# Impact Fracture Behavior and Damage Mechanisms of PP/EVOH Blends Compatibilized with Ionomer $Zn^{2+}$

**M. Montoya,[1] M. J. Abad,[1] L. Barral Losada,[1] V. Pettarin,[2] C. Bernal[3]**

[1]*Grupo de Polímeros, E.U.P.-Ferrol, Universidad de A Coruña, Avda. 19 febrero, s/n, Ferrol 15405, Spain*
[2]*Grupo de Ciencia e Ingeniería de Polímeros, INTEMA (UNMdP-CONICET), Departamento de Ingeniería en Materiales, Universidad Nacional de Mar del Plata, Av. J.B. Justo 4302, Mar del Plata B7608FDQ, Argentina*
[3]*Grupo de Materiales Avanzados, INTECIN (UBA-CONICET), Departamento de Ingeniería Mecánica, Facultad de Ingeniería, Universidad de Buenos Aires, Av. Paseo Colón 850, Buenos Aires C1063ACV, Argentina*

**ABSTRACT:** In this work, the impact fracture behavior and the damage mechanisms of PP/EVOH blends compatibilized with ionomer $Zn^{2+}$ were investigated, focusing on the effect of the compatibilizer and the EVOH content. Initiation energy release rate ($G_{IC}$) values for the blends with EVOH content lower than 30 wt % were slightly lower or similar to that of neat PP, probably due to the premature failure induced by the presence of critical-size flaws derived from debonding of second phase particles. However, blends with 40 wt % EVOH exhibited higher $G_{IC}$ values than neat PP as a result of the increased number of EVOH particles able to induce energy-absorption mechanisms. An increase in the work of fracture values with EVOH content was also observed, especially for the blends with EVOH content above 30 wt %. Therefore, the incorpo-

ration of EVOH to PP led to blends more prone to ductile behavior than neat PP. Furthermore, Pukánszky and Maurer model was successfully applied to fit experimental data of $G_{IC}$ as a function of EVOH content and to confirm the lack of a significant effect of the ionomer $Zn^{2+}$ on the impact fracture properties observed. Finally, from the study of the main deformation mechanisms it was established that the toughening effect of debonding of EVOH particles and subsequent ductile tearing of PP matrix around them which developed under quasi-static stresses were not able to develop under impact loading conditions. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2515–2522, 2010

**Key words:** polypropylene; blends; mechanical properties; impact fracture; damage mechanisms

## INTRODUCTION

To obtain a low-cost recyclable material, easy to process with good barrier, optical, and mechanical properties, is a common difficult problem in the packaging and hydrocarbons transport industries. To solve this problem, a widely used practice in industry is to blend a small quantity of a barrier material with a low-cost one.

This is the case of the combination of polypropylene (PP) and the copolymer of ethylene vinyl alcohol (EVOH), to produce a material with good barrier properties at relatively low cost.[1] The former is a semicrystalline polymer with good mechanical, thermal, and barrier properties to water but with poor barrier properties to oxygen, which can be used for food packaging. In contrast, EVOH has high barrier properties to oxygen and carbon dioxide,[1,2] high resistance to hydrocarbons and good processability.[3]

However, PP and EVOH have a poor miscibility; hence, a compatibilizer is commonly used in the formulations. Many works have been done concerning the compatibilization and the physical properties of PP/EVOH blends.[1–5]

In addition, mechanical properties frequently play a significant role in many applications of polymers. In particular, the characterization of the mechanical performance of polymers under impact (high strain rates) to obtain reliable data relevant to practical applications for the design purposes is a subject of much interest.

Although polypropylene exhibits relatively ductile behavior at room temperature, it has the disadvantage of having insufficient toughness at low temperatures and in the presence of notches.[6] Therefore, its use is still limited in many engineering applications.[7,8]

Several studies regarding the tensile properties of PP/EVOH blends have been published in the literature[1,3–5] as well as significant effort has been devoted on the fracture behavior of impact-modified PP blends.[8–13] However, only a few studies have been focused on the fracture behavior of PP/EVOH blends,[14,15] and particularly fracture properties at the extreme conditions of impact loading have not been already investigated.

The aim of this work was to study the impact fracture behavior and the damage mechanisms of PP/EVOH blends compatibilized with ionomer $Zn^{2+}$. Impact fracture tests on single-edge notched bending SENB specimens were performed on neat PP and on PP/EVOH blends with different EVOH content. The effect of the ionomer $Zn^{2+}$ content was also analyzed. In addition, the blends damage mechanisms under both quasi static and impact loading conditions were investigated.

## EXPERIMENTAL

### Materials

An extrusion grade of PP synthesized by Repsol (ISPLEN PP044W3f) was used. Its melt flow index (MFI) value is 3.02 g/10 min (230°C, 2160 g), and its density is 0.90 g $cm^{-3}$.

The EVOH copolymer from EVAL Europe (grade: F101B) has an ethylene content of 32.9%, a MFI of 1.51 g/10 min (190°C, 2160 g), and density equal to 1.19 g $cm^{-3}$.

