

# Impact Toughening of Polypropylene by Ethylene Vinyl Acetate Copolymer

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## SYNOPSIS

In this article we studied the potential of ethylene vinyl acetate copolymer (EVA) as an impact modifier for isotactic polypropylene (PP). PP/EVA blend in the range 0–40 wt % EVA content is studied by using three grades of EVA containing 9, 12, and 19 wt % VA. Izod impact strength measurements were made at temperatures ranging from liquid nitrogen temperature to 60°C to explore the impact-toughening effect as a function of blending ratio both at low and above ambient temperatures. The results are compared with various reported blends of PP with other elastomers. Morphological studies through scanning electron microscopy on etched impact-fractured surfaces are carried out and a correlation of morphology and impact properties at various blending ratios is presented. Finally, a mathematical analysis of the data is performed in terms of second-degree polynomial to express impact strength as a simultaneous function of two variables, and an equation is proposed that shows the best fit with the experimental data. Relevant contour diagrams, based on the proposed equation, for optimization of properties are also presented.

## INTRODUCTION

Blending of polypropylene (PP) with elastomers has generated considerable interest for improvement of impact properties of PP, particularly at low temperatures. Various elastomers have been investigated for this purpose.<sup>1–10</sup> Most elastomers go up to a factor 1.5 in the low-temperature impact strength improvement, while styrene-ethylene-butylene-styrene triblock copolymer (SEBS) has been distinctly superior in this regard as it is reported<sup>7</sup> to improve low-temperature impact strength by a factor of 2.

Ethylene vinyl acetate copolymer (EVA) may also prove a suitable candidate for improving impact properties owing to the presence of olefinic segments and interactive vinyl acetate groups. In addition, the vinyl acetate concentration (VA%) may provide an additional variable to EVA for its role as impact modifier of PP. Furthermore, the glass transition temperature of EVA is quite low, which also indicates the possibility of achieving better low-temperature impact properties for the PP/EVA blend.

In this article, a study of impact properties of PP/EVA blend is presented at varying blending ratios from 0–40 wt % EVA content using EVA with three different VA% (9, 12, and 19 wt %). Impact properties are measured at various temperatures from liquid nitrogen temperature up to 60°C. The results are presented as variations of impact strength with various experimental variables. Mathematical analysis of the data is performed to establish a suitable equation representing the impact strength as a function of two variables: (1) the blending ratio or EVA content of the blend and (2) the temperature. Contour diagrams plotted from this equation have been presented for the optimization of the properties in a practical application and designing a material with a desired range of properties.

## EXPERIMENTAL

### Materials

Isotactic PP used was Koylene M-0030 grade (MFI-10) supplied by Indian Petrochemicals Corporation Ltd. EVA copolymer containing 12% VA (grade ELVAX-3134) supplied by du Pont was used and

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has an MFI of 8. The other two EVA samples containing 9 and 19% VA were obtained from U.S.I. Chemicals Co. The three samples are abbreviated as EVA-9, EVA-12 and EVA-19, where the number denotes VA% in each sample.

### Preparation of Blends

The binary blend of PP/EVA in the composition range 0–40 wt % EVA were prepared by melt mixing the appropriate quantities of polymers in a single-screw extruder (Betol BM-1820). Screw speed was 30 rpm and the preheating zones were maintained at 200, 200, and 210°C with die zone at 215°C. Blend samples obtained from the extruder in the form of long strands were chopped into granules in a granulator and dried at 70°C for 10 h.

### Test Specimens

Test specimens, the rectangular bars ( $6.4 \times 0.38 \times 1.25$  cm), (as per ASTM D-256) were prepared by injection molding on a Windsor SP-1 Injection Moulding Machine. A triangular notch of depth 2.5 mm and tip angle 45° was cut on these test specimens.

### Measurements

Izod impact strength of these specimens was measured on a falling hammer-type impact tester (FIE Impact Tester Model 042).

For impact testing at temperatures other than the ambient, specimens were kept for sufficiently long duration (around 12 h) in a constant-temperature bath or chamber and then quickly mounted and tested on the impact tester with minimum possible exposure to ambient condition. The risk of temperature variation in the interior of the sample was negligible due to the poor thermal conductivity of the samples. Test temperatures used were 60, 30, 0, -20, and -196°C. Measurements were made on at least five samples in each case and an average value was taken; the deviation was less than 5%.

Scanning electron microscopy (SEM) of the impact-fractured surfaces was carried out on Stereoscan (Model S360) of Cambridge Instruments. Samples were etched in toluene at 40°C for 2 h to dissolve out the EVA component.

