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OF COMMERCIAL POLYMERS*

PROPERTIES OF ETHYLENE–DIMETHYLAMINOETHYLMETHACRYLATE COPOLYMERS AS POLY(VINYL CHLORIDE) RESIN MODIFIER

(Technical Report)

Prepared for publication by

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†1989–91 ‡1987–89

Properties of ethylene-dimethylaminoethyl-methacrylate copolymers as poly(vinyl chloride) resin modifier

ABSTRACT : Morphological, physical, and mechanical properties of the blends of poly(vinyl chloride) (PVC) with (ethylene-dimethylaminoethylmethacrylate copolymer) (E-DAM) were studied. From the dynamic mechanical characterization of the PVC/E-DAM blends, it was concluded that E-DAM was slightly compatible with PVC due to the specific interaction between the α-hydrogen of PVC and the tertiary amine group of E-DAM. Measurements of the tensile stress-strain behavior and of the Izod notched impact strength were carried out for a series of PVC/E-DAM blends in the composition range of 0 to 15 wt% of E-DAM. Improved toughness and impact strength is observed in the case when the amount of E-DAM is 10 wt%. Transmission and scanning electron micrographs of PVC/E-DAM blends show E-DAM domain sizes ranging from 0.1 to 1 μm. E-DAM forms the continuous phase when the composition exceeds 12 wt%. In the ternary blend of PVC/E-DAM/PE, E-DAM acts as a compatibilizer for PVC/PE system. Addition of small amount of PE into PVC/E-DAM blend enhances the toughness of the mixture.

INTRODUCTION

PVC is a versatile commodity polymer with relatively low price and easiness of the property modification. The impact modification of PVC by the introduction of a rubbery polymer is a common industrial practice. The properties of the modified PVC depend on the morphology, the physical properties of the rubbery modifier, and the interfacial adhesion between the rubber and PVC.[1,2]

Methods and conditions of blending are very important to the resulting morphology and subsequently the properties of the blends.[3] The secondary grain structure (50-250 μm) of PVC is broken down during processing, and is reduced to the 1 μm primary grain structure. The rubbery impact modifier should fill the interstitial space between the grains.[4]

E-DAM is a partially crystalline copolymer which has a tertiary amine group branch in the flexible and chemically stable PE chain. The amine groups are partially compatible with the weakly acidic PVC containing α-hydrogen. The addition of a small amount of E-DAM to PVC yields toughened plastics which are easily processed and possess good mechanical properties. The morphology and properties of E-DAM-toughened PVC through melt blending were analyzed in this paper.

EXPERIMENTAL

Materials and blend preparation

The materials used in this study are as follows, and the properties of E-DAM copolymers are listed in Table 1.

PVC : P-800 (Han Yang Chem. Co., Korea, $\overline{M_n}$ = 50 000)
E-DAM : three grades with varying DAM content (Sumitomo Chem. Co., Japan)
DA3005(15 wt% of DAM, MI=6) (coded as DAM15)
DA1701(28 wt% of DAM, MI=100) (coded as DAM28)
DA3032(39 wt% of DAM, MI=300) (coded as DAM39)
LDPE : 5316 (Han Yang Chem. Co., Korea, MI=0.8)
HDPE : E-308 (Korea Petrochemical Co., Korea, MI=0.8)
EPDM : Roy.521 (Uniroyal Co., USA, PE/PP=52/48 mol%)

PVC with a tin stabilizer at a mass fraction of 2% were preblended in a Henschel mixer. PVC/E-DAM blends were prepared by melt blending, using a Brabender roller mixer. First, the roller mixer was charged with PVC and was rotated at 160℃. After 5 minutes, gelling of PVC was observed and E-DAM with 1% Irganox 1010 as the antioxidant were added in the composition range of 0 to 15 wt%. The mixer was set at 40 rpm and blending was carried out at 180℃ for 5 minutes. The resulting blend was further mixed at 180℃ for 5 minutes on a two roll mill (3″ × 7″ roll) to assure homogeneity and to obtain sheet-form samples for the compression molding. The blends were molded to desired thickness in a preheated press at 180℃ for 2~3 minutes and quenched in cold water.

Measurement

The dynamic mechanical properties were measured with a du Pont model 981 Dynamic Mechanical Analyzer. The temperature scanning range was from -150 to 140℃ and the heating rate was set at 10℃/min. The tensile properties were measured by an Instron at room temperature in accordance with the procedure described in ASTM D 1708-66.