Since PP and EVOH have a poor miscibility,[4] ionomer $Zn^{2+}$ was used as a compatibilizer. It was expected to interact by complexation with the OH groups of EVOH.[3] The used ionomer $Zn^{2+}$ (Surlyn 9970) from Du Pont, is a random ethylene/methacrylic acid copolymer, with a MFI of 14 g/10 min (190°C, 2160 g) and density equal to 0.94 $gcm^{-3}$.[14]

The melting points of the pure components and the blends determined by differential scanning calorimetry (DSC) have been previously reported.[14]

### Blends preparation

Prior to processing, EVOH and the ionomer were dried in a vacuum oven for a period of 24 h at 80°C and 8 h at 60°C, respectively. Blends of PP/EVOH and PP/EVOH/ionomer were prepared using a corotating twin-screw extruder (Brabender DSE20) operating at a speed of 45 rpm. The barrel temperature was 215°C, and the die temperature was 220°C. All components were premixed by tumbling and simultaneously fed into the twin-screw extruder.

Binary blends were prepared in proportions of 90/10, 80/20, 70/30 and 60/40, w/w PP/EVOH, respectively. The compatibilized blends were made with amounts of 2, 5, 10, and 20% of ionomer $Zn^{2+}$ respect the EVOH mass in the blend.

### Sample preparation and impact characterization

Pellets of neat PP and the blends were compression-molded into plaques at 220°C, under 1 MPa for 15 min followed by 10 MPa for 8 min. Then the plaques were rapidly cooled down by circulating water

within the press plates under a pressure of 10 MPa. Thermal stresses generated during molding were released by annealing the plaques in an oven for 3 h at 100°C.

Fracture characterization was carried out on single-edge notched bend SENB specimens cut out from compression-molded thick plaques (thickness, $B = 8$ mm). Sharp notches were introduced by sliding a fresh razor blade into a machined slot. Crack-to-depth ($a/W$), thickness-to-depth ($B/W$) and span-to-depth ($S/W$) ratios were always kept equal to 0.5, 0.5, and 4, respectively.

Impact fracture tests were performed in three-point bending in a falling weight Fractovis of Ceast at an impact velocity of 1 m/s.

Energy release rate values at initiation ($G_{IC}$) were obtained by following ISO 17281:2002 standard recommendations.[16]

As the blends exhibited a semi-controlled propagation way, i.e., load did not suddenly drop to zero after the critical load was reached, the work of fracture ($W_f$) was also determined. It was calculated from the total area under the load-displacement curve ($U_T$) divided by twice the area of the fracture surface (since two new faces are created), as follows[17,18]:

$$W_f = U_T / 2B(W - a) \tag{1}$$

The work of fracture was defined simply as the total energy consumed to produce a unit area of fracture surface during the "complete" fracture process.

### Fracture surface analysis

The fracture surfaces of SENB specimens tested in impact were examined using a JEOL JSM-6460LV scanning electron microscope (SEM) at an accelerating voltage of 20 kV. The samples were sputter coated with a thin layer of gold before they were observed.

### Investigation of the damage mechanisms

To study the damage mechanisms, SENB fracture specimens of the blends were also tested in three-point bending in an Instron dynamometer 4467 at a crosshead speed of 1 mm/min. The specimens were tested up to subcritical displacement levels until a significant deformation zone was developed. To study damage mechanisms acting under impact conditions, low-energy impact (low blow) tests were also performed on some blend samples.

Side surfaces of samples tested under quasi static and low blow conditions were observed by scanning

electron microscopy (SEM) after they had been coated with a thin layer of gold.

All tests were carried out at room temperature.

## RESULTS AND DISCUSSION

### Impact fracture behavior

Figure 1(a,b) shows typical load-deflection curves obtained in impact for neat PP and their 70/30/5 blend, respectively as an example. Neat polypropylene exhibited completely brittle behavior, characterized by a linear elastic response up to fracture followed by a sudden drop of load to zero. Hence, nearly all the impact energy was involved in crack initiation and no additional energy was needed for fracture propagation. This means that the stored energy in the sample at the moment of crack initiation was enough to propagate the crack through the entire specimen[9] and unstable crack propagation with a very high fracture speed was developed. On the other hand, the blends displayed some amount of post-maximum displacement (propagation behav-

ior), which was found to be higher for the blends with EVOH content equal to or higher than 30 wt %.

It is well established in the literature[10] that the fracture process can be divided into an initiation stage, where the stress builds up at the notch tip without crack initiation, and a crack propagation stage where the crack runs through the sample. If the material exhibits brittle fracture behavior, the crack propagation speed will be very high and the displacement during crack propagation will be very small. When the material fracture behavior is ductile, on the other hand, the crack propagation speed is much lower, and the propagation displacement significantly exceeds displacement during brittle fracture. Therefore, the amount of displacement during crack propagation is a measure of the ductile crack propagation. In our case, the higher post-maximum displacement levels for the blends with EVOH content equal to or higher than 30 wt % indicate the higher ductility of these blends.