## RESULTS AND DISCUSSION

### Ambient Temperature

#### Constant VA Content

The impact strength for the PP/EVA-12 blend varies as a function of blending ratio as shown in Figure 1. As the EVA content of the blend increases from 0–40 wt %, the impact strength increases, initially slowly up to 30 wt % EVA content and then quite rapidly at higher EVA contents. The impact strength of the blend at 40% EVA content is higher than that

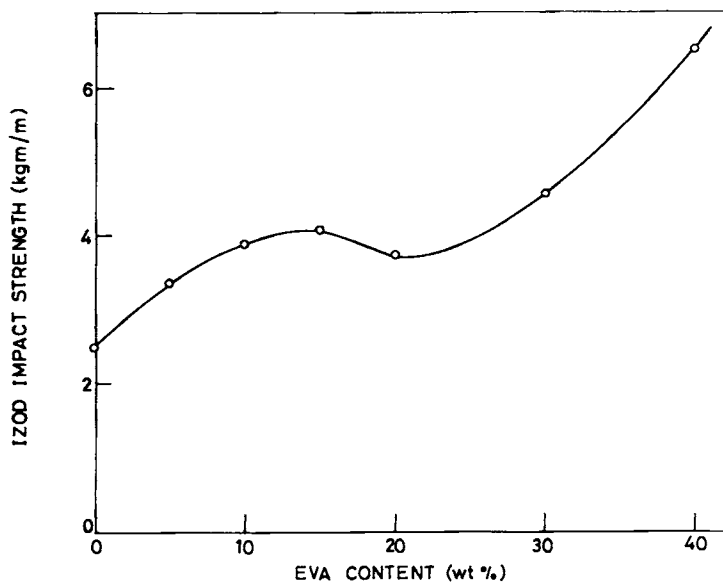


Figure 1 Impact strength as a function of composition of PP/EVA-12 blend.

**Table I Values of Relative Impact Strengths of the Blends of PP with Various Elastomers and Copolymers**

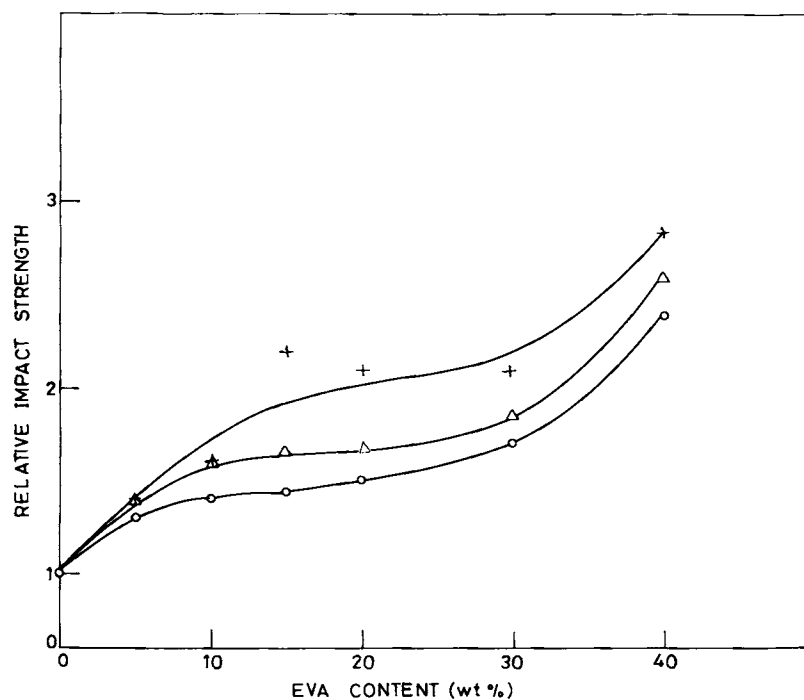
Blending Ratio	Elastomer/Copolymer					
	EVA-12	PBu	SEBS	ABS	EPDM	EPR
95/5	1.4	1.4	1.5	2.1	—	—
90/10	1.6	1.45	2.3	2.3	1.35	—
85/15	1.7	1.45	3.0	—	2.0	1.9
80/20	1.6	—	5.5	1.8	2.1	—
75/25	—	1.5	—	—	—	—
70/30	1.85	1.5	—	1.7	4.5	—
60/40	2.6	—	—	1.6	—	—
50/50	—	—	—	1.6	—	—

of pure PP by a factor of 2.6. The ratio of impact strength of the blend to that of pure PP (called relative impact strength) compares well with the blends of PP with various other elastomers and copolymers as seen from the data given in Table I. It is seen that at ambient temperature SEBS is the best impact modifier of PP while EPDM is next. EVA, which falls lower than EPDM in terms of the maximum improvement achieved (which is at 30% EPDM level), shows better impact strength improvement than EPDM at lower blending ratios.

Compared to polybutadiene (PBu), EVA produces better impact strength improvement in the entire range of blending ratios studied. Thus, EVA-12 seems a good candidate for impact strength improvement of PP and even superior than other elastomers and copolymers depending on the blending ratio.

