

Blends of Low Density Polyethylene /Plasticized Poly(vinyl Chloride): The Rheological, Morphological, and Mechanical Characterization

RAIJA MIKKONEN and ANTTI SAVOLAINEN, *Institute of
Plastics Technology, Tampere University of Technology,
P. O. Box 527, SF-33101 Tampere, Finland*

Synopsis

An experimental study was conducted to investigate the rheological, morphological, and mechanical properties of a heterogeneous polymer blend system consisting of low density polyethylene (LDPE) and plasticized poly(vinyl chloride) (PVC). The components were mixed using a single-screw extruder, which was equipped with a special measuring head for the determination of rheological quantities. The morphology of blends was examined by scanning electron microscopy. Die swell was determined by photography. The velocity of ultrasound through the polymer melt was also measured. The dependencies of viscosity, die swell, and ultrasonic velocity on blend composition were qualitatively similar, exhibiting a minimum at about 70 wt % PVC. The morphology of the blend system at this blending ratio was different from morphologies of the other blends. Tensile properties of blends, except elongation at break, were not significantly inferior to those of the LDPE component.

INTRODUCTION

Polymer blends constitute about 15% of all consumed plastics. Their consumption is increasing at a rate twice as high as that for all plastics.¹ Advantages of blending are not only for engineering plastics, but also for commodity resins. Modification of impact strength, especially at low temperatures, dimensional stability, stress cracking, and improving of processability have been the prime goals of blending. The recycling of plastic wastes has also increased both academic and industrial interest in polymer blends.

Low density polyethylene is a major component of waste plastics. Wastes from different sources are frequently mixtures of LDPE with other volume plastics, as polystyrene, high density polyethylene, polypropylene, and poly(vinyl chloride). Several researchers have studied blends of LDPE with PS, HDPE, and PP. There are far fewer papers concerning to LDPE/PVC blends.

Scott et al.²⁻⁴ have examined the use of solid phase dispersants (compatibilizers) to improve mechanical properties of LDPE/PVC blends. They found that EPDM was very effective in increasing the impact strength and elongation at the break. Chlorinated polyethylene (CPE) was expected, on the basis of previous studies,⁵ to improve the ductility of blends, but proved to be quite ineffective. Bataille et al.⁶ have studied the influence of CPE, EVA, and the terpolymer plasticizer Elvaloy on the physical and processing properties of

LDPE/PVC mixtures. They suggest the possible usefulness of more complex mixtures, involving EVA and CPE, in quantities adjusted so as to combine some of the benefits in ultimate properties due to CPE with those in elastic modulus and processability due to EVA. Boutevin et al.⁷ investigated P(E-g-MMA) copolymers as a compatibilizer to LDPE/PVC blends. They found values for tensile strength to be almost double compared to those of homopolymer mixtures.

In the present study we have investigated the rheological, morphological, and mechanical properties of LDPE/plasticized PVC blends. We have also used ultrasonic velocity measurements to characterize blend properties. The correlations between the ultrasonic velocity behavior, the morphology, and the rheological behavior are discussed.

EXPERIMENTAL

Materials used were pipe and cable grade LDPE A 3522 (MFI 0.35 g/10 min, density = 922 kg/m³) and cable grade plasticized (DOP) PVC, Pekevic 295/00 PE (Pb-stabilized, density = 1320 kg/m³, Shore A Hardness 95). Both were supplied by Neste Corp.

A Nokia MP40-24D single-screw extruder was used to prepare the blends. The screw used was an experimental PVC screw with the following geometry:

feed	$L/D = 4$, height 7.0 mm
compression	$L/D = 7.5$, compression 1:2.7
metering	$L/D = 8.75$, height 2.6 mm

There was the Maddock type mixing section [Fig. 1(a)] at the end of the screw. The screw speeds were 50, 80, 110, and 140 min⁻¹.

The extruder was equipped with a special measuring head [Fig. 1(b)]. The width, height, and length of the slit die were 14.0, 3.1, and 140 mm, respectively. The pressure gradient was measured along a section 60 mm in length and at a distance of 40 mm from the lip.

The temperature profile in the extruder and the die was as follows: 160 170 180 180 180 (°C). The composition of blends is presented in Table I. Ultrasonic transducers (2.0 MHz) with a specialized electronic unit⁸ were used to measure the time taken by a short ultrasonic pulse to traverse the melt stream (30 mm), (Fig. 1). The probes were cooled on one end by a cooling chamber and heated on the other by the melt.

The swell of extrudates emerging vertically from the die exit into the air was determined by photography. Extrudates were first cut into sections 5 cm in length and then photographed. The length of extrudates was kept constant so that the effects due to gravity would be consistent. The measurements from photos were made approximately 5–10 mm from the lower end, where the elongation was negligible.

The morphology of extrudates was investigated by scanning electron microscopy (ISI-40/Robinson backscattered electron detector). Sample surfaces were ground and polished. Fracture surfaces, prepared in liquid nitrogen, were also studied.

