

# iPP/HDPE Blends. II. Modification with EPDM and EVA

H. P. BLOM, J. W. TEH,\* and A. RUDIN†

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

## SYNOPSIS

Past work has shown that addition of high-density polyethylene (HDPE) to polypropylene (PP) resulted in a significant reduction in the elongation at break and in the gate-region impact strength of injection molded articles. In this study, we report on the compatibilization of these blends with ethylene/propylene/diene monomer (EPDM) or ethylene/vinyl acetate (EVA) copolymers. EPDM is effective at improving the impact strength and gate puncture resistance of a 90/10 PP/HDPE blend. EVA, on the other hand, is effective at improving the impact strength and the elongation at break of this material. It was also found that EVA is a better impact modifier for PP than is EPDM. DSC analysis indicated that EPDM, when blended with PP, caused a significant reduction in the degree of crystallinity of the PP. This was not observed in the case of EVA/PP blends. Further, our results indicate that care must be taken in designating a particular material as a better compatibilizer than some other material. It is crucial that conditions be attached to the label compatibilizer, indicating in particular the desired mechanical properties of the blend. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

In an earlier publication<sup>1</sup> we reported on the effect of addition of high-density polyethylene (HDPE) to polypropylene (PP). We concluded that PP and HDPE are incompatible and immiscible and that HDPE caused a deterioration in the tensile properties, especially the elongation at break. We also observed a deficiency in the gate puncture strength of the blend. The purpose of the present study was to modify the blends of PP and HDPE, in particular the 90/10 PP/HDPE blend, with a view to compatibilizing the two homopolymers and restoring the mechanical properties back to those of the neat PP.

A number of methods exist for modifying incompatible blends to improve the adhesion between the phases. One is by chemical modification carried out by reactive extrusion. Typically, a peroxide is added to the melt blend in the extruder. In the case of a gross viscosity mismatch, peroxides can reduce the

viscosity of the PP phase through chain scission and increase the viscosity of the PE phase through crosslinking, as has been shown by Yu et al.<sup>2</sup> Another option is to add a third component that can act as a polymeric surfactant, situating itself at the interface of the two homopolymers. The polymeric compatibilizer is ideally a block copolymer of the two homopolymers in the blend.

This latter approach is the one that we have chosen, partly because others have had some success with the compatibilization of PP/HDPE blends with this method,<sup>3</sup> and partly because this is seen to be the most economical and the easiest to implement in a production environment. All that would be required is the addition of the suitable copolymer resin to the recycled material as it is extruded and pelletized during the recycling process.

We chose to study the potential of ethylene/propylene/diene monomer (EPDM) and ethylene/vinyl acetate (EVA) as compatibilizers for PP/HDPE blends. Choudhary et al.<sup>3</sup> and Stehling et al.<sup>4</sup> used EP rubbers as compatibilizers for PP/HDPE systems with good success. Both groups reported that addition of EP rubbers to PP/HDPE blends greatly improved the impact strength of the material. EVA is at least partially compatible with PP<sup>5</sup> and with

\*Present address: Novacor Research and Technology Corporation, 2928 16th Street N.E., Calgary, Alberta T2E 7K7, Canada.

† To whom correspondence should be addressed.

**Table I Properties and Molecular Characteristics of Polymers**

| Resin  | $M_n$  | $M_w$   | $M_z$   | MFI (dg/min)    | $\rho$ (g/cm <sup>3</sup> ) |
|--------|--------|---------|---------|-----------------|-----------------------------|
| PP     | 21,700 | 166,000 | 509,000 | 20 <sup>a</sup> | 0.91                        |
| HDPE   | 16,000 | 72,600  | 256,000 | 5 <sup>b</sup>  | 0.96                        |
| EPDM   | 65,700 | 165,000 | 379,000 | 50 <sup>c</sup> | 0.87                        |
| EVA-28 | 19,700 | 76,900  | 219,000 | 3 <sup>b</sup>  | 0.95                        |
| EVA-33 | 12,200 | 53,400  | 167,000 | 43 <sup>b</sup> | 0.95                        |

$M_n$ ,  $M_w$ , and  $M_z$  were determined in TCB at 145°C.<sup>7</sup>

<sup>a</sup> ASTM D1238, 230°C, 2.16 kg.

<sup>b</sup> ASTM D1238, 190°C, 2.16 kg.

<sup>c</sup> Mooney viscosity (ASTM D6146) ML 1 + 8 (125°C).

HDPE.<sup>6</sup> It is therefore expected that EVA might act as a compatibilizer for PP/HDPE blends. We studied two EVAs differing in their VA content in an attempt to determine the effect of the degree of crystallinity of the EVA on its ability to compatibilize PP and HDPE.

## EXPERIMENTAL

### Materials

Injection molding grade isotactic polypropylene (iPP) was supplied by Montell Canada Inc. HDPE was supplied by DuPont Canada Inc. The EPDM copolymer was supplied by Bayer Rubber Inc., and had an ethylene content of ~ 80%. EVA copolymers EVA-28 and EVA-33 were supplied by AT Plastics. The VA contents were 28 and 33%, respectively. Molecular weight (from size exclusion chromatography),<sup>7</sup> melt flow, and density data for all the materials are listed in Table I. The compositions of the blends investigated in this study are listed in Table II. The ternary blends were prepared in such a way as to retain a constant iPP/HDPE ratio of 90/10.

**Table II Blend Compositions (Wt %)**

| PP    | HDPE | Copolymer <sup>a</sup> |
|-------|------|------------------------|
| 100.0 | —    | —                      |
| 90.0  | 10.0 | —                      |
| 98.9  | —    | 1.1                    |
| 96.7  | —    | 3.3                    |
| 94.5  | —    | 5.5                    |
| 89.1  | 9.9  | 1.0                    |
| 87.3  | 9.7  | 3.0                    |
| 85.5  | 9.5  | 5.0                    |

<sup>a</sup> For each blend containing a copolymer, there are three samples containing EPDM, EVA-28, or EVA-33, respectively, for a total of 20 blends.

The binary blends of PP and copolymer were prepared in a manner to retain the PP/copolymer ratio in the corresponding ternary blends.

### Extrusion

All samples were tumble blended prior to melt blending in a Leistritz LSM corotating intermeshing twin-screw extruder. The feed rate was  $100 \pm 10$  g/min, the screw speed was 35 rpm, the die temperature was 190°C, and the die pressure was ~ 17 bar. The barrel was purged between batches with 2 kg of the new blend to ensure that all traces of the previous blend had been removed. The extrudate was frozen in-line in a water bath (~ 10°C), air dried, and pelletized. In the case of the ternary blends, all three resins were melt blended simultaneously. Details of the extruder setup are given in an earlier publication.<sup>1</sup>

### Specimen Preparation

Impact bars (6.2 × 12.7 × 76 mm) and dumbbell tensile test pieces (ASTM D638 type I) were prepared by injection molding on a Battenfeld BSKM 50-ton press (190–210°C barrel temperature, 3.22-MPa injection pressure, 40°C mold, and 1.2-s injection time). Thin-walled containers (635- $\mu$ m thick) were injection molded on an Engel ES-125 injection molder. The barrel temperature varied from 230°C at the feed port to 270°C at the nozzle. The mold temperature was set at 30°C, the injection pressure was 12.4 MPa, and the average injection velocity was 14.7 cm/min.

### Annealing

Notched impact bars, tensile bars, and thin-walled containers were annealed in hot air (75°C) in an

oven for 1 week. Fresh and annealed samples were left for 5–7 days at room temperature prior to testing.