#### Effect of VA Content

Effect of VA% on the impact strength vs. blending ratio curves is shown in Figure 2. The general shape of the curve is similar for all three VA% studied, showing a rapid increase of impact strength value up to 5% EVA content, followed by a slow rise up to 30% EVA content, and then a rapid increase of impact strength with increasing EVA content of the blend. These differences of impact strength in the different regions of blending ratios are accompanied by the differences in the morphology of dispersion, as will be discussed subsequently. The impact strength at a constant blending ratio increases with increasing VA% of the EVA used. However, at the highest VA% (i.e., EVA-19) there is a considerable scatter of data points that might be the effect of the abundance of strongly interacting vinyl acetate groups. Values of the relative impact strength are presented in Table II for the PP/EVA blend using



**Figure 2** Relative impact strength as a function of composition of PP/EVA blend at varying VA%: (○), 9; (△), 12; (+), 19.

**Table II** Relative Impact Strength of PP/EVA Blend Using EVA of Varying VA Contents

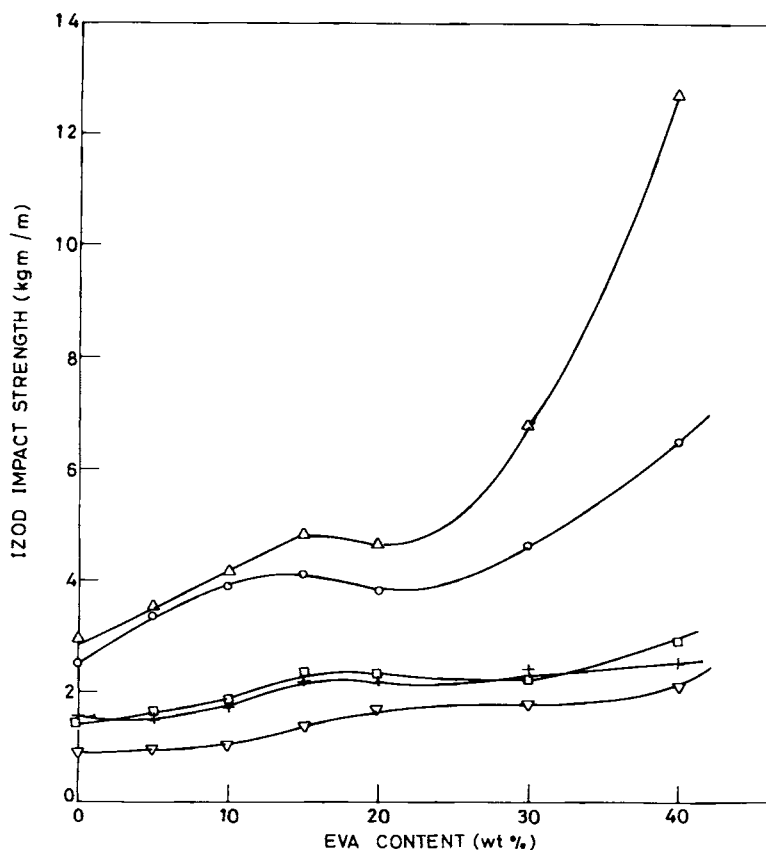
Blending Ratio (wt % EVA Content)	VA Content (wt %)		
	9	12	19
5	1.3	1.4	1.4
10	1.4	1.6	1.6
15	1.45	1.7	2.2
20	1.5	1.6	2.1
30	1.7	1.85	2.1
40	2.4	2.6	2.85

EVA of varying VA%. This observed increase of impact strength with increasing VA% of the EVA used is apparently due to the increasing elastomer character of EVA with increasing VA%.<sup>11</sup>

#### Effect of Temperature

The effect of temperature is studied only at a fixed VA%, the EVA-12. The impact strength vs. blending

ratio curve changes its character with variation of temperature as shown in Figure 3. For PP/EVA-12 blend, the curve at 60°C shows the steepest increase of impact strength and has similar features as described in the previous section for the case of ambient temperature. At temperatures of 0°C and below, the overall increase of impact strength becomes very small and the distinction of sharpness of variations in the two regions of blending ratio [viz. (1) 5–30% EVA content and (2) above 30% EVA content] becomes negligible. This is the effect of formation of glassy state of the matrix or both the components of the blend. At 0 and –20°C, the matrix component PP goes into its glassy state, while at –196°C both the matrix as well as the elastomer inclusions are in their glassy state. The impact strength is distinctly lower at all blending ratios when both components are in their glassy state than when only the matrix is in the glassy state. This is obvious because for impact toughening the rubbery character of the dispersed phase droplets is essential for the required instantaneous dissipation of energy through deformation of the droplets and subsequent



**Figure 3** Impact strength as a function of composition of PP/EVA-12 blend at varying temperatures (°C): (∇), –196; (+), –20; (□), 0; (○), 30; (Δ), 60.

formation of crazes and/or shear bands in the adjoining matrix. Several previous studies<sup>1-3</sup> have shown that the impact improvement becomes insignificant below the  $T_g$  of the elastomer.