Tensile property measurements were done on a JJ tensile testing machine T5000 at room temperature. A cross head speed of 50 mm/min was used.

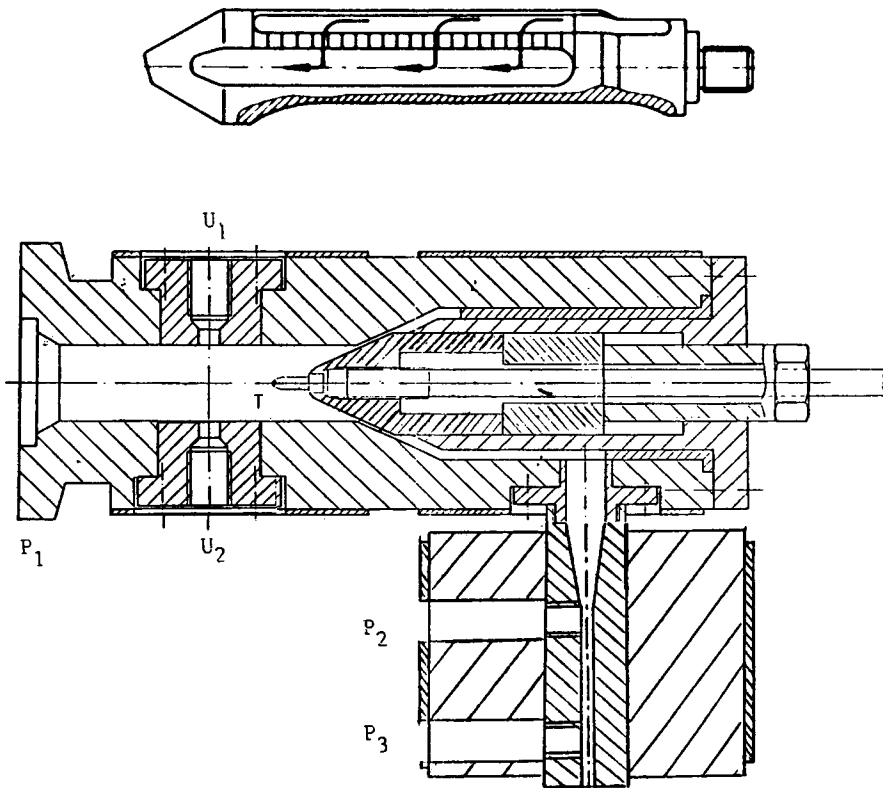


Fig. 1. (a) The Maddock mixing section of the screw. (b) The measuring extruder head: P_1 , P_2 , P_3 pressure transducers, T temperature transducer, U_1 , U_2 ultrasonic transducers.

TABLE I
Composition and Power Law Exponents of LDPE/Plasticized PVC Blends

Composition	wt %	n
LDPE/PVC	100/0	0.260
LDPE/PVC	75/25	0.218
LDPE/PVC	50/50	0.205
LDPE/PVC	25/75	0.228
LDPE/PVC	0/100	0.144

RESULTS AND DISCUSSION

Melt flow characteristics were determined from measurements of volumetric flow rate and the pressure gradient in the slit die using the following equations to calculate the shear rate $\dot{\gamma}$, shear stress τ_w , and viscosity $\eta^{9,10}$:

$$\dot{\gamma} = [(2n + 1)/3n] \dot{\gamma}_{app} \tag{1}$$

$$\tau_w = (-\delta p/\delta z)h/2 \tag{2}$$

$$\eta = \tau_w/\dot{\gamma} \tag{3}$$

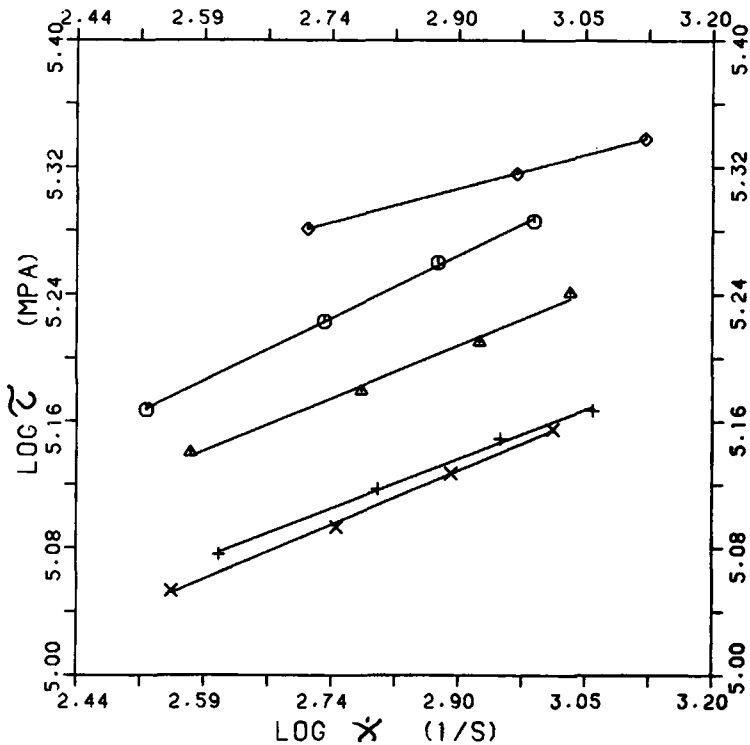


Fig. 2. The flow curves of LDPE/plasticized PVC blends: (○) LDPE/PVC 100/0; (△) LDPE/PVC 75/25; (+) LDPE 50/50; (×) LDPE/PVC 25/75; (◇) LDPE/PVC 0/100.