The plane-strain fracture toughness K_{Ic}, and the fracture energy G_{Ic} were also measured (ASTM E399). The notched Izod impact tests were performed by the standard ASTM D256-81 method. The densities of the deformed and undeformed specimens were measured with a pycnometer at room temperature. Light transmission experiments as a measure of the clarity of the PVC/E-DAM film were performed using a He/Ne Laser with wavelength of 632.8 nm. The thickness of the sample was kept constant at 2 mm.

Table 1. Characteristics of E-DAM Copolymers.

	Unit	Commercial Name(Coded Name)		
		DA3005(DAM15)	DA1701(DAM28)	DA3032(DAM39)
DAM content	wt%	15	28	39
Density	g/cm^3	0.9317	0.9358	0.9392
Melt Index	g/10min	6	100	300
[η]$^{1)}$		0.79	0.59	0.49
Tensile strength	kg/cm^2	73	47	15
Elongation	%	550	708	258
T_m	℃	98	88	66
T_g	℃	80	68	48

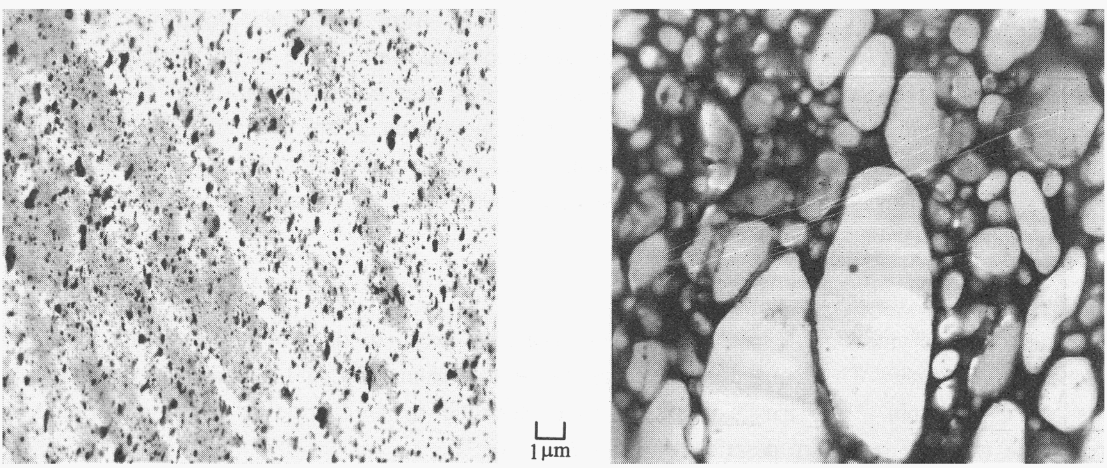
1) intrinsic viscosity ; tetralin solution at 135℃

RESULTS AND DISCUSSION

Morphology

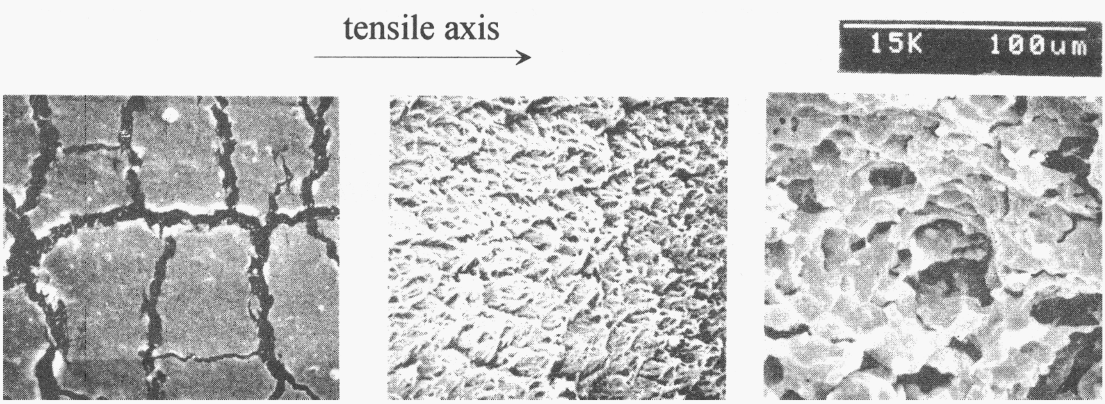
The morphology of the blend was analyzed by transmission electron microscopy, where the rubber particles were stained with 10 wt% phosphowolframic acid at 60℃ for 30 minutes. Blends with 9 wt% DAM28 exhibited uniformly dispersed particles of DAM28 in the range of 0.1 to 1 μm (dark areas in Figure 1(a)). In the case of 15 wt% DAM28 blend, morphological changes were observed and E-DAM formed interconnected phases between PVC grains (Figure 1(b)).