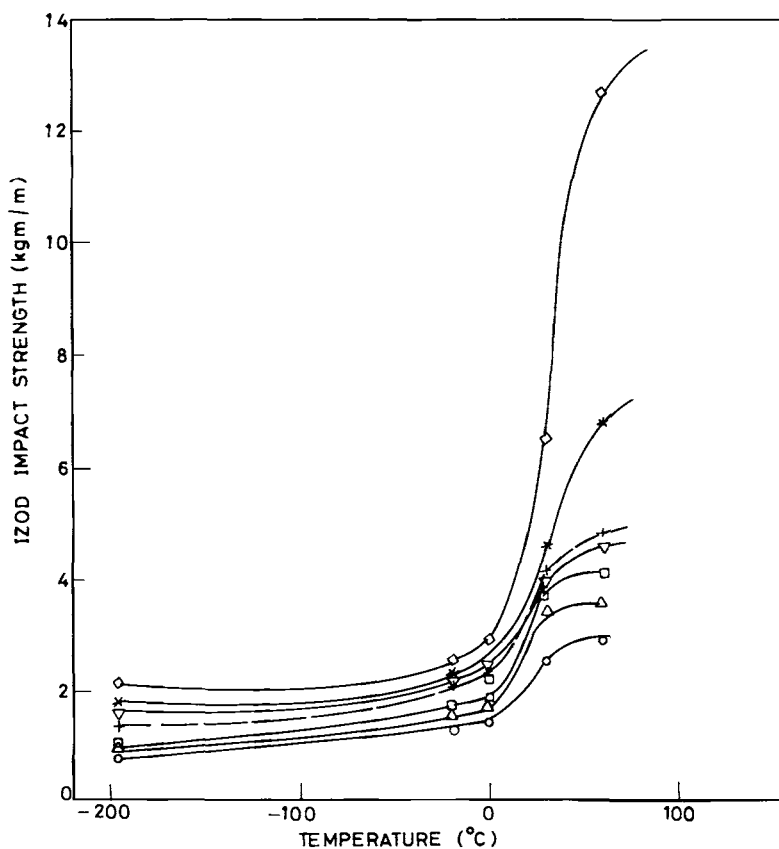
At constant blending ratios, the impact strength of the PP/EVA-12 blend varies with temperature as shown in Figure 4. Initially, from  $-196$  up to  $0^\circ\text{C}$  the impact strength shows a very small increase, and thereafter it rises rapidly, reaching a plateau around  $60^\circ\text{C}$ . This high-impact strength and its variation with temperature above the  $T_g$  of PP seems to suggest that glassy or rubbery state of the matrix plays an important role in impact toughening of polymers. The total increase of impact strength in this temperature range  $0$ – $60^\circ\text{C}$  varies with EVA content of the blend, implying the predominance of the role of EVA in impact toughening even when the matrix PP is in its flexible state, i.e., above its  $T_g$ .

Some observations of the stress-whitening effect in the impact fracture surfaces of these samples are quite systematic and noteworthy. At high EVA content (i.e., 30 and 40%) and at high temperatures

(i.e.,  $30$  and  $60^\circ\text{C}$ ), the stress whitening around the notch region was considerably greater than at other temperatures and blending ratios. At conditions favoring craze formation, viz., low temperatures, the stress-whitening effect was completely absent. However, at high temperatures (i.e.,  $30$  and  $60^\circ\text{C}$ ) but low EVA content ( $< 30$  wt %) the stress whitening was also not significant. It seems that this stress whitening is due to the formation of shear bands. Crazeing, which occurs in the glassy matrix, does not produce the stress whitening at the notch tip. As the temperature of the matrix becomes favorable for shear deformation of the matrix (i.e., above its  $T_g$ ), the shear bands form. These shear bands are induced by the dispersed phase droplets, which is clearly confirmed by the observation that at low EVA content the stress whitening is insignificant even at high temperatures.