### Mechanical Properties

Notched Charpy impact properties were determined using an instrumented impact tester.<sup>8</sup> The hammer velocity was  $1.0 \pm 0.1$  m/s. The impact strength was determined from the kinetic energy loss of the hammer, and was an average of 10 specimens. Tensile properties were obtained using an Instron tensile tester at a crosshead speed of 25.4 cm/min and an initial jaw separation of 10 cm. Results were averages for seven specimens. The gate puncture test was performed on selected samples. This test was carried out on a modified Instron tensile tester fitted with a dart head that descended at 1 m/s, striking the gate region of the thin-walled container. The gate puncture strength, arbitrarily defined as the maximum load, which occurred just prior to the break of the specimen, was averaged from 10 specimens. Further details can be found in Blom et al.<sup>1</sup>

### DSC

A Perkin–Elmer DSC-2 was used to investigate the melting and crystallization behavior of the blends. All samples were approximately 10 mg in weight. Each sample was analyzed in the following manner.

1. The encapsulated sample was placed in the sample holder cell, heated to 200°C at 160°C/min, and held for 10 min.
2. The sample was then cooled from 200°C to 0°C at 10°C/min (crystallization).
3. After that, the sample was immediately heated from 0 to 200°C at 10°C/min (melting).

Data were collected in parts 1 and 3. In the crystallization experiments, only one peak was observed in all blends, in contrast to the previous observation of two peaks. This is probably a result of the different cooling rates used in this study. For the melting experiments, blends containing both PP and HDPE showed two peaks. The following assumptions were made in the data analysis:

1. The enthalpy of fusion of 100% crystalline iPP was taken to be 138 J/g.<sup>9</sup>
2. The enthalpy of fusion of 100% crystalline linear PE was taken to be 290 J/g.<sup>10</sup>
3. For blends containing a copolymer (EPDM, EVA-28, or EVA-33), it was assumed that the

copolymers did not contribute to the enthalpy of fusion or enthalpy of melting for either PP or HDPE for the crystallization and melting experiments, respectively.

4. For the 90/10 PP/HDPE blend, the enthalpy of fusion for a 100% crystalline sample was taken to be  $(0.9 \times 138) + (0.1 \times 290) = 153$  J/g.

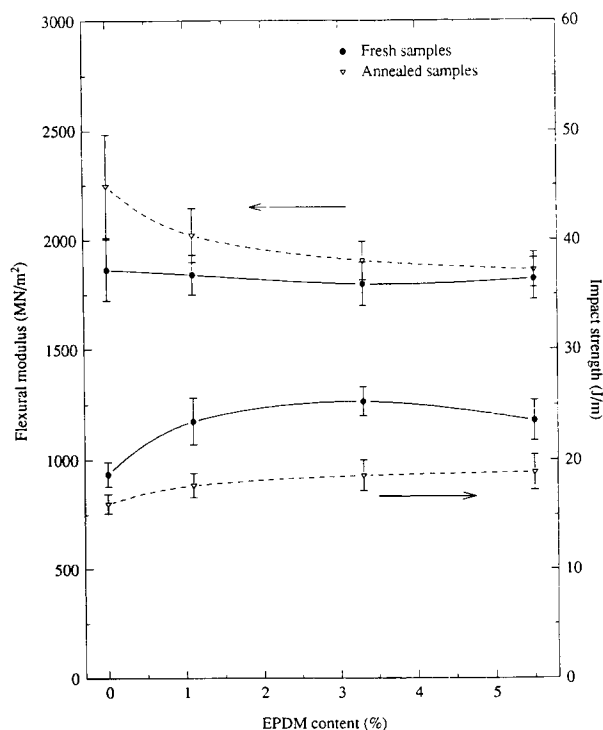
## RESULTS AND DISCUSSION

### EPDM Systems

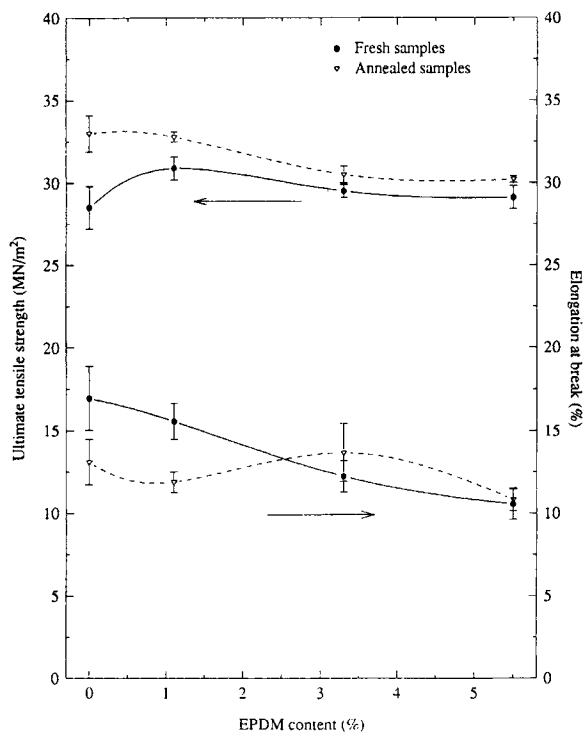
#### PP/EPDM Blends

It is apparent from Figure 1 that addition of up to 5.5% EPDM to PP resulted in only a slight increase in the Charpy impact strength, with no change in the flexural modulus of the fresh samples. The increase in the impact strength was manifested upon the addition of only 1.1% EPDM, after which no further change took place.

Although there was an observable decrease in yield strain and yield stress, this change was insignificant. In fact, for all blends discussed in this report, the tensile yield properties showed only slight



**Figure 1** Effect of EPDM content on the impact properties of PP.



**Figure 2** Effect of EPDM content on the tensile properties of PP.

variations, and hence the tensile yield properties will not be discussed further. More significant was the change in the elongation at break. Figure 2 outlines the change in the ultimate tensile properties of EPDM-modified PP with increasing amount of EPDM. Here we observed that elongation at break decreased with increasing EPDM content, with a

40% loss in ultimate elongation at 5% EPDM content. However, addition of 1.1% EPDM caused an initial increase in the ultimate tensile strength (UTS), and further addition of EPDM resulted in a small decline in this property.

As seen in Table III, the gate puncture strength of neat PP was found to be 17.4 kgf. Addition of 5% EPDM improved this by ~ 25%, to 21.7 kgf.

The DSC results for the neat PP and for the 94.5/5.5 PP/EPDM blend are shown in Table III. Both crystallization and melting thermograms indicated that addition of EPDM to PP resulted in a significant reduction in the crystallinity of the PP (59 to 44%).