The scanning electron microscopy examination of the failure zone after the tensile test is shown in Figure 2. The fracture surface of PVC showed cracks developed perpendicular to the tensile stress axis (Figure 2(a)). In the 10 wt% DAM28 blend, fine fibrils of oriented polymer parallel to the stress axis were formed, whereby crack propagation was suppressed (Figure 2(b)). In Figure 2(c), because of the poor adhesion of LDPE to PVC matrix, failure appeared to have taken place easily at the PVC-LDPE interface.



(a) PVC/DAM28 (91/9)   (b) PVC/DAM28 (85/15)

Figure 1. Transmission electron micrographs of PVC/DAM28 blends.



(a) PVC   (b) PVC/DAM28 (90/10)   (c) PVC/LDPE (90/10)

Figure 2. Scanning electron micrographs of the fracture surface of elongated specimens.

Dynamic Mechanical Analysis

The storage modulus E' and the loss tangent of the PVC/DAM28 blend are shown in Figure 3 and 4, respectively. Figure 3 shows T_g's of DAM28 and PVC as 0℃ and 110℃, respectively. In the PVC/DAM28 blend, the glass transition region is generally broadened by the addition of DAM28. When 10 wt% DAM28 was blended with PVC, PVC phase formed the continuous matrix and the modulus of the blend was close to that of PVC. But, in the case of 20 wt% DAM28 blend, morphological changes were observed and the DAM28 copolymer with low viscosity formed the continuous matrix and the modulus of the blend approached to that of the pure DAM28. Figure 4 shows that the blend has a two phase structure with somewhat shifted low temperature transition of DAM28 phase, which indicates partial compatibility with PVC. The transition of the PVC rich phase is also somewhat lower than that of the pure PVC, probably due to the partial compatibility with DAM28.

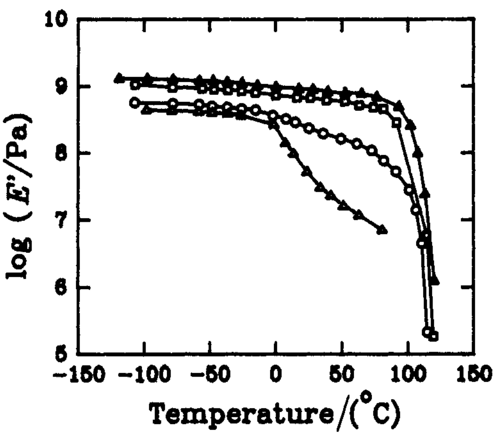


Figure 3. Young's modulus E' as a function of temperature for PVC/DAM28 blend and component polymers.
▲ PVC ; □ PVC/DAM28 (90/10) ; ○ PVC/DAM28 (80/20) ; △ DAM28.

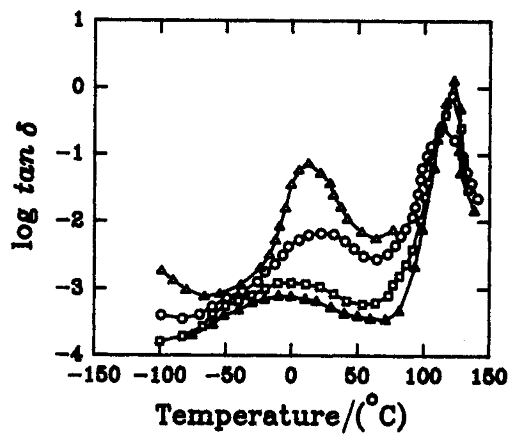


Figure 4. Mechanical loss tangent as a function of temperature for PVC/DAM28 blends.
▲ PVC ; □ PVC/DAM28 (90/10) ; ○ PVC/DAM28 (80/20) ; △ DAM28.