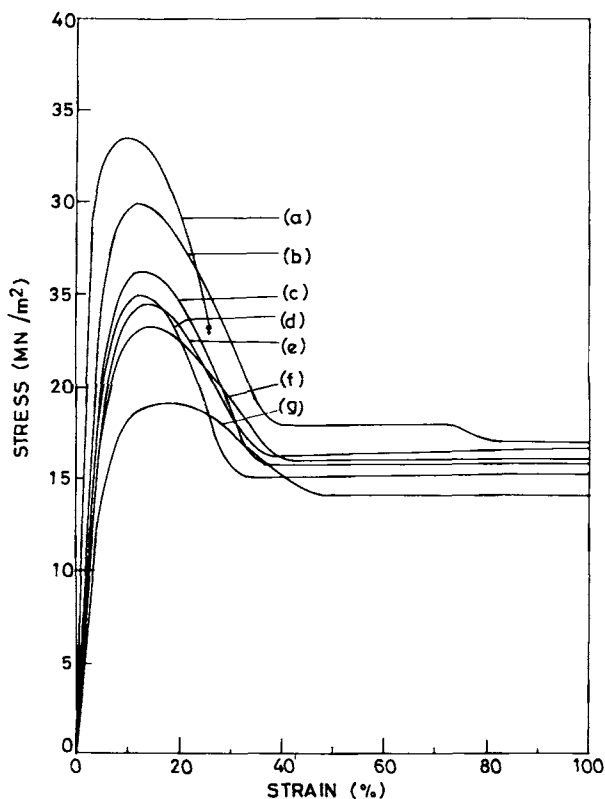
### Work of Yield

The area under the tensile stress-strain curve up to the end of the yield peak is defined as "work of



**Figure 4** Impact strength as a function of temperature of PP/EVA-12 blend at varying EVA content (wt %): (○), 0; (Δ), 5; (□), 10; (+), 15; (▽), 20; (\*), 30; (◇), 40.

yield." This is a measure of total energy of deformation in the yield region. Tensile stress-strain curves at ambient temperature for PP/EVA-12 blend at varying blending ratio are presented in Figure 5 to illustrate the effect of blending on the yield behavior. The work of yield increases with increasing EVA content as shown in Table III. Variation of impact strength with work of yield for the PP/EVA-12 blend, shown in Figure 6, is quite linear; the higher the impact strength the higher the work of yield. This linear correlation of impact strength with tensile work of yield indicates that the dispersed EVA domains have some similarity in their effect on tensile yielding and impact toughening of the PP/EVA blend. Tensile yielding is essentially a manifestation of molecular chain mobility, which is eased in the presence of the dispersed EVA domains. Thus, the present correlation seems to suggest that in the impact toughening (at ambient temperature) the molecular chain mobility plays an important role, which confirms the predominance of shear yielding over the crazing mechanism of toughening of this blend at ambient temperature.



**Figure 5** Stress-strain curves for PP/EVA-12 blend with varying EVA content (wt %): (a), 0; (b), 5; (c), 10; (d), 15; (e), 20; (f), 30; (g), 40. All samples, except PP, break beyond the scale of the figure at 100–400% strain.

**Table III** Area Under the Yield Peak of PP/EVA-12 Blend with Varying EVA Content

EVA (wt %)	Area under Yield Peak (Arbitrary units)
0	10.3
5	13.0
10	13.5
15	13.9
20	13.6
30	16.3
40	16.3

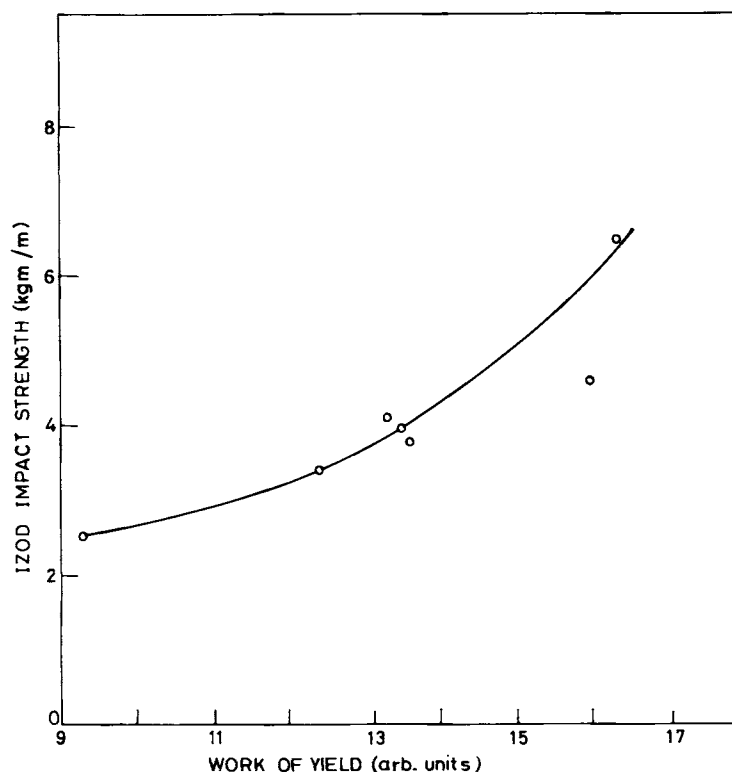
### Morphology

SEMs of the etched impact fracture surfaces are shown in Figure 7. The two-phase morphology is clearly visible at all compositions of the blend, confirming the immiscibility of EVA with PP. The holes represent the EVA droplets, which are dissolved out on etching. The dispersion of the EVA droplets is quite fine and uniform at all blending ratios. The average droplet size, calculated after measuring the diameters of 100 droplets in each case, is in the range 0.5–2  $\mu\text{m}$ , at all blending ratios except at the highest (40% EVA content), where the droplets are larger and elongated. A correlation of mean droplet size with the rheological properties of the two phases, their blending ratios, and the shear rate of mixing was possible from these data and will be presented in a subsequent publication.<sup>13</sup>

Though the dispersed phase droplets are quite circular, there is a distribution of droplet size at each blending ratio. The average size is within the range recognized as the optimum diameter by other authors<sup>1,2</sup> for rubber toughening of polymers.