Figures 1 and 2 also show the effect of annealing on the impact and tensile properties. The first observation to note is that the flexural modulus and the UTS increased as a result of the annealing treatment. On the other hand, the impact strength decreased with annealing. The effect of annealing on the elongation at break varied with composition. At less than 1.1% EPDM content, annealing reduced the elongation at break. The elongation at break of the samples containing 3.3 or 5.5% EPDM remained the same or increased slightly upon annealing. It is interesting to note that the effect of annealing is more pronounced for the PP than for the blends. The flexural modulus of the pure PP was seen to increase dramatically upon annealing (21%), whereas the amount of this increase diminished as EPDM was added (10 to 2%). The same was true for the UTS, and, incidentally, also in the yield stress. Annealing of the neat PP resulted in a large

**Table III** Properties of Blends of PP, HDPE, and EPDM

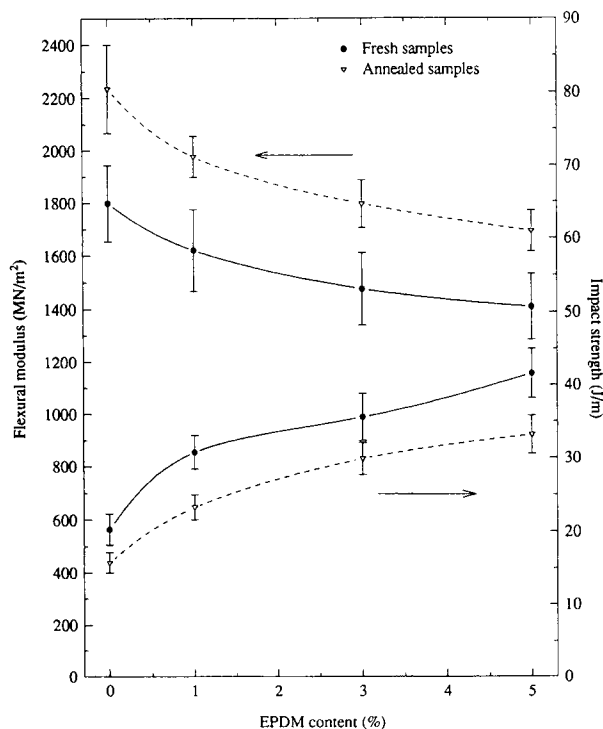
| Property   | PP/HDPE/EPDM |            |            |              |
|--|--------------|------------|------------|--------------|
|  | 100/0/0      | 90/10/0    | 94.5/0/5.5 | 85.5/9.5/5.0 |
| <b>Impact properties</b>                                 |              |            |            |              |
| Flexural modulus (MN/m <sup>2</sup> )                    | 1860 ± 140   | 1800 ± 145 | 1820 ± 96  | 1410 ± 120   |
| Impact strength (J/m)                                    | 18.7 ± 1.1   | 20.3 ± 2.1 | 23.6 ± 1.1 | 41.6 ± 3.4   |
| <b>Tensile properties</b>                                |              |            |            |              |
| Yield stress (MN/m <sup>2</sup> )                        | 35.3 ± 0.2   | 35.7 ± 0.4 | 30.4 ± 0.4 | 32.3 ± 0.4   |
| Yield strain (%)   | 8.1 ± 0.4    | 7.7 ± 0.4  | 6.6 ± 0.4  | 7.5 ± 0.6    |
| Ultimate tensile strength (MN/m <sup>2</sup> )           | 28.5 ± 1.3   | 30.9 ± 1.4 | 29.1 ± 0.7 | 30.1 ± 0.7   |
| Elongation at break (%)                                  | 17.0 ± 1.9   | 12.9 ± 1.6 | 10.5 ± 0.9 | 11.8 ± 0.8   |
| <b>Gate-region impact strength</b>                       |              |            |            |              |
| Gate puncture strength (kgf)                             | 17.4 ± 3.7   | 4.4 ± 0.7  | 21.7 ± 2.7 | 20.7 ± 2.8   |
| <b>Thermal properties (DSC), <math>\chi_c</math> (%)</b> |              |            |            |              |
| PP + PE, crystallization                                 | 59           | 56         | 44         | 58           |
| PP, from melting   | 59           | 53         | 44         | 54           |
| HDPE, from melting                                       | —            | 66         | —          | 68           |

drop in the gate puncture strength, from 17.4 kgf for fresh PP to 4.2 kgf for the annealed material. Annealing of the PP/EPDM blend resulted in a slight drop compared to the fresh PP/EPDM material, from 21.7 to 17.4 kgf.

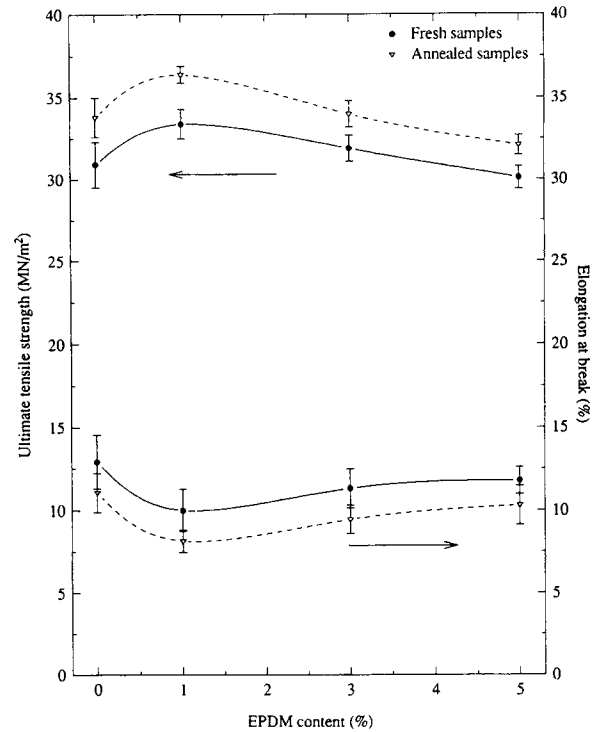
### PP/HDPE/EPDM Ternary Blends

The effect of adding EPDM to a 90/10 blend of PP and HDPE on the notched Charpy impact properties is shown in Figure 3. There was a slight softening of the material as indicated by a drop in the flexural modulus, compared with no change in the case of PP/EPDM blends. In addition, there was a large increase ( $\sim 105\%$  at 5% EPDM content) in the impact strength of the blend.

Addition of EPDM to the 90/10 PP/HDPE blend had no effect on the tensile yield strain and caused only a slight drop in the yield stress ( $\sim 10\%$  at a 5.0% EPDM loading). A greater effect was seen in the ultimate tensile properties (Fig. 4). One percent EPDM enhanced the UTS, but further addition caused a decrease in this property. The ultimate elongation, on the other hand, reacted in the opposite trend, with 1% EPDM reducing the elongation at break and further addition improving this property. The net effect was that addition of 5%



**Figure 3** Effect of EPDM content on the impact properties of a 90/10 PP/HDPE blend.



**Figure 4** Effect of EPDM content on the tensile properties of a 90/10 PP/HDPE blend.

EPDM resulted in no change in either UTS or ultimate elongation of the PP/HDPE blend.

The gate puncture strength of the 90/10 PP/HDPE blend was greatly enhanced by addition of EPDM (Table III). Whereas the load at failure for the 90/10 blend was 4.4 kgf, EPDM improved this by 370%, to 20.7 kgf.

A comparison of the degree of PP and HDPE crystallinity of the 90/10 PP/HDPE blend with the EPDM-modified blend, as determined from the DSC, showed that EPDM had no effect on the crystallinity of the PP and HDPE phases (Table III).

The effect of annealing the ternary blends is also shown in Figures 3 and 4 (dashed lines). Exposing these samples to 75°C for 7 days resulted in an increase in the flexural modulus and the UTS, and a decrease in the impact strength and the elongation at break. The trends exhibited by the fresh samples due to the effect of EPDM content were also shown by the annealed samples. Annealing also resulted in a small drop in the gate puncture strength of the 85.5/9.5/5.0 PP/HDPE/EPDM system from 20.7 kgf for the fresh material to 16.7 kgf for the annealed material.