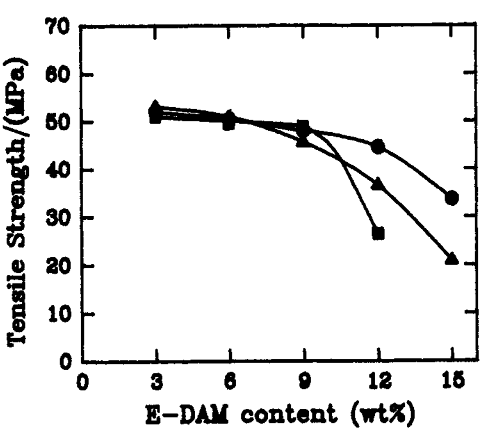


Figure 5. Effect of E-DAM content on the tensile strength.
■ DAM39 ; ● DAM28 ; ▲ DAM15.

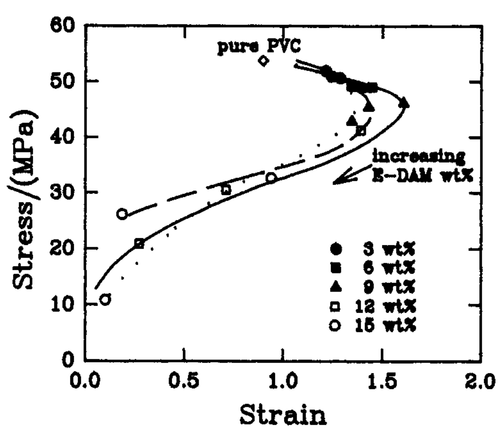


Figure 6. Failure envelope of PVC/E-DAM blends with different E-DAM content.
—— DAM39 ; ----- DAM28 ; ······ DAM15.

Tensile Properties

The effect of E-DAM content on the tensile strength of the PVC/E-DAM blends for three different grades of E-DAM is shown in Figure 5. With small amount of E-DAM (3-9 wt%), PVC formed the matrix phase and the tensile strength of the blend was dominated by the PVC matrix and was in a similar range as the latter.[5] When more than 12 wt% of E-DAM was blended, the tensile strength of the blend decreased due to the phase inversion occurring. Here, E-DAM with the much lower melt viscosity forms the continuous matrix.

The failure envelope schematically representing the dependence of the stress-strain curve of PVC/E-DAM blends on the E-DAM content is shown in Figure 6. As the PVC was blended with increasing amount of E-DAM, the elongation at the break increased owing to the craze formation and shear yielding in the blend. At about 9 wt% E-DAM concentration the maximum elongation was obtained, being highest for the relatively more compatible DAM39 blends.

The theoretical prediction of the composite modulus proposed by Kerner[6] was compared with the experimental data of PVC/DAM28 blends (Figure 7). The Kerner model may be written as

$$\frac{1}{E_b} = \frac{1}{E_m}\left[1 + \frac{15(1-\nu_m)}{(7-5\nu_m)} - \frac{\phi_d}{\phi_m}\right]$$

where, E is the tensile modulus, ϕ is the volume fraction, and ν is the Poisson's ratio. The subscripts b, m, and d refer to the blend, the matrix, and the dispersion, respectively. The ν_m of PVC is 0.38 and the densities of PVC and DAM28 were 1.392 and 0.939 g/cm^3, respectively. The experimental data fitted well with Kerner's model up to 12 wt% E-DAM concentration, but, above that point, deviations were observed due to the morphological changes.

The energy required to break the samples was calculated from the area under the stress-strain curve and was defined as the toughness plotted in Figure 8. The PVC/DAM39 blends had the highest toughness, since DAM39 had better compatibility with PVC and had better interfacial adhesion.

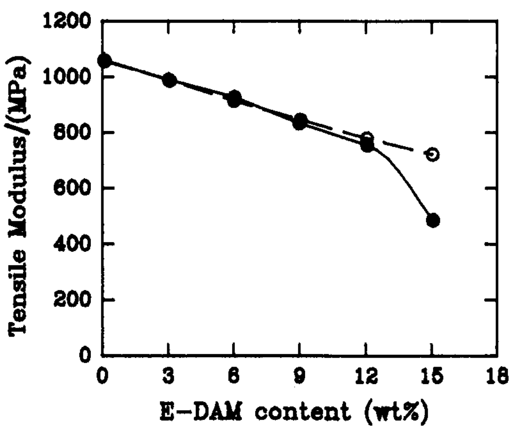


Figure 7. Tensile modulus vs. E-DAM content for PVC/DAM28 blends.
○ theoretical prediction by Kerner ;
● experimental data.