Macroscopically, all the fracture surfaces appeared relatively flat and smooth with the mirror-like appearance characteristic of unstable crack growth and without any signs of stress whitening (Fig. 2), resembling brittle fracture behavior under impact loading. Similar findings have been reported by Thio et al.[6] for composites of isotactic polypropylene and $CaCO_3$ even when a significant improvement in toughness was achieved. These authors observed that fracture surfaces of notched Izod specimens displayed a brittle mode of separation with some evidence of plastic deformation only very near the notch root.

Critical initiation energy release rate values ($G_{IC}$) as a function of EVOH content are shown in Figure 3 along with their deviations. In spite of the high scatter of experimental data which was expected in impact tests, it was observed that $G_{IC}$ values for the
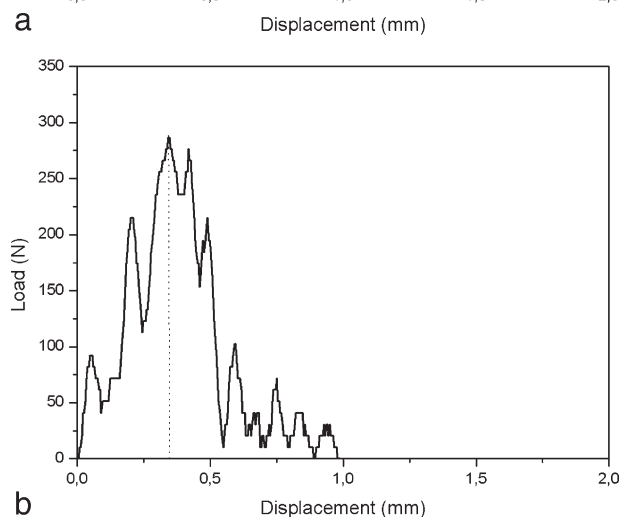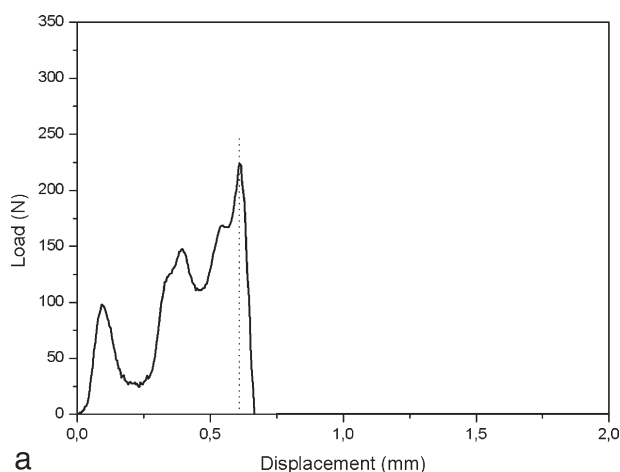




**Figure 1** Typical impact load-deflection curves for neat polypropylene and one of the blends. (a) Neat PP. (b) 70/30/5 blend.
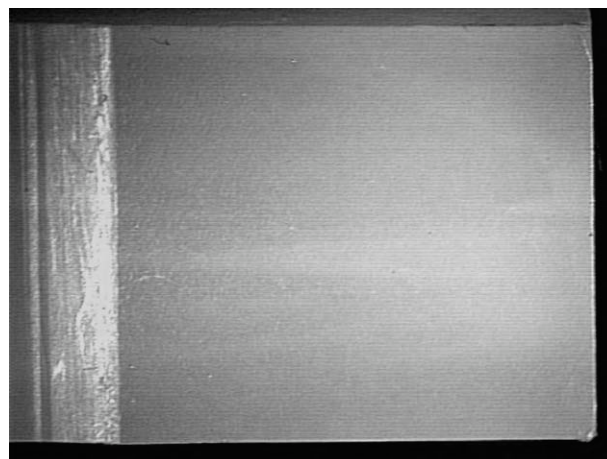
**Figure 2** Typical macrograph of the fracture surface of a 90/10/10 blend sample broken under impact loading conditions.
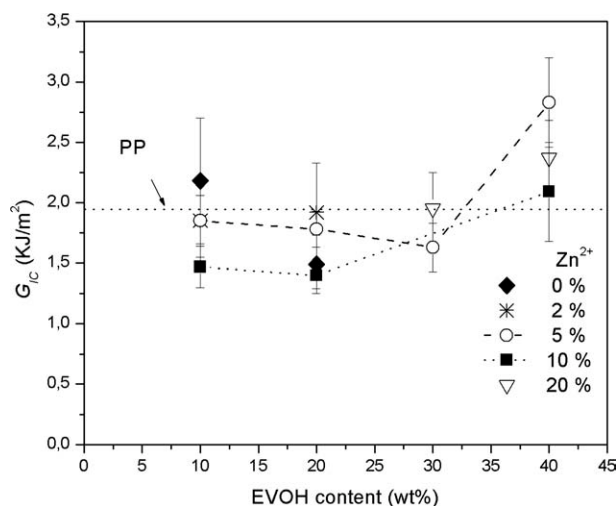
**Figure 3** Critical energy release rate values ($G_{IC}$) for the different blends as a function of EVOH content.