With increasing EVA content of the blend, the number density of dispersed EVA domains increases considerably while the average diameter increases only slightly. This large number of dispersed droplets may be responsible for impact strength improvement. At 40% EVA content, the EVA droplets show a wide distribution of size and shape. Small droplets retain their circular (or spherical) shape while the large ones are quite elongated, apparently formed by coalescence of several small droplets.

This variation of average droplet size is quite consistent with the variation of the impact strength with EVA content described earlier. In the region 5–30% EVA content, the impact strength increase is quite small, while in the region 30–40% EVA content the impact strength shows a rather steep rise that may be due to the sudden change in morphology of dispersed phase in this region.



**Figure 6** Variation of impact strength with work of yield for PP/EVA-12 blend.

A correlation of morphology with impact strength may be described as follows. In the case of the blend having 5% EVA-12 content, the presence of a small number of EVA droplets accounts for the observed high-impact strength of the blend at this EVA content. From 5–30% EVA content, the change is essentially in the number density of EVA droplets while the average size of the droplets increases slightly with increasing EVA content of the blend, which seems consistent with the rather slow increase of impact strength in this region of blend compositions. This suggests that an increase of number density of dispersed domains of the elastomer has little effect on the impact toughening.

#### Impact Strength as a Function of Two Variables

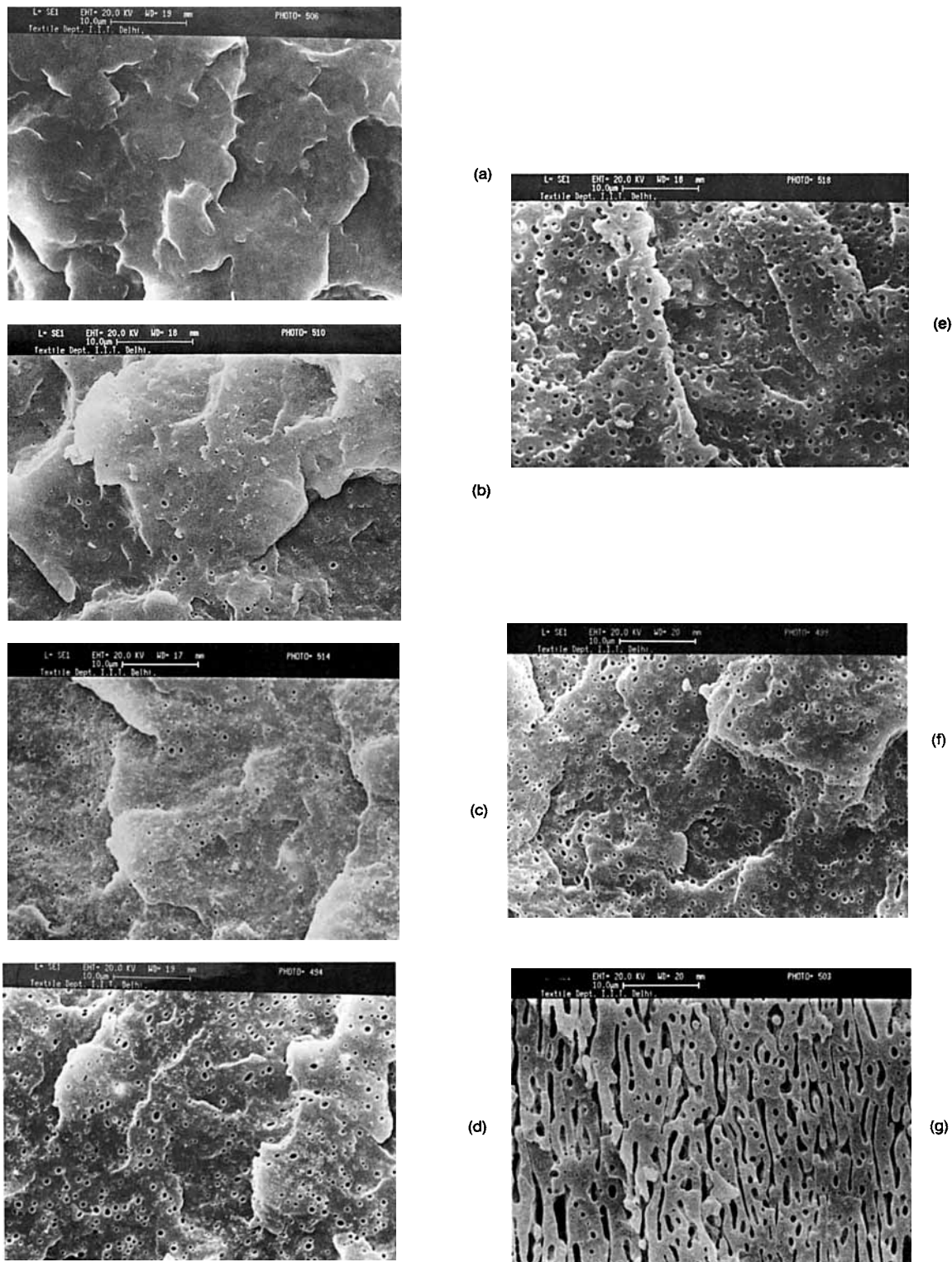
We have attempted an analysis of these data to determine the equation representing the impact strength as a simultaneous function of the experimental variables. The above-stated results show that the impact strength of PP/EVA blend is a function of two variables, viz., the blending ratio (or EVA weight fraction) and temperature. The third variable, viz., the VA% is not included in this analysis owing to smaller number of data points; hence, the