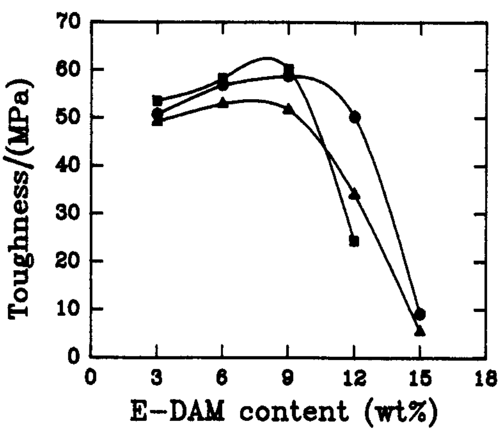


Figure 8. Toughness vs. E-DAM content.
■ DAM39 ; ● DAM28 ; ▲ DAM15.

It is evident that E-DAM with increasing amounts of DAM in the copolymer shows better compatibility with PVC due to the interaction between the amine of DAM and α-hydrogen of PVC. The compatibility of two polymers can also be predicted by considering the solubility parameters. The solubility parameters (δ) of PVC and PE are 19.7 ($J^{0.5}/cm^{1.5}$) and 16.0 ($J^{0.5}/cm^{1.5}$), respectively.[7] The incorporation of DAM to PE makes the solubilty parameter to increase, since the polarity and hydrogen bonding forces are increased. The calculated δ-values by the group contribution theory are δ(DAM15) = 17.26, δ(DAM28) = 17.88, and δ(DAM39) = 18.26($J^{0.5}/cm^{1.5}$). With increasing DAM content, the δ-value of E-DAM approaches that of PVC, and thus E-DAM becomes more compatible with PVC.

Impact Behavior

Figure 9 shows the change of notched Izod impact strength as a function of E-DAM content. When DAM39 or DAM28 was blended with PVC, the impact strength increased by approximately twenty times to 800-910 J/m. However, when DAM15 was added to PVC, the impact strength increased only by four times. The commercial high impact PVC, modified with a conventional impact modifier such as CPE, MBS, and ABS shows 1070-1337 J/m of notched Izod impact strength.[8] The impact strengh of the blends reach its maximum value at 10 - 12 wt% E-DAM content but drops sharply at higher E-DAM content due to the morphological changes.

The effects of DAM28 on K_{1c} and G_{1c} evaluated by three point bending test are shown in Figure 10 and 11. K_{1c}, often referred to as the fracture toughness, indicates the stress field intensity factor around a sharp crack. G_{1c} is called the fracture energy or critical strain-energy release rate and provides a measure of the energy required to extend a crack over a unit area.[9,10] When DAM28 is added to PVC, K_{1c} of the blends increases slightly initially, but roughly K_{1c} values remain constant within the error range. The G_{1c} of the PVC/DAM28 blends increased as the amount of DAM28 was increased (Figure 10). The energy dissipation around the crack tip during the crack propagation increased due to the viscoelastic and plastic deformations with increasing amount of DAM28 copolymer. The G_{1c} of PVC/E-DAM blend increased as the DAM content of E-DAM was increased due to the increased compatibility with PVC, but K_{1c} remained constant (Figure 11).

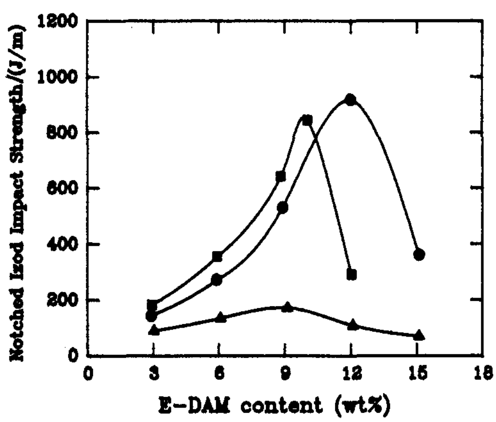


Figure 9. Effect of E-DAM content on the impact strength.
■ DAM39 ; ● DAM28 ; ▲ DAM15.