### EPDM Systems

To facilitate the discussion of the effect of addition of EPDM to PP and to the 90/10 PP/HDPE blend,

the relevant results have been summarized and tabulated in Table III. Reading across each row allows us to compare the results for pure PP, the 90/10 PP/HDPE blend, addition of 5.5% EPDM to PP, and the addition of 5% EPDM to the 90/10 PP/HDPE blend. These results are for fresh samples only.

Choudhary and coworkers<sup>11</sup> recently reported on the effect of EPDM on the mechanical properties of PP/EPDM blends. They found that addition of up to 15% of an EPDM improved the impact strength of PP only very slightly. A greater enhancement of this property was observed at EPDM contents in excess of 20%. This improvement was accompanied by losses in the tensile yield stress and Young's modulus and by an increase in the elongation at break of the material, although addition of only 5% EPDM caused a slight decrease in the elongation at break. From wide angle X-ray diffraction as well as from DSC experiments, these authors also found that addition of EPDM to PP reduced the overall crystallinity of the PP. It is clear that our own results from Table III closely match those reported by Choudhary et al.<sup>11</sup> In essence, addition of small amounts of EPDM (~ 5%) to PP resulted in a slight improvement in the impact strength, a slight decrease in the elongation at break, and a significant reduction in the apparent crystallinity of the material.

From Table III it can be seen that addition of EPDM to the 90/10 PP/HDPE blend resulted in a considerable decrease in the flexural modulus and a small decrease in the elongation at break. However, EPDM served to improve the impact properties of the 90/10 blend, doubling the Charpy impact strength and enhancing the gate puncture resistance by 370%. This indicates that EPDM is effective at compatibilizing PP and HDPE from an impact failure perspective.

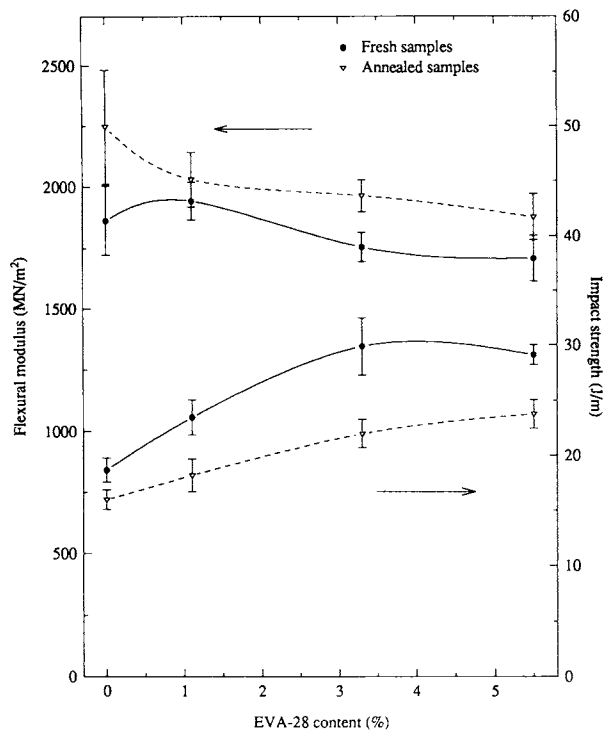
Choudhary et al.<sup>3</sup> reported that addition of up to 5% EPDM rubber to a 90/10 PP/HDPE blend resulted in an initial decrease in the elongation at break. However, further addition resulted in an increase in this property to values well above that of neat PP (10–15% EPDM) and even above neat HDPE (20% EPDM). This increase was accompanied by a small decrease in the tensile yield stress (<10% drop) and a large increase in the Izod impact strength. They concluded that addition of 5–10% EPDM aided the compatibilization of blends of iPP and HDPE.

In the case of ternary blends of PP, HDPE, and EPDM, our results are again consistent with those of Choudhary et al.<sup>3</sup> However, whereas these authors

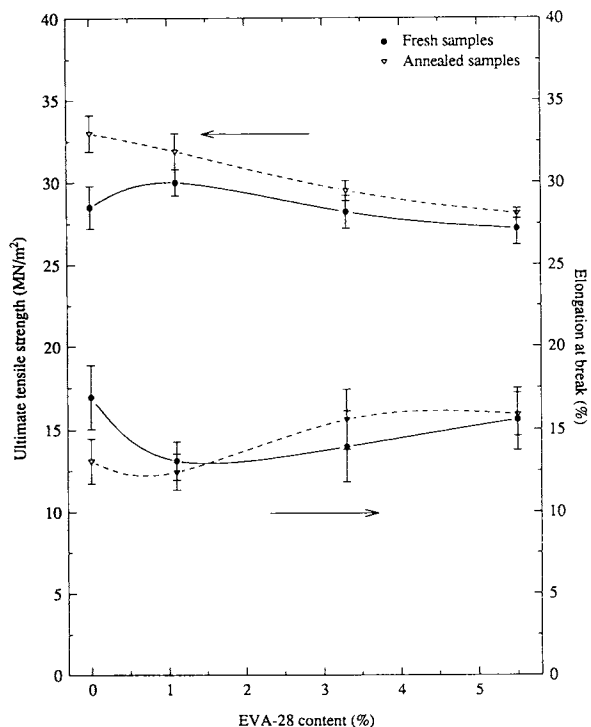
considered EPDM to be an effective compatibilizer for PP and HDPE, our results indicated that more care must be taken in making that statement. The desired final properties, determined from the expected end use, must also be stated. Addition of 5% EPDM greatly improved the impact strength and the gate puncture strength of the 90/10 PP/HDPE blend, but left the elongation at break unchanged, about 30% lower than that of neat PP. Thus, it would be more appropriate to argue that EPDM is a good compatibilizer of PP and HDPE so long as failure at low tensile deformation rate is not critical and only the high rate impact performance is important. Conversely, if the criterion of elongation at break at low deformation rate is important, then it must be concluded that EPDM (at a loading of 5% or less) is a poor compatibilizer for PP/HDPE blends.

We observed that addition of 10% HDPE to PP resulted in a small increase in the impact strength of the PP (~ 9%), and that addition of 5.5% EPDM rubber to PP increased the impact strength of the PP by 27%. It is interesting to note, therefore, that addition of both EPDM and HDPE to PP resulted in a large increase (>105%) in the impact strength. This observation was made by Stehling and coworkers,<sup>4</sup> who investigated the properties of rubber-modified PP. They found that addition of HDPE to PP did not improve the unnotched Izod impact strength (-18°C) of the PP, presumably due to the poor adhesion between PP and HDPE, and possibly also due to the nonrubbery nature of the HDPE. Addition of 20% EP rubber to the PP resulted in an increase in the Izod impact strength from 2.6 to 6.4 J/cm. However, when both HDPE and EP rubber (EPR) were added to PP (80 PP/10/7 EPR/9.3 HDPE), the unnotched Izod impact strength at -18°C increased to 16 J/cm. Study of these blends by SEM revealed that HDPE and EPR may form either a core-shell or interpenetrating network (IPN) morphology, depending on the mixing method. Melt blending of HDPE and EPR (50/50 wt %) resulted in a cocontinuous morphology. This morphology was retained by the larger particles in a ternary blend of PP and HDPE/EPR with PP as the matrix. However, if all three materials were melt blended simultaneously, a core-shell morphology was observed. No effect of morphology on the impact strength was observed. The observed synergism between HDPE and EPR was postulated by the authors to arise from these core-shell and IPN structures.