proposed equations should be valid for the given sample of EVA, viz., the EVA-12 for which the data are used in this analysis. However, since the trend of variation of impact strength (see Fig. 2) is similar for all VA%*s* studied, the optimization equation should be useful for any other EVA sample with appropriate modification.

The individual effects of temperature and the EVA content on the impact strength of the blend can be quantified and compared by establishing a relationship of the type:

$$Y = f(x) \quad (1)$$

where  $Y$  is the impact strength and  $x$  may be either temperature or weight fraction of EVA. With increasing temperature and EVA content, the impact strength increases. But, it is not necessary that the variations of impact strength with EVA content and temperature may follow identical relationships. Since the temperature dependence and EVA content dependence of impact strength are different, the expression (1) will be replaced by two similar equations with the variables  $x_1$  and  $x_2$  instead of the single variable  $x$ .



**Figure 7** SEMs of etched impact-fractured samples of PP/EVA-12 blend at varying EVA content (wt %): (a), 0; (b), 5; (c), 10; (d), 15; (e), 20; (f), 30; (g), 40.



$$Y = f(x_1) \quad (2)$$

for one variable (say, EVA content)

$$Y = f(x_2) \quad (3)$$

for another variable (say, temperature).

If eq. (2) is expressed as a linear relationship, say  $Y = mx_1 + C$ , and  $m$  and  $C$  are evaluated, then the  $m$  and  $C$  at one temperature (or variable  $x_2$ ) may not be the same as at another temperature. Hence, the second variable is to be introduced in eq. (2). Thus, the following relationship should represent a combined effect of the eqs. (2) and (3), i.e.,

$$Y = f(x_1, x_2) \quad (4)$$

The most common mathematical approach to establish such relationship of any property with one or more variable is in terms of a linear polynomial of the form

$$Y = \text{constant} + ax + bx^2 + cx^3 \quad (5)$$

(for single variable  $x$ )

$$Y = \text{constant} + Ax_1 + Bx_2 + Cx_1x_2 + D(x_1)^2 + E(x_2)^2 + Fx_1^2x_2 + Gx_1x_2^2 + Hx_1^3 + Ix_2^3 \quad (6)$$

(for two variables  $x_1$  and  $x_2$ )

From the general expression, eq. (6), we take a simpler expression involving only the second-degree terms as expressed by eq. 7 below. Similar second-degree equations are proposed by Arroyo et al.<sup>12</sup> for other systems.

$$Y = \text{constant} + Ax_1 + Bx_2 + Cx_1x_2 + Dx_1^2 + Ex_2^2 \quad (7)$$

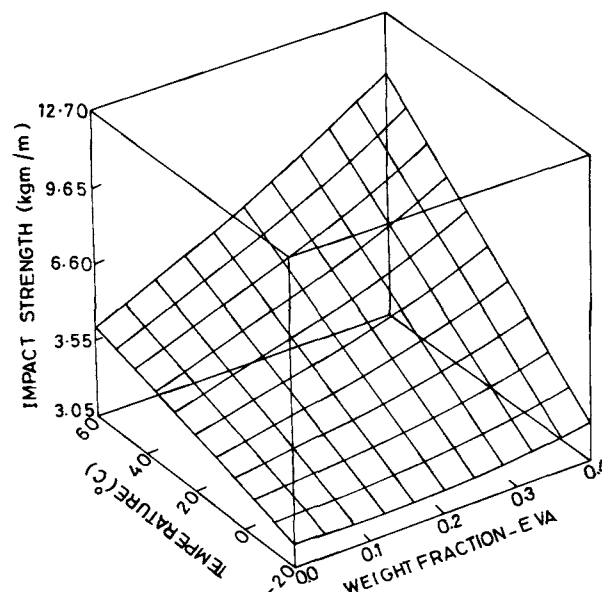
The coefficients  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $E$  in eq. (7) have been determined for the present data on PP/EVA-12 blend using a computer with relevant software. The best-fitting equation thus determined is given below [eq. (8)], where  $Y$ ,  $x_1$  and  $x_2$  are replaced by the impact strength ( $I$ ), the weight fraction of EVA ( $W$ ), and the temperature ( $T$ ), respectively.