**Figure 4** Work of fracture values ($W_f$) for the different blends as a function of EVOH content.

blends with EVOH content equal to or lower than 30 wt % were slightly lower or similar to that of neat PP. Probably, premature failure was induced by the presence of critical-size flaws derived from debonding of second phase particles.[12] During impact, where the plastic resistance of PP is raised considerably in the local condition of high strain rate near the notch root[6] and the glass transition temperature of the PP matrix is shifted from about 5°C at quasi-static conditions to room temperature at impact conditions (according to the time-temperature superposition principle), some of the voids that were created by debonding of EVOH particles from the matrix were not stable and grew to a size where crack initiation occurs.

On the other hand, irrespectively of the ionomer $Zn^{2+}$ content, blends with 40 wt % EVOH exhibited $G_{IC}$ values slightly higher than that of PP, probably as a result of an increased number of active EVOH particles able to induce energy-absorption mechanisms.

Work of fracture values for the different blends as a function of EVOH content are presented in Figure 4, along with their deviations. An increase in the work of fracture values with the EVOH content was also observed, and this increase was significantly higher for the blends with EVOH content above 30 wt %. A trend of PP/EVOH blends to be more prone to ductile fracture behavior than neat PP has been already reported in previous investigations under quasi-static regime.[14,15] In addition, impacted specimens of 40 wt % EVOH blends presented hinging between both halves confirming the higher ductility of these blends.

It should also be noted that the compatilizer had no significant influence on both fracture initiation and work of fracture values, probably as a result of the presence of different counteracting effects, as it will be explained later.
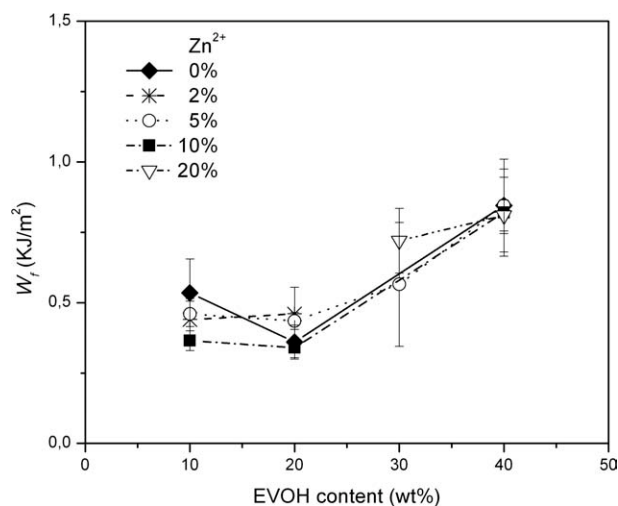
Figure 5(a,b) presents SEM micrographs of the fracture surfaces of impacted samples of neat PP and the 60/40/10 blend, as an example while Figure 5(c,d) are closer views of those figures. A typical brittle-appearance fracture surface is observed for neat PP in Figure 5(a,c). In PP/EVOH micrographs [Fig. 5(b,d)] it can be seen that EVOH particles debonded from the PP matrix leading to the formation of voids. No signs of shear yielding of the matrix ligaments between particles were observed. Similar findings have been previously reported by Fasce et al.[19] for polypropylene modified with elastomeric metallocene-catalyzed polyolefin blends. These authors have been attributed the increase in the impact toughness of their blends to the formation of free surfaces (voids) which acted as craze initiation sites. Similarly in our blends, debonding of EVOH particles would have led to the formation of voids that would have acted as craze initiation sites, thus contributing to higher energy absorption.

The $G_{IC}$ values observed for the blends with EVOH content lower than 40 wt %, could be due to the insufficient number of active EVOH particles able to induce the energy-absorption mechanisms mentioned above.

The increase in the work of fracture with EVOH content observed could be also a consequence of the higher energy consumed during crack propagation, as a result of the increase in the number of particles inducing the toughening mechanisms of debonding of particles and subsequent craze initiation.

