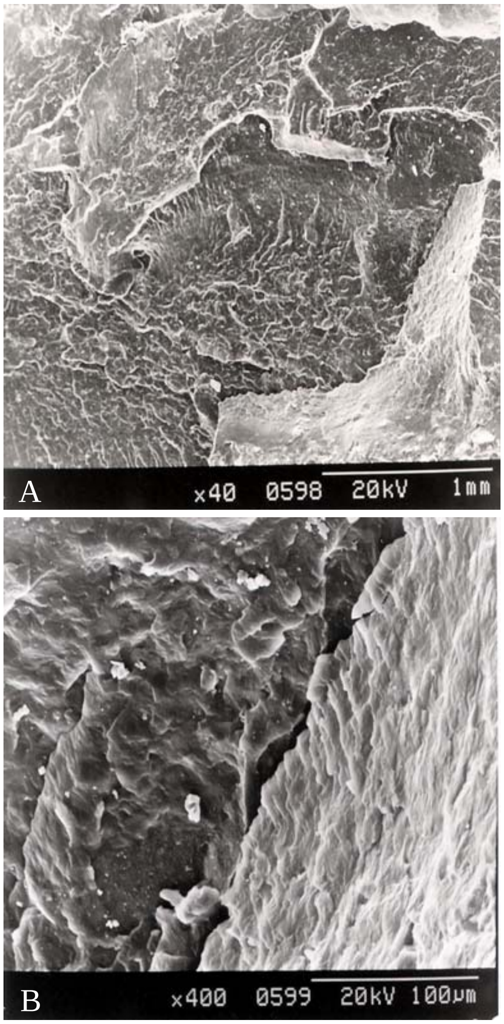

Fig. 3. SEM micrographs taken from the impact fracture surface of PP/SBS 85/15 SV blends. A. 40x, B. 400x.

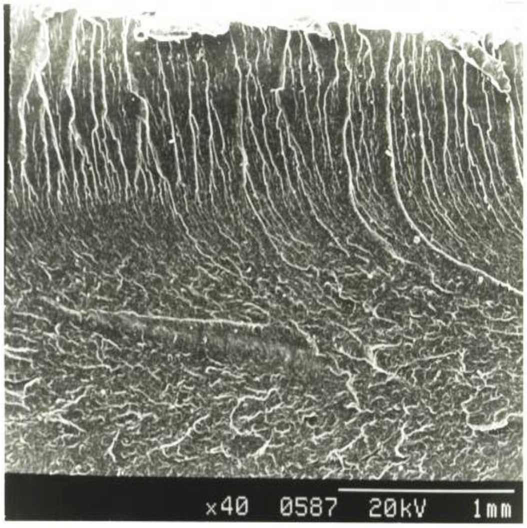

Fig. 4. SEM micrographs taken from the impact fracture surface of PP/SBS 70/30 DV blends.

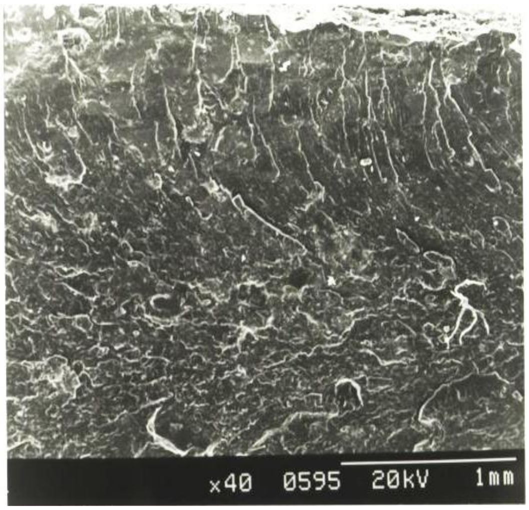

Fig. 5. SEM micrographs taken from the impact fracture surface of PP/SBS 70/30 SV blends.

As a reminder, the term dynamic or "in situ" cross-linking means the simultaneous curing of the rubber component and its fine dispersion in a molten thermoplastic resin via an intensive mixing and kneading process [9]. In this research, this process took place in an extruder.

As the cross-linking reaction occurs, both the viscosity of the rubber and the viscosity of the whole system increase. This rise in viscosity is accompanied by increasing shear stresses, which break up the continuous rubber phase more efficiently, so the size of the rubber particles is reduced, improving the interfacial adhesion [9].

CONCLUSIONS

Drop weight measurements showed that pure PP has extremely low impact strength. Improved impact strength can be achieved by blending PP with SBS via dynamic vulcanization. However, static vulcanization proved to be not as efficient as dynamic vulcanization for improving impact resistance. Finally, SEM observations indicate that for PP/SBS blends, a small particle size and a strong rubber/matrix adhesion are extremely important if a high impact resistance is to be achieved.

ACKNOWLEDGEMENTS

The authors wish to thank the Venezuelan Scientific Research Council FONACIT, the Centre Catalá del Plastic for the financial support and UCV. Also, the authors are very grateful to the people of Laboratorio "E" - Universidad Simón Bolívar, especially Engineer Héctor Rojas and TSU Fabio Albán.

REFERENCES

[1] Hernández M., González J., Albano C., Ichazo M.N., Lovera D. (2003) "Effects of Composition and Dynamic Vulcanization on the Rheological Properties of PP/NBR blends" *Polym. Bull.* 50:205-212.

[2] Ichazo M., Hernández M., González J., Albano C. (2004) "Comparison of Rheological and Mechanical Behavior of Dynamically and Statically Vulcanized PP/SBS Blends" *Polym. Bull.* 51:419-427.

[3] Hernández M., Albano C., González J., Ichazo M. (2006) "Influence of Type of Vulcanization on Rheological and Thermal Properties of PP/NR Blends" *Polym. Bull.* 56(2-3):285-291.

[4] Hernández M., González J., Albano C., Ichazo M.N., Lovera D. (2006) "Thermal and Mechanical Characterization of PP/NBR Blends" *Revista de la Facultad de Ingeniería UCV* 21(1):5-12.

[5] Karger-Kocsis J. (2000) *Structure Development during Polymer Processing*, The Netherlands, Kluwer Academic Publishers, pp. 163-179.

[6] Tjong S.C., Xu S, Mai Y (2002) "Impact-Specific Essential Work of Fracture of Maleic Anhydride-Compatibilized Polypropylene/Elastomer Blends and Their Composites" *J. Polym. Sci.* 40:1881-1892.

[7] Saroop M., Mathur G.N. (1997) "Studies on the Dynamically Vulcanized Polypropylene (PP)/Butadiene Styrene Block Copolymer (SBS) Blends: Mechanical Properties" *J. Appl. Polym. Sci.* 65:2691-2701.

[8] Zebarjad S.M., Lazzeri A., Bagheri R., Seyed Reihani S.M., Frounchi M. (2003) “Fracture mechanism under dynamic loading of elastomer-modified polypropylene” *Mater. Letters* 57:2733-2741.

[9] Karger-Kocsis J. (1999) “Thermoplastic Rubber via Dynamic Vulcanization” in *Polymer Blends and Alloys*, New York, Marcel Dekker, pp.125-153.