Our SEM investigation on the fracture surfaces of the PP/EPDM, PP/HDPE, and PP/HDPE/EPDM blends failed to reveal any significant dif-



**Figure 5** Effect of EVA-28 content on the impact properties of PP.



**Figure 6** Effect of EVA-28 content on the tensile properties of PP.

ference in morphology. However, our DSC study rendered indirect evidence that an IPN morphology was obtained in the case of the PP/HDPE/EPDM blend. The summary of thermal properties in Table III shows that addition of EPDM to PP greatly reduced the crystallinity of the PP, while addition of HDPE to PP resulted in only a slight reduction in the overall crystallinity of the PP. However, when both HDPE and EPDM were added to PP, the overall crystallinity of the PP in the ternary blend was unaffected, compared to that of neat PP. This suggests that the EPDM is not in intimate contact with the PP, because the crystallization behavior of the PP in the ternary blend was not affected. This affords indirect evidence for the formation of an IPN morphology.

The annealing of the binary blends of PP and EPDM displayed some interesting behavior that warrants further comment. We noted that addition of EPDM reduced the response of the system to annealing for the modulus-type properties. Aging of PP that resulted in a change in modulus is generally believed to arise from perfection of existing crystallites and in the crystallization of amorphous material. There are two possible explanations for the observed phenomenon of nonresponse of the PP/EPDM blends toward annealing: either EPDM increases the crystallinity of fresh PP such that aging has no further effect, or EPDM hinders the rearrangement, perfection, and crystallization of amorphous material of the PP upon aging. In light of the DSC results, which show that addition of EPDM to PP reduces the crystallinity of the PP, the latter explanation seems more likely. How this restriction occurs is not clear, and further work is required to understand this phenomenon more fully.

## EVA Systems

### PP/EVA-28 Binary Blends

The variation of the impact strength of blends of PP and EVA-28 with EVA content is shown in Figure 5. While addition of EVA-28 to PP resulted in only a small change in the flexural modulus of the blend, it improved the impact strength by about 56% for EVA contents greater than 3.3%.

Once again, very little change was observed in the tensile yield behavior. The variation of ultimate tensile properties is outlined in Figure 6. Addition of 1.1% EVA-28 caused a drop in the elongation at break and a rise in the UTS. Further addition reversed the changes made upon the initial addition of EVA-28, with the UTS being reduced to the neat

PP values and the ultimate elongation being increased to near the neat PP levels.

The effect of EVA-28 on the gate puncture strength of PP is shown in Table IV. Addition of 5.5% EVA-28 improved this property by about 30%, from 17.4 to 22.8 kgf.

The DSC results shown in Table IV indicate that addition of 5.5% EVA-28 to PP reduced the crystallinity of the PP in the crystallization experiment from 59 to 49%. However, on melting, this difference is not observed (59% crystallinity for the neat PP, and 58% for PP in the binary blend).

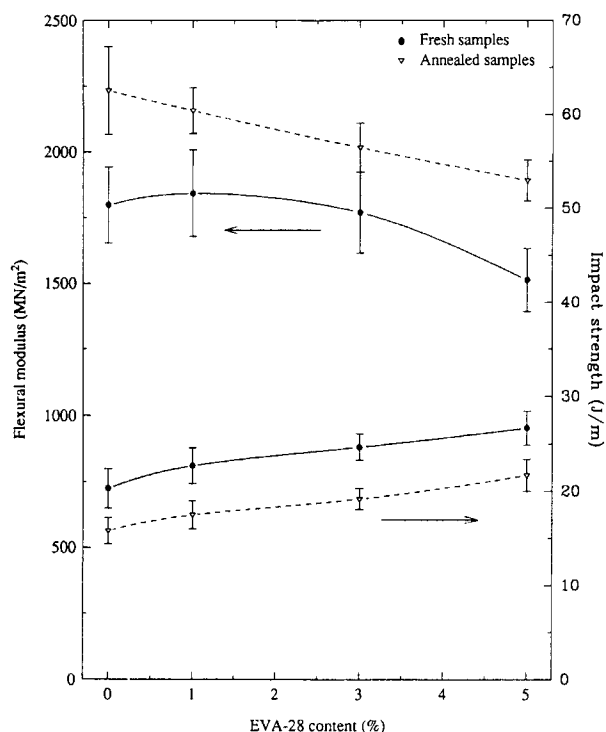
The effect of annealing is indicated by the dashed lines in Figures 5 and 6. The results are similar to those of PP/EPDM blends discussed previously.

### PP/HDPE/EVA-28 Ternary Blends

Addition of up to 3.3% EVA-28 to a 90/10 PP/HDPE blend had no effect on the flexural modulus (Fig. 7). Addition of 5.5% EVA-28 resulted in a decrease in this property. The impact strength increased monotonously with EVA-28 content. Addition of 5.5% EVA-28 increased the impact strength of the material by about 30%.

The tensile properties of the ternary blends containing EVA-28 are shown in Figure 8. Incorporation of EVA-28 into the 90/10 PP/HDPE blend had no effect on the tensile yield behavior of the material. In fact, the observable change in tensile property was the UTS, which dropped slightly ( $\sim 8\%$ ).

Table IV indicates that EVA-28 improved the gate puncture strength of the 90/10 PP/HDPE blend from 4.4 to 10.1 kgf, an increase of more than 125%.



**Figure 7** Effect of EVA-28 content on the impact properties of a 90/10 PP/HDPE blend.

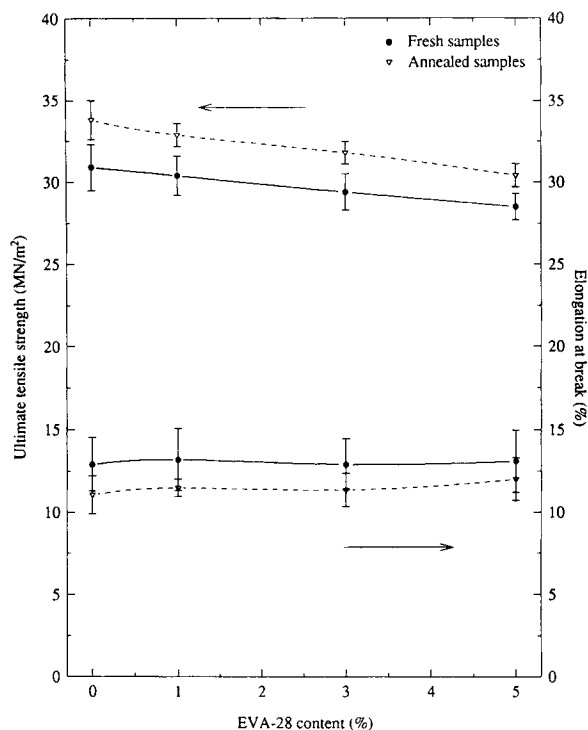
There was essentially no change in the degree of crystallinity as determined by DSC analysis for the ternary blends containing EVA-28 (Table IV).