$$I = 2.0 + 0.01T + 0.23WT + 13.3W^2 \quad (8)$$

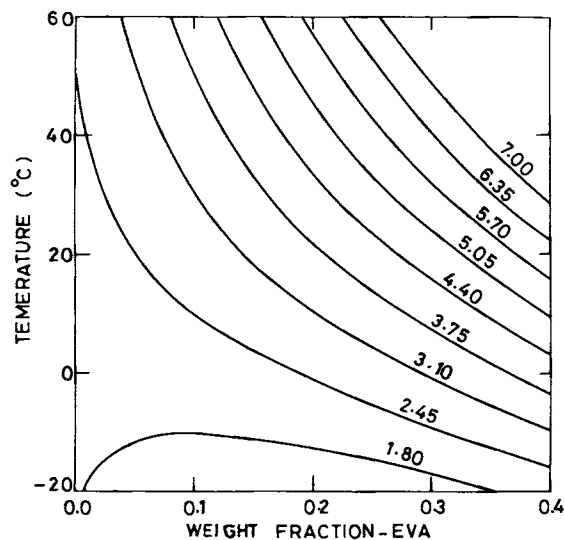
The coefficients of the other terms were zero or negligibly small; hence, they are not present in eq. (8). A three-dimensional plot of  $I$  vs  $T$  and  $W$  using eq. (8) was made for the data on PP/EVA-12 blend,

which is as shown in Figure 8. The experimental points of Figure 4 do not fall exactly on the theoretical surface, shown in Figure 8 representing the three-dimensional plot of eq. (8). However, the experimental points are not very far from the theoretical prediction, as is clear from the sufficiently high value of the multiple regression coefficient,  $r^2 = 0.88$ . Thus, Figure 8 approximates the behavior of the system with reasonable accuracy for the values of  $W$  and  $T$  in this studied range. The square term in the equation indicates a curvature in the surface obtained in the three-dimensional plot. The presence of the interaction term, i.e., the term  $WT$  in eq. 8, shows that the effects of temperature and composition are interdependent and the positive sign of its coefficient suggests that this effect is reinforcing. But, the total effect is not very large as indicated by the small value of the coefficient.

In the second-degree equation thus obtained, we can substitute only one value for  $T$  (or  $W$ ) and can calculate impact strength at different values of  $W$  (or  $T$ ). The same procedure can be repeated for all temperature values. The results can be presented in terms of contour plots as shown in Figure 9. The practical use of such contour plots is that, given the value of the property (which need not be any experimental data point itself), the temperature and the EVA content needed to attain that value of the property (i.e., impact strength) can be directly ob-



**Figure 8** Three-dimensional representation of the equation describing the variation of impact strength with weight fraction of EVA in the blend and temperature for the PP/EVA-12 blend.



**Figure 9** Contour plot obtained from the three-dimensional plot (Fig. 8).

tained from the plot. That is, the procedure optimizes the value of the variables needed to get any desired value of the property.

## CONCLUSION

EVA is a good impact modifier for PP, both at ambient and low temperature, and compares well with other impact modifiers of PP. At the blending ratio 90/10, EVA produces better impact toughening than EPDM. With increasing EVA content the impact strength increases initially rapidly up to 5 wt % EVA content and then slowly up to 30 wt % EVA content and then again rapidly at higher EVA content. Furthermore, the higher the VA% of the EVA the higher is the impact strength improvement.

Impact toughening at ambient temperature is essentially due to shear yielding mechanism as suggested by the observed stress whitening in the fractured samples and the correlation of impact strength with work of yield.

The dispersion of EVA in PP is quite fine and homogeneous. The increase in number density of

the dispersed droplets has less effect on the impact toughening than the variation of mean diameter of the droplets as shown by the correlation of the morphology and impact strength.

The impact strength can be represented as a simultaneous function of two variables (composition and temperature) by a second-degree polynomial equation. The positive sign of the coefficient of the term dependent on both the variables indicates that although the temperature and composition effects are independent they have slight reinforcing effect on the impact strength.

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Received April 29, 1991

Accepted August 19, 1991