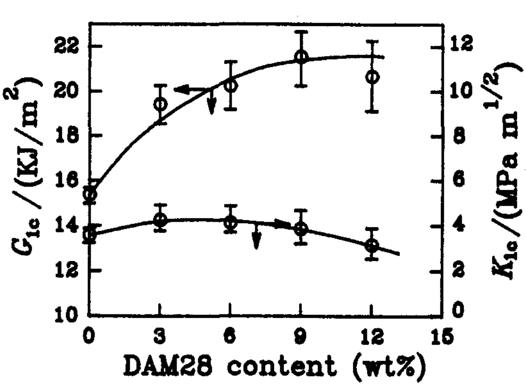


Figure 10. Effect of DAM28 content on the fracture energy (G_{1c}) and fracture toughness (K_{1c}) of the blends.

Clarity & Density

The clarity of the blend is shown in Figure 12 as a function of E-DAM content. When E-DAM containing increasing amounts of DAM was blended with PVC, the clarity of the blend increased due to the increased compatibility. The morphological changes in the PVC/E-DAM blend were also shown as the rapid drop of the transmitted light intensity as the amount of E-DAM exceeded 10 wt%.

The densities of the five different compositions of the PVC/DAM28 blend before and after tensile deformation are shown in Figure 13. The calculated densities based on the volume additive rule are represented by the dotted line. The deformed specimens showed the stress-whitening phenomenon. When DAM28 was added up to 12 wt%, the densities of the blends were slightly higher than the calculated densities. It is likely that partial intermixing between PVC and DAM28 chain segments at the interface might lead blends to show densification.

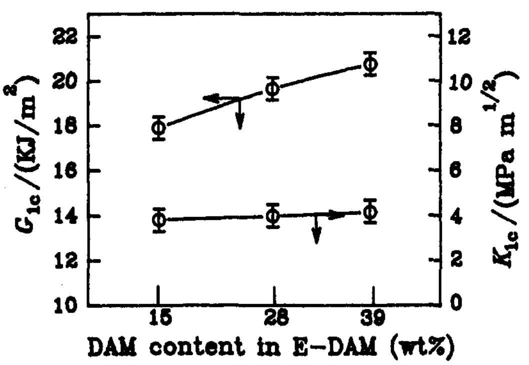


Figure 11. Effect of DAM content in E-DAM on G_{1c} and K_{1c} of PVC/E-DAM (91/9) blends.

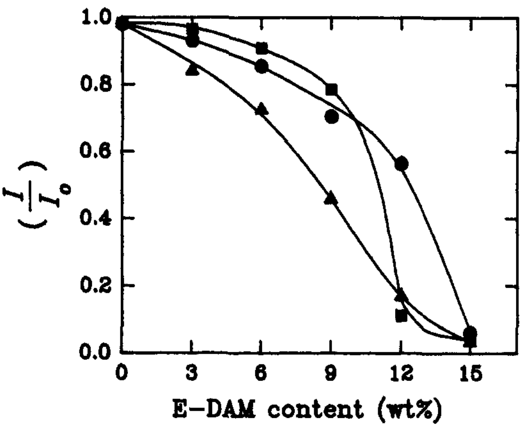


Figure 12. Transmitted light intensity ratio of blend(I) and PVC(I_o) in PVC/E-DAM blends. ■ DAM39 ; ● DAM28 ; ▲ DAM15.

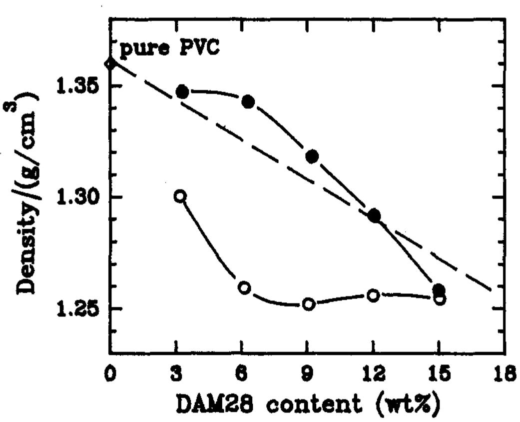


Figure 13. Density vs. DAM28 content in PVC/DAM28 blends.
● PVC/DAM28 blends ;
○ stress-whitened zone of sample after tensile test.