Figures 7 and 8 also show the effect of annealing on the mechanical properties of the ternary blends. Similar to previous observations, the flexural modulus and UTS both increased with aging, and the

**Table IV** Properties of Blends of PP, HDPE, and EVA-28

| Property   | PP/HDPE/EVA-28 |            |            |              |
|--|----------------|------------|------------|--------------|
|  | 100/0/0        | 90/10/0    | 94.5/0/5.5 | 85.5/9.5/5.0 |
| <b>Impact properties</b>                                 |                |            |            |              |
| Flexural modulus (MN/m <sup>2</sup> )                    | 1860 ± 140     | 1800 ± 145 | 1708 ± 94  | 1514 ± 120   |
| Impact strength (J/m)                                    | 18.7 ± 1.1     | 20.3 ± 2.1 | 29.1 ± 0.9 | 26.7 ± 1.8   |
| <b>Tensile properties</b>                                |                |            |            |              |
| Yield stress (MN/m <sup>2</sup> )                        | 35.3 ± 0.2     | 35.7 ± 0.4 | 32.7 ± 0.5 | 33.7 ± 0.4   |
| Yield strain (%)   | 8.1 ± 0.4      | 7.7 ± 0.4  | 7.6 ± 0.4  | 7.2 ± 0.6    |
| Ultimate tensile strength (MN/m <sup>2</sup> )           | 28.5 ± 1.3     | 30.9 ± 1.4 | 27.2 ± 1.0 | 28.5 ± 0.8   |
| Elongation at break (%)                                  | 17.0 ± 1.9     | 12.9 ± 1.6 | 15.6 ± 1.9 | 13.1 ± 1.9   |
| <b>Gate-region impact strength</b>                       |                |            |            |              |
| Gate puncture strength (kgf)                             | 17.4 ± 3.7     | 4.4 ± 0.7  | 22.8 ± 1.5 | 10.1 ± 1.3   |
| <b>Thermal properties (DSC), <math>\chi_c</math> (%)</b> |                |            |            |              |
| PP + PE, crystallization                                 | 59             | 56         | 49         | 57           |
| PP, from melting   | 59             | 53         | 58         | 53           |
| HDPE, from melting                                       | —              | 66         | —          | 69           |





**Figure 8** Effect of EVA-28 content on the tensile properties of a 90/10 PP/HDPE blend.

impact strength and ultimate elongation decreased with aging. The gate puncture resistance also decreased, from 10.1 to 7.1 kgf.

### EVA-28 Systems

To the best of our knowledge, only a few publications have appeared on the study of EVA/PP blends,<sup>5,12-15</sup> and no work has been published on ternary blends of PP, HDPE, and EVA. We briefly summarize here the results of the studies dealing with PP/EVA blends. Thomas<sup>12</sup> studied the effect of blend ratio on tensile impact behavior and found that the tensile impact strength (TIS) was dependent on the size, shape, and the continuity of the EVA phase. Small particle sizes encountered at low EVA loadings (<30%) greatly enhanced the TIS. Thomas et al.<sup>13</sup> also studied the wear and tear behavior of PP/EVA blends in which the rubbery phase (EVA) was dynamically crosslinked with dicumyl peroxide. It was found that the wear and tear resistance was optimal when the rubber phase was continuous, which occurred at > 60% EVA content. In both of these studies, the EVA contained 45% VA.

Gupta et al. studied the mechanical<sup>15</sup> and the melt-rheological<sup>5</sup> behavior of PP/EVA blends. The study included the effect of blending ratio (0-40%),

VA content (9, 12, and 19%), and temperature (-196-60°C) on the Izod impact strength of blends of PP and EVA. They found that for a particular EVA, the Izod impact strength increased with up to 10% EVA content, leveled off, and then began to increase with EVA loadings of greater than 30%. They also reported that an increase in VA content increased the effectiveness of the EVA as an impact toughener for PP. The best EVA (containing 19% VA) was shown to provide better impact strength improvement than EPDM at the same blending ratio of 90/10 PP/rubber.

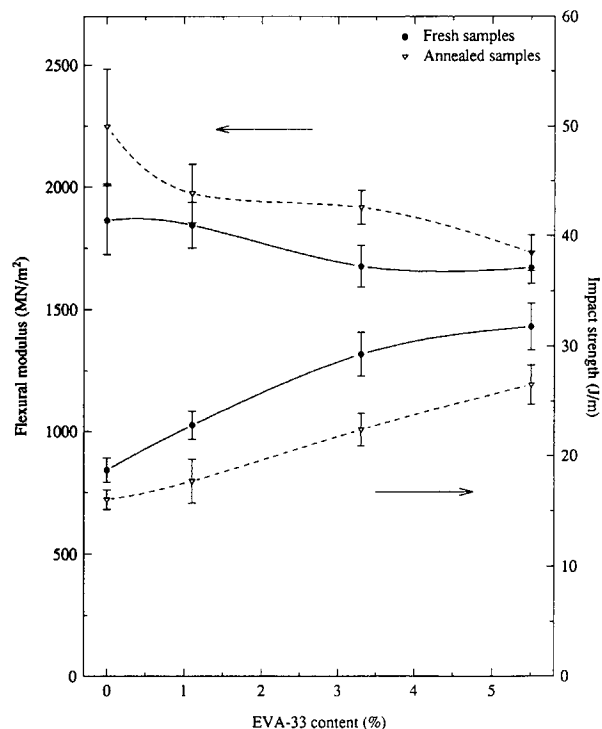
Our results, which are summarized in Table IV, are in good agreement with those of Gupta et al.<sup>15</sup> It is clear from our results that addition of 5.5% EVA-28 to PP enhanced the Charpy impact strength of the PP. In fact, we also found that EVA-28 was a better impact modifier than EPDM for PP. However, in the case of ternary blends of PP/HDPE/EVA, we observed only a small improvement in impact strength, in contrast to the large enhancement observed in the PP/HDPE/EPDM systems. Thus, while EPDM is more efficient at improving the impact strength of a 90/10 PP/HDPE blend, EVA-28 is more effective at improving the impact strength of PP.

This observation is also true in the case of the gate puncture strength results (Tables III, IV). EVA-28 improved the gate puncture strength of PP slightly better than EPDM; however, EPDM outperformed EVA-28 in improving the gate puncture strength of the 90/10 PP/HDPE blend.

Turning to the tensile properties, however, we see a different picture emerge. We observed that addition of EPDM to the 90/10 PP/HDPE blend caused a decline in the ultimate elongation. Although EVA-28 did not bring the elongation at break back to the neat PP levels, it also did not have any detrimental effect. EVA-28 left the ultimate elongation unchanged. The effects of EPDM and EVA-28 on the 90/10 PP/HDPE blend are essentially the same for the other tensile properties. Thus, it is clear that as far as the tensile properties are concerned, EVA-28 is a better compatibilizer than EPDM.

### PP/EVA-33 Binary Blends

The effect of EVA-33 content of the impact and tensile properties of PP are shown in Figures 9 and 10. The behavior of PP/EVA-33 blends is very similar to that of PP/EVA-28 blends, with the following notable differences. EVA-33 imparted a better impact strength to PP than did the EVA-28. However, the elongation at break of the PP/EVA-33 blend



**Figure 9** Effect of EVA-33 content on the impact properties of PP.

was inferior to that of the PP/EVA-28 blend. Further, there was no observed effect of annealing on the ultimate tensile strength for the PP/EVA-33 blends. The UTS of the neat PP increased upon annealing, but the UTS of the blends was unaffected by annealing. Annealing of the thin-walled containers resulted in a drop in the gate puncture strength from 22.9 to 15.9 kgf, a smaller change than for the corresponding PP/EVA-28 system.

#### PP/HDPE/EVA-33 Ternary Blends

It is clear from Figure 11 that addition of EVA-33 to a 90/10 blend of PP and HDPE enhanced the impact strength of the PP/HDPE material. While incorporation of EVA-33 did cause some unsystematic variation in the flexural modulus, it also increased the impact strength by  $\sim 50\%$ .

Once again, the tensile yield properties showed very little variation with EVA-33 content. Figure 12, however, indicates that addition of EVA-33 to the 90/10 PP/HDPE material resulted in a larger decrease ( $\sim 11\%$ ) in the UTS, but a slight increase ( $\sim 11\%$ ) in the elongation at break, as contrasted to previous blends discussed.