## Modeling of fracture properties

The dependence of fracture toughness on composition can be analyzed using the following expression derived by Pukánszky and Maurer.[20] The change in
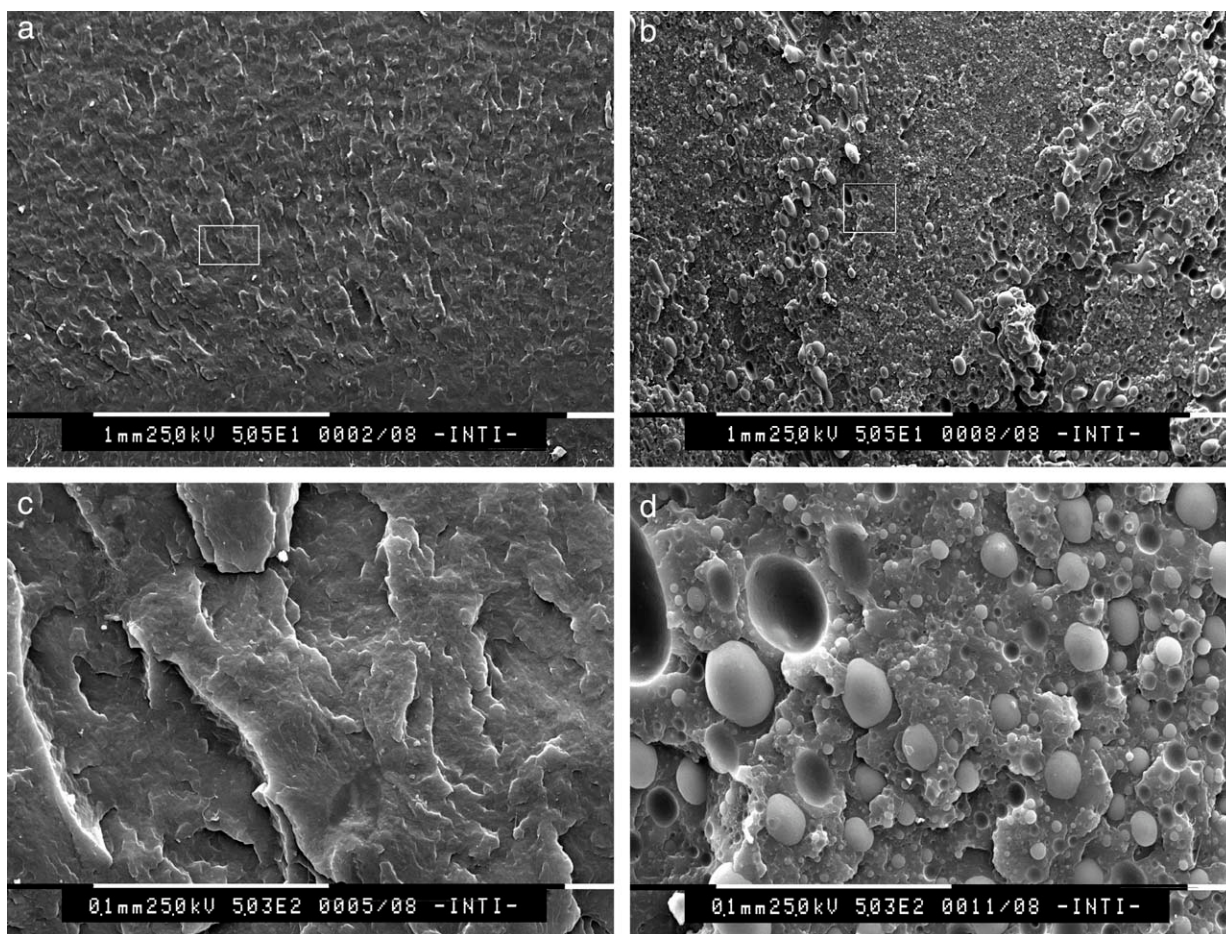
**Figure 5** SEM micrographs of the fracture surfaces of SENB samples broken in impact. (a) Neat PP. (b) 60/40/10 blend. (c) Closer view of a. (d) Closer view of b.

the property due to the interaction between components has been considered proportional to the actual value of that property in this analysis[20]:

$$G_{IC} = G_{ICm}(E_m/E)(1 - v_f)/(1 + 2.5v_f)\exp(B_{Gc}v_f) \quad (2)$$

where $E_m$ and $E$ are the modulus of the matrix and the composite, respectively, $v_f$ is the second phase volume fraction and $E_m/E$ accounts for the inverse correlation that exists between fracture resistance and stiffness of the material. The term $(1 - v_f)/(1 + 2.5\,v_f)$ represents the change in the effective load-bearing cross-section of the matrix due to the presence of the second phase and $B_{Gc}$ is related to interfacial properties[21] and is particular to each system.

The effect of the reduced load-bearing cross-section can be eliminated, if the reduced property is plotted against second phase content in the linearized form of eq. (2):

$$ln\,G_{ICred} = ln\,G_{ICm} + B_{Gc}v_f, \quad (3)$$

where

$$G_{ICred} = G_{IC}E/E_m(1 + 2.5v_f)/(1 - v_f).$$

From the slope of the linear regression of experimental data, the $B_{Gc}$ parameter can be easily obtained. Its value can be used for determining the effect of component interaction on fracture resistance.