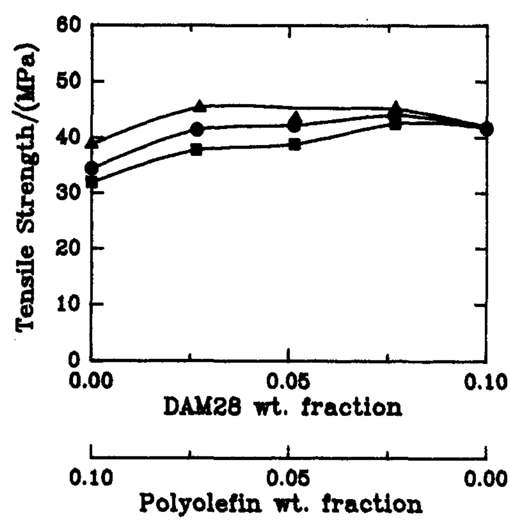


Figure 14. Tensile strength vs. DAM28 wt. fraction in PVC/DAM28/PE blends (PVC wt. fraction is constant at 0.9).
▲ HDPE ; ● LDPE ; ■ EPDM.

When specimens were stretched, crazes appeared which yielded a volume change of the sample. The reduction of the densities with craze formation is indicated in Figure 13 by open circles.

PVC/DAM28/PE Ternary Blend

PVC/DAM28/PE ternary blends were prepared maintaining the PVC content at 90 wt% and varying the DAM28/PE (or EPDM) ratio for the remaining 10 wt%. The tensile strength of the ternary blend was plotted against DAM28 weight fraction in Figure 14. The crystallinity of the polyolefin had an effect on the tensile strength of the blends, and HDPE showed higher tensile strength.

Figure 15 shows that the addition of DAM28 in PVC/PE blends increases the elongation at break of the blend remarkably and may act as a compatibilizer for the PVC/PE system. The effect of the DAM28 on increasing the elongation at break was somewhat smaller when EPDM was incorporated as the polyolefin component compared to the blends with HDPE and LDPE.

The impact strength behavior shown in Figure 16 indicates that the addition of 0.05-0.075 weight fraction of DAM28 in PVC/DAM28/PE (LDPE or EPDM) ternary blends exhibits a significant enhancement while the addition of DAM28 in PVC/DAM28/HDPE ternary blend does not show significant enhancement in Izod impact strength.

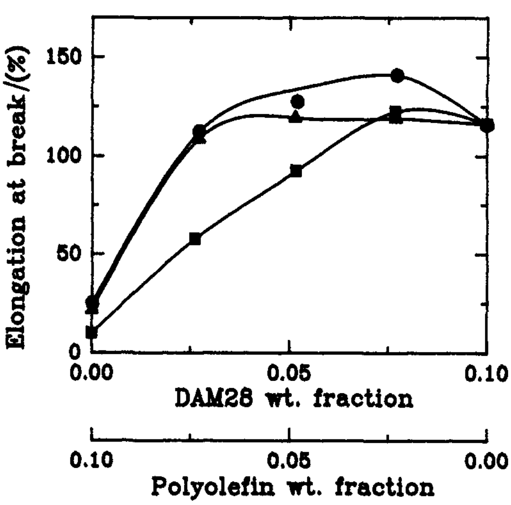


Figure 15. Elongation at break vs. DAM28 wt. fraction in PVC/DAM28/PE blends. (PVC wt. fraction is constant at 0.9). ▲ HDPE ; ● LDPE ; ■ EPDM.

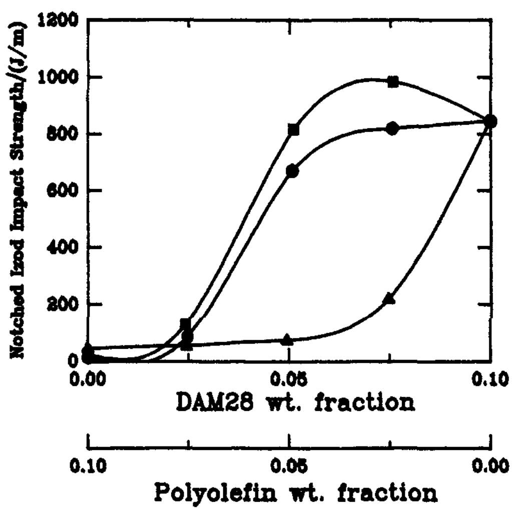


Figure 16. Notched Izod impact strength vs. DAM28 wt. fraction in PVC/DAM28/PE blends. (PVC wt. fraction is constant at 0.9). ▲ HDPE ; ● LDPE ; ■ EPDM.

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