EVA-33 only marginally improved the gate puncture strength of the PP/HDPE blend from 4.4 to 6.6 kgf (Table V).

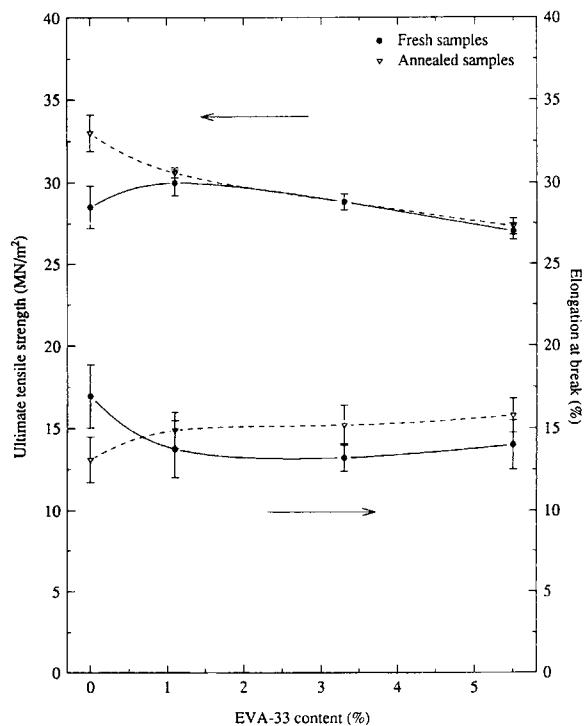
Modification of the 90/10 PP/HDPE blend with EVA-33 increased the degree of crystallinity of the HDPE phase, and left the PP crystallinity unchanged in the melting experiment, as shown in Table V.

Annealing of these ternary blends (Figs. 11, 12) resulted in an increase in the flexural modulus and UTS and a decrease in the impact strength and elongation at break. The gate puncture strength was greatly reduced (50%, 6.6 to 3.3 kgf) by annealing. This result is also lower than the result for the fresh 90/10 PP/HDPE blend (4.4 kgf).

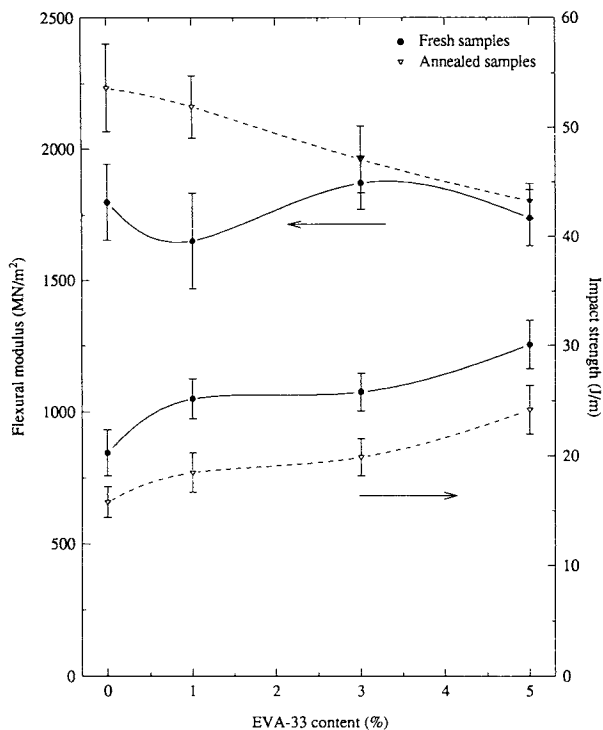
#### EVA-33 Systems

The salient results for the EVA-33 blends are summarized in Table V. It is clear from the impact and tensile data on PP/EVA-33 blends that EVA-33 is a good impact modifier for PP. This improvement is accompanied by a slight decrease in the elongation at break. EVA-33 is also effective at enhancing the gate-region impact strength of PP.

As a compatibilizer for the 90/10 PP/HDPE blend, EVA-33 was found to enhance the impact strength, and the elongation at break was also significantly improved. However, the gate puncture strength was not improved significantly.



**Figure 10** Effect of EVA-33 content on the tensile properties of PP.



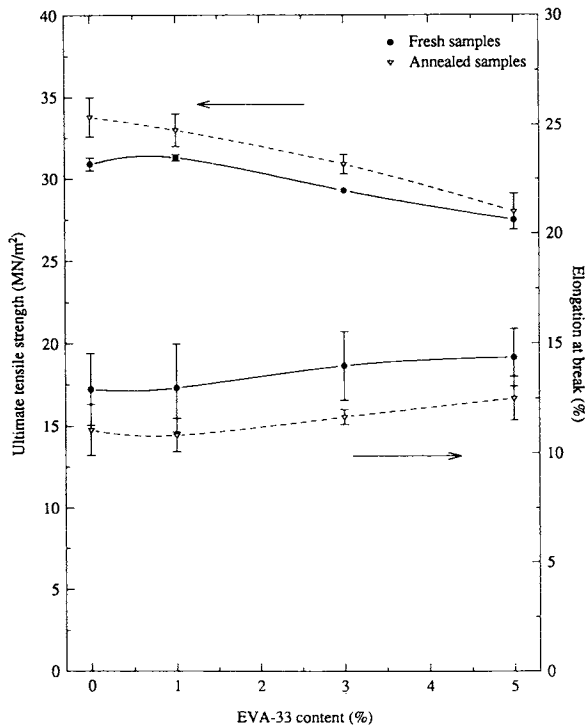
**Figure 11** Effect of EVA-33 content on the impact properties of a 90/10 PP/HDPE blend.

### General Discussion

One of the results of the work of Gupta et al.<sup>15</sup> was that the effectiveness of EVA as an impact modifier for PP was related to the VA content of the EVA. The higher the VA content, the better the improvement in impact strength. This is attributed to the increasing elastomeric character of the EVA with increasing VA content. As the VA content increases, the degree of crystallinity of the EVA decreases. (There are, of course, other factors that govern the degree of crystallinity, such as short and long chain branching frequency and distribution.) The bulkiness of the acetoxy side chain disrupts regular chain packing, and this effect increases with increasing VA content. Typically, an EVA with a VA content of 10% will have a degree of crystallinity in the range of 30%. The crystallinity is halved to 15% if the VA content is increased to 20%.<sup>16</sup> Thus in the study of Gupta et al.<sup>15</sup> the degree of crystallinity of the EVAs used varied between 15 and 30%. Hence, large differences were observed in the elastomeric nature of the EVAs. It is well known that an important factor in impact modification of PP is the rubbery nature of the impact modifier. Hence, it is not surprising that Gupta et al.<sup>15</sup> found a correlation between VA content and impact improvement.

Our own results also show this behavior, but to a much lesser extent. EVA-33 is more effective at improving the impact strength of PP than EVA-28. The effect is quite small, however, owing to the small difference in VA content (28 and 33%). At these VA contents the crystallinity of the sample is very small. EVA-28 has a degree of crystallinity of about 12%, and the EVA-33 has a degree of crystallinity of about 9%. The EVA-33 will therefore be slightly more elastomeric than the EVA-28, and one would expect, therefore, that EVA-33 will be a more effective impact modifier for PP than EVA-28.