Figure 6 shows the results obtained from the application of eq. (3) to the blends with 0, 2, and 10 wt % ionomer $Zn^{2+}$. Volume fraction values were obtained by taking into account the density of PP and EVOH and neglecting the density of the compatibilizer. The values of stiffness ($E$) were adopted to be the dynamic flexural modulus values determined under impact at the same test speed used in the fracture tests by following the procedure proposed by Grellmann et al.[22] Experimental data of $G_{IC}$ were reasonably fitted by Pukánszky and Maurer model,[20] as good linear regressions were found between reduced energy release rate values and EVOH volume fraction values.
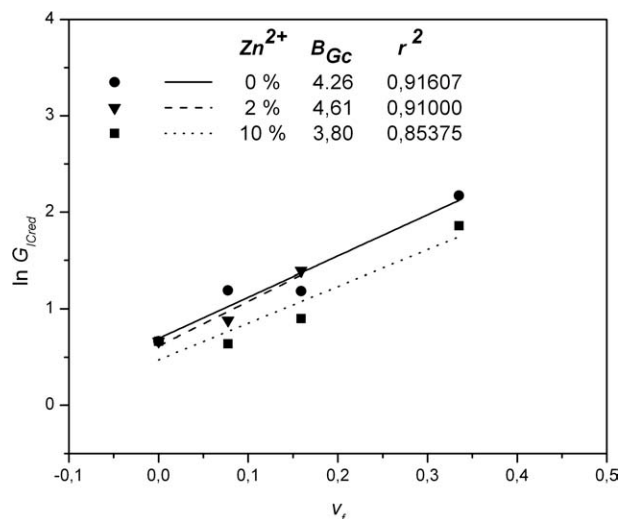
**Figure 6** Results obtained from the application of Pukánzsky and Maurer model for the blends with different ionomer $Zn^{2+}$ content.

It can also be observed in Figure 6 that the incorporation of ionomer $Zn^{2+}$ did not lead to remarkable differences in the values of the $B_{Gc}$ parameter, confirming the lack of a significant influence of the ionomer content on the initiation energy values. However, as it can be seen in the SEM micrographs of Figure 7 and the particle size distributions of Figure 8, the increase in the ionomer $Zn^{2+}$ content led to more homogeneous blends that exhibit decreased second phase particle sizes and narrower particle size distributions. These observations confirmed the compatibilizing effect of the ionomer $Zn^{2+}$ originally reported in Ref. 4.

## Damage mechanisms

Figure 9 shows a SEM micrograph of a typical side surface around the damaged zone of a PP/EVOH blend sample. It was tested under quasi-static loading conditions at 1 mm/min under the same geometrical conditions of the impact tests. It is clearly observed in this figure that under some deformation at low strain rates and temperatures above the glass transition of the PP matrix, EVOH particles debonded from the PP matrix which subsequently underwent ductile tearing around these particles. Due to the difference in the elastic properties between PP and EVOH (stiffness of EVOH is about three times that of PP[1]), second phase particles acted as stress concentrators during deformation processes and the triaxial stress around them started to build up. Interfacial debonding, i.e., separation of the particles from the matrix, occurred changing the stress state in the surrounding matrix. Volume strain was released, reducing the sensitivity of the matrix polymer toward crazing and shear yielding was favored.
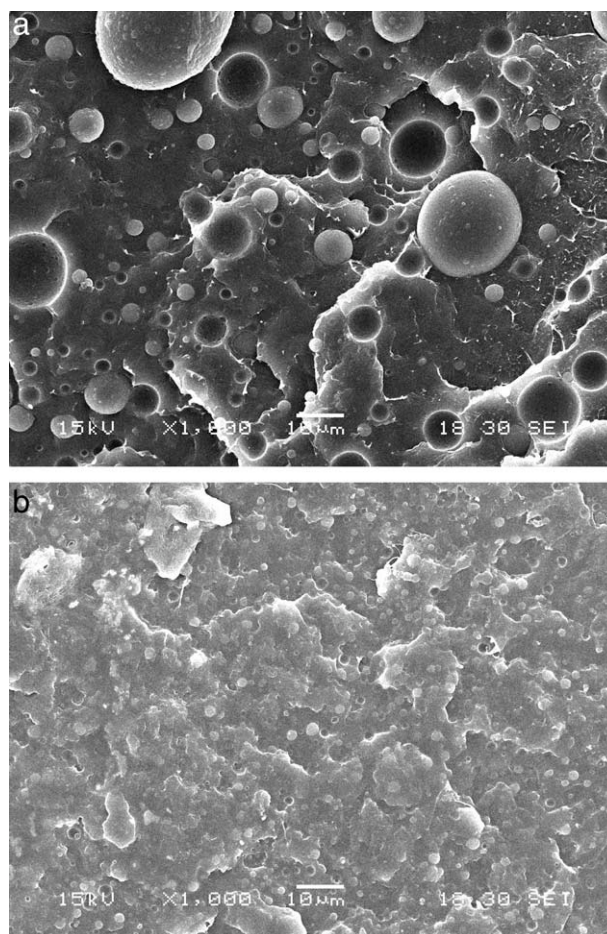


**Figure 7** SEM micrographs of the fracture surfaces of two blends with different ionomer $Zn^{2+}$ contents. (a) 80/20/2 blend. (b) 80/20/10 blend.