Our results also indicate that both EVAs are more effective at improving the impact strength of PP than EPDM. This was the main point of the article by Gupta et al.,<sup>15</sup> but they give no indication as to why this is the case. There are three main factors that govern the impact modification of PP: the elastomeric nature of the impact modifier, the interfacial adhesion of the impact modifier and the PP, and the particle size and distribution of the impact modifier in the PP. Increased impact improvement can be obtained by increasing the elastomeric nature of the material, increasing the interfacial adhesion, decreasing the particle size, and reducing the polydispersity of the rubber phase. It would seem, based on our results, that the three copolymers used in



**Figure 12** Effect of EVA-33 content on the tensile properties of a 90/10 PP/HDPE blend.

**Table V Properties of Blends of PP, HDPE, and EVA-33**

| Property   | PP/HDPE/EVA-33 |            |            |              |
|--|----------------|------------|------------|--------------|
|  | 100/0/0        | 90/10/0    | 94.5/0/5.5 | 85.5/9.5/5.0 |
| <b>Impact properties</b>                                 |                |            |            |              |
| Flexural modulus (MN/m <sup>2</sup> )                    | 1860 ± 140     | 1800 ± 145 | 1670 ± 65  | 1739 ± 107   |
| Impact strength (J/m)                                    | 18.7 ± 1.1     | 20.3 ± 2.1 | 31.8 ± 2.1 | 30.1 ± 2.2   |
| <b>Tensile properties</b>                                |                |            |            |              |
| Yield stress (MN/m <sup>2</sup> )                        | 35.3 ± 0.2     | 35.7 ± 0.4 | 31.9 ± 0.1 | 33.1 ± 0.1   |
| Yield strain (%)   | 8.1 ± 0.4      | 7.7 ± 0.4  | 7.9 ± 0.3  | 7.5 ± 0.5    |
| Ultimate tensile strength (MN/m <sup>2</sup> )           | 28.5 ± 1.3     | 30.9 ± 1.4 | 27.0 ± 0.5 | 27.5 ± 1.0   |
| Elongation at break (%)                                  | 17.0 ± 1.9     | 12.9 ± 1.6 | 14.0 ± 1.5 | 14.4 ± 1.31  |
| <b>Gate-region impact strength</b>                       |                |            |            |              |
| Gate puncture strength (kgf)                             | 17.4 ± 3.7     | 4.4 ± 0.7  | 22.9 ± 1.1 | 6.6 ± 0.9    |
| <b>Thermal properties (DSC), <math>\chi_c</math> (%)</b> |                |            |            |              |
| PP + PE, crystallization                                 | 59             | 56         | 50         | 57           |
| PP, from melting   | 59             | 53         | 60         | 52           |
| HDPE, from melting                                       | —              | 66         | —          | 72           |

this research may be ranked in order of increasing elastomeric nature as follows: EVA-33 > EVA-28 > EPDM. This is supported also by considering the ethylene content of the three materials, which decreases in the above sequence. It would be expected that increasing the ethylene content would decrease the elastomeric nature of the material, because ethylene sequences would be "hard" materials.

Turning our attention to the compatibilization of the 90/10 PP/HDPE blend, we see that it is important to clarify and specify the desired mechanical properties before judging one copolymer as being a better compatibilizer than another. Clearly, if one is concerned about the strength of the high-shear flow regions of thin-walled containers and not too concerned about a slight deterioration in tensile properties, then EPDM is the best compatibilizer for these systems. On the other hand, if good tensile properties are important, then EVA-33 would be the compatibilizer of choice, because it enhanced the elongation at break. In fact, EVA-33 is the worst compatibilizer for improving gate-region impact strength, and EPDM is a poor compatibilizer for tensile properties. It is evident from this discussion that the term compatibilizer must be used in reference to the desired end-use properties.

## CONCLUSIONS

1. Assessment of the effectiveness of EPDM, EVA-28, and EVA-33 as compatibilizers for PP/HDPE blends indicates that these co-

polymers can be ordered in terms of increasing compatibilization as follows: for impact properties, EVA-33 < EVA-28 < EPDM, and for tensile properties, EPDM < EVA-28 < EVA-33.

2. EPDM and both EVAs are equally efficient when it comes to improving the gate puncture strength of PP. However, in the case of PP/HDPE blends, it was found that the gate puncture strength was enhanced greatly by EPDM, but only marginally by the EVAs. Neither EVA is suitable as a compatibilizer for PP/HDPE in this regard.
3. The EPDM/HDPE combination demonstrated a synergistic interaction in its effect on the impact strength of PP. Our earlier results indicate that HDPE is a poor impact modifier for PP. Generally, EPR are good impact modifiers if the particle size and distribution can be optimized. In our case, the EPDM used was a poor impact modifier, indicating that this material was poorly dispersed in the PP, as might be expected due to the high viscosity of the EPDM compared to the PP. However, when both HDPE and EPDM were added to PP, the resultant material had a good impact strength, because the HDPE improved the dispersion of the EPDM phase. This can be attributed to the mixing of the HDPE and EPDM phases to form either a core-shell or an IPN system.
4. We verified the findings of others who state that increasing the VA content in an EVA

yields a material that is better able to improve the impact strength of PP.

5. As an impact modifier for PP, EVA-28 and EVA-33 are far superior to the EPDM studied.

The authors gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada, the University Research Incentive Fund of Ontario, and Montell Canada Limited. The authors also acknowledge the assistance of G. Shields with the gate puncture testing, and the fruitful discussions with J. Keung and D. Pauk of Montell.

## REFERENCES

1. H. P. Blom, J. W. The, and A. Rudin, *J. Appl. Polym. Sci.*, **58**, 995 (1995).
2. D. W. Yu, M. Xanthos, and C. G. Gogos, *Adv. Polym. Technol.*, **11**, 295 (1992).
3. V. Choudhary, H. S. Varma, and I. K. Varma, *Polymer*, **32**, 2541 (1991).
4. F. C. Stehling, T. Huff, C. S. Speed, and G. Wissler, *J. Appl. Polym. Sci.*, **26**, 2693 (1981).
5. A. K. Gupta, B. K. Ratnam, and K. R. Srinivasan, *J. Appl. Polym. Sci.*, **46**, 281 (1992).
6. Z. Fang, Y. Tang, C. Chen, Q. Li, and C. Xu, *Hecheng Xiangjiao Gongye*, **15**, 290 (1992).
7. S. Pang and A. Rudin, *ACS Symp. Ser.*, **521**, (1993).
8. D. G. Cook, A. Rudin, and A. Plumtree, *Polym. Eng. Sci.*, **30**, 596 (1990).
9. I. Campoy, J. M. Arribas, M. A. Zaporta, C. Marco, M. A. Gomez, and J. G. Fatou, *Eur. Polym. J.*, **5**, 475 (1995).
10. R. L. Blaine, *Application Brief Number TA-12*, DuPont Company, Wilmington, DE.
11. V. Choudhary, H. S. Varma, and I. K. Varma, *Polymer*, **32**, 2534 (1991).
12. S. Thomas, *Mater. Lett.*, **5**, 360 (1987).
13. S. Thomas, B. R. Gupta, and S. K. De, *J. Mater. Sci.*, **22**, 3209 (1987).
14. X. M. Xie, M. Matsuoka, and K. Takemura, *Polymer*, **33**, 1996 (1992).
15. A. K. Gupta, B. K. Ratnam, and K. R. Srinivasan, *J. Appl. Polym. Sci.*, **45**, 1303 (1992).
16. *EVA Copolymers* [Technical literature], AT Plastics Inc, Brampton, Ontario, Canada.

Received August 9, 1995

Accepted October 27, 1995