This mechanism of toughening has been proposed by Kim and Michler[23,24] for particle-filled semicrystalline polymers and also observed by others[25–27] on different polypropylene composites.
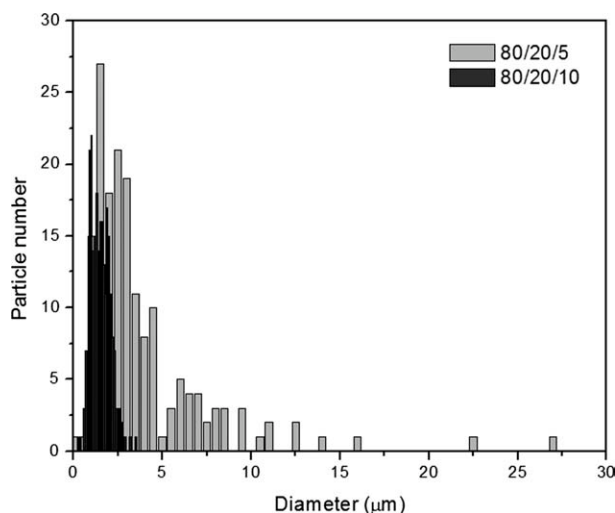


**Figure 8** Particle size distributions for two 80/20 blends with different ionomer $Zn^{2+}$ contents.
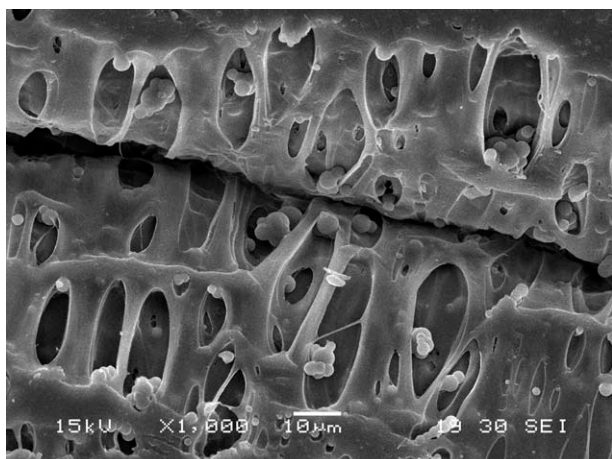
**Figure 9** SEM micrograph of a typical side surface around the damaged zone of a blend sample tested under quasi-static loading conditions at 1 mm/min.

The damage mechanism described above was also found around damaged zones in PP/EVOH blend samples tested at 100 mm/min (not shown).

However, side surfaces of low-blow impact tests (Fig. 10) only showed small signs of lateral damage and the toughening mechanism observed under quasi-static loading was absent. Instead, debonding of EVOH particles would have led to the formation of voids that would have acted as craze initiation sites as mentioned before.

Our results suggest that during impact, in the presence of notches and high strain rates, the time required for the relaxation of stress concentrations at the crack tip becomes comparable with, and eventually exceeds the effective time available.[13] Hence, the interparticle ligaments of polymer were not able to deform plastically to a significant extent[28] and the mechanism of toughening via particle debonding fol-
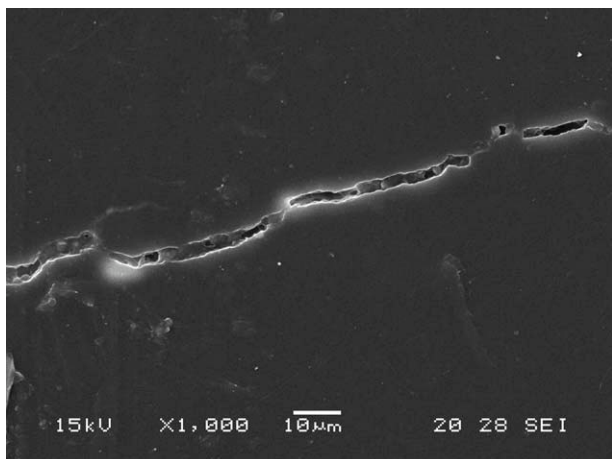


**Figure 10** SEM micrograph of a typical side surface around the damaged zone of a blend sample tested in low blow tests.

lowed by matrix ductile tearing observed under quasi-static loading could not be developed.

From the results of this investigation, the different impact fracture behavior observed in our blends could be explained in terms of different counteracting effects.

At low EVOH content, there is an insufficient number of active EVOH particles able to induce toughening mechanisms and the creation of critical-sized flaws from debonding of EVOH particles becomes dominant. At higher EVOH content, in contrast, matrix toughening mechanisms prevail.

Regarding the effect of the compatibilizer, the addition of the ionomer $Zn^{2+}$ on one hand, leads to a better dispersion of EVOH particles in PP and a decrease in the second phase particle size that would be beneficial to avoid the formation of critical-sized flaws and to induce the matrix toughening mechanisms probably via the creation of voids able to act as craze initiation sites. On the other hand, the presence of the compatibilizer is expected to increase interfacial adhesion between both phases, hindering debonding of EVOH particles from the matrix with the subsequent well-known detrimental effect on toughening.[28] Therefore, these counteracting effects could explain the absence of a significant influence of the compatibilizer on the impact fracture properties of our blends.

## CONCLUSIONS

The impact fracture behavior and the damage mechanisms of PP/EVOH blends compatibilized with ionomer $Zn^{2+}$ were investigated.

It was observed that the impact initiation energy release rate values $G_{IC}$ for all PP/EVOH blends with EVOH content lower than 30 wt % were slightly lower or similar to that of neat PP. However, blends with 40 wt % EVOH exhibited slightly higher $G_{IC}$ values than PP as a result of the increased number of active EVOH particles able to induce energy-absorption mechanisms.

A change in the fracture behavior of PP was found from the incorporation of EVOH. The blends were more prone to ductile fracture in comparison to neat PP presenting some propagation energy after fracture initiation.

Pukánszky and Maurer model was successfully applied to these blends. The lack of a significant influence of the ionomer content on the materials impact fracture behavior was confirmed from model results.

Under quasi-static loading conditions the damage mechanism in PP/EVOH blends was found to be the debonding of EVOH particles with a subsequent matrix ductile tearing around these particles. On the other hand, under impact conditions, EVOH

particles debonded from the PP matrix leading to the formation of voids which seem to act as craze initiation sites.

The impact fracture behavior observed in the investigated PP/EVOH blends could be explained in terms of different effects. The formation of critical-sized flaws against the development of matrix toughening from debonding of EVOH particles could explain the effect of EVOH content. On the other side, the lack of a significant influence of the ionomer content on the fracture properties could be attributed to the counteracting effects of the beneficial improvement in the particle dispersion and particle size distribution versus the detrimental increase in the interfacial adhesion promoted by the compatibilizer.

## References

1. Faisant, J. B.; Ait-Kadi, A.; Bousmina, M.; Deschenes, L. Polymer 1998, 39, 533.
2. Demarquette, N. R.; Kamal, M. R. J Appl Polym Sci 1998, 70, 75.
3. Kalfoglou, N. K.; Samios, C. K.; Papadopoulou, C. P. J Appl Polym Sci 1998, 68, 589.
4. Abad, M. J.; Ares, A.; Barral, L.; Cano, J.; Díez, F. J.; García-Garabal, S.; López, J.; Ramírez, C. J Appl Polym Sci 2004, 94, 1763.
5. Abad, M. J.; Ares, A.; Barral, L.; Eguiazábal, J. I. Polym Int 2005, 54, 673.
6. Thio, Y. S.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 2002, 43, 3661.
7. Frontini, P. M.; Fave, A. J Mater Sci 1995, 30, 2446.
8. Van Del Wal, A.; Gaymans, R. J. Polymer 1999, 40, 6045.
9. Van Del Wal, A.; Nijhol, R.; Gaymans, R. J. Polymer 1999, 40, 6031.
10. Van Del Wal, A.; Verheul, A. J. J.; Gaymans, R. J. Polymer 1999, 40, 6057.
11. Van Del Wal, A.; Gaymans, R. J. Polymer 1999, 40, 6067.
12. Wong, S.-C.; Mai, Y.-W. Polymer 1999, 40, 1553.
13. Gensler, R.; Plummer, C. J. G.; Grein, C.; Kausch, H. H. Polymer 2000, 41, 3809.
14. Montoya, M.; Abad, M. J.; Barral Losada, L.; Bernal, C. J Appl Polym Sci 2005, 98, 1271.
15. Montoya, M.; Abad, M. J.; Barral Losada, L.; Bernal, C. Eur Polym J 2006, 42, 265.
16. ISO Standard 17281:2002: Plastics-Determination of fracture toughness (GIC and KIC) at moderately high loading rates (1 m/s); 2002.
17. Aksel, C.; Warren, P. D. Compos Sci Technol 2003, 63, 1433.
18. Nuñez, A. Ph.D. Dissertation, Royal Institute of Technology, Lightweight Structures, National University of Mar del Plata, Argentina, June 2005.
19. Fasce, L. A.; Frontini, P. M.; Wong, S.-C.; Mai, Y.-W. J Polym Sci Part B: Polym Phys 2004, 42, 1075.
20. Pukánszky, B.; Maurer, F. H. Polymer 1995, 36, 1617.
21. Bezerédi, A.; Demjén, Z.; Pukánszky, B. Die Angew Makrom Chem 1998, 61, 256.
22. Grellmann, W.; Seidler, S.; Hesse, W. Martin-Luther-Universität Halle-Wittenberg Procedure for Testing of Plastic, Instrumented Charpy Impact Test (ICIT). Procedure for Determining the Crack Resistance Behaviour Using the Instrumented Impact Test, MPK-ICIT, 2001–11.
23. Kim, G. M.; Michler, G. H. Polymer 1998, 39, 5689.
24. Kim, G. M.; Michler, G. H. Polymer 1998, 39, 5699.
25. Zuiderduin, W. C. J.; Westzaan, C.; Huétink, J.; Gaymans, R. J. Polymer 2003, 44, 261.
26. Lazzeri, A.; Zebarjad, S. M.; Pracella, M.; Cavalier, K.; Rosa, R. Polymer 2005, 46, 827.
27. Vu-Khanh, T.; Fisa, B. Theor Appl Fracture Mech 1990, 13, 11.
28. Thio, Y. S.; Argon, A. S.; Cohen, R. E. Polymer 2004, 45, 3139.