in which $\dot{\gamma}_{app}$ and n are defined by

$$\dot{\gamma}_{app} = 6Q/wh^2 \quad (4)$$

$$n = d \ln \tau_w / d \ln \dot{\gamma}_{app} \quad (5)$$

Q is the volumetric flow rate, $-\delta p/\delta z$ is the pressure gradient, and w and h are the width and the height of the slit.

The flow curves, shear stress vs shear rate, are presented in Figure 2. The curves are linear over the entire range of measurements implying the validity of the power law relationship:

$$\tau_w = K \dot{\gamma}^n \quad (6)$$

The values of the power law exponent are between 0.26 and 0.14 (Table I). They do not show a regular change with varying blend composition. The shear stress-shear rate relations for blends are below those of each of the pure components.

Figure 3 shows plots of viscosity vs. shear stress. The viscosity increases dramatically with decreasing shear stress. The rate of viscosity increase becomes more pronounced with increasing PVC content except for the

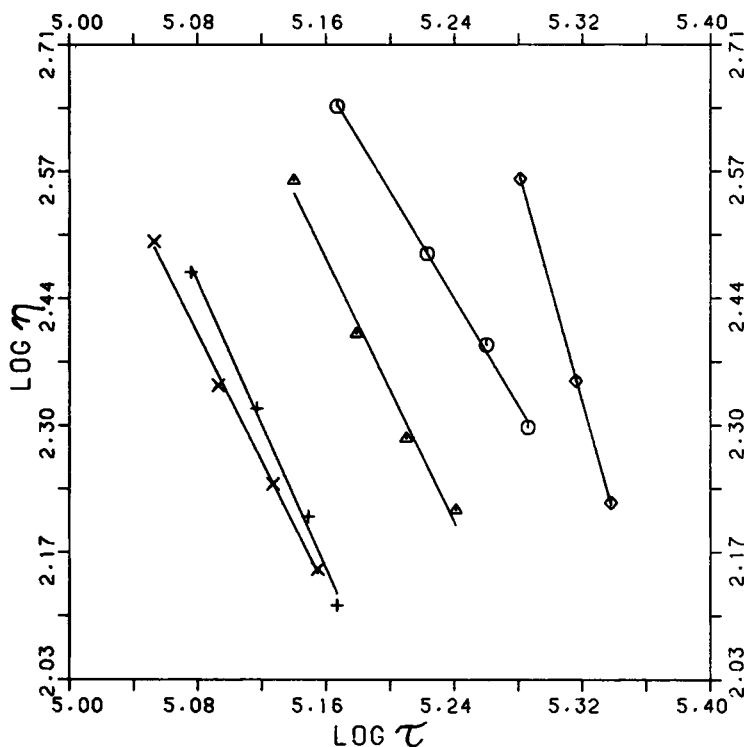


Fig. 3. The viscosity as a function of shear stress: (○) LDPE/PVC 100/0; (▲) LDPE/PVC 75/25; (+) LDPE/PVC 50/50; (×) LDPE/PVC 25/75; (◇) LDPE/PVC 0/100.

LDPE/PVC 25/75 blend. The viscosity increase of this blend is less than in the 50/50 and 75/25 blends.

The effect of blending ratio on the melt viscosity at constant shear stress (150 kPa) is shown in Figure 4 and at different shear rates in Figure 5. The dependence of viscosity on blending ratio shows the same trend whether shear stress or shear rate is used. The viscosity goes through a minimum at the blending ratio of 60–70% PVC.

The composition dependence of melt rheology of the blends is as a rule nonadditive, displaying maxima and/or minima on the rheology–composition graphs.^{10–12} In a recent review Utracki¹² has divided the polymer blends into three groups: those which show positive deviations from the additivity, those which show negative deviations, and the remainder, where both types of deviations are observed. The method should be based on zero shear viscosity–composition dependence. Since these data are not always available, the second best criterion has been accepted the viscosity at constant shear stress.^{10, 12} Shear rate may not be continuous due to formation of discontinuous phases between polymers.^{10, 12}

Miscible blends and those with strong interdomain interactions has been found to show positive deviations from the additivity rule.¹² The blends in which the interactions are weak have been found to show negative deviations and the blends in which there is a concentration-dependent transition of structure (phase inversion, etc.), positive and negative deviations.¹² Han^{10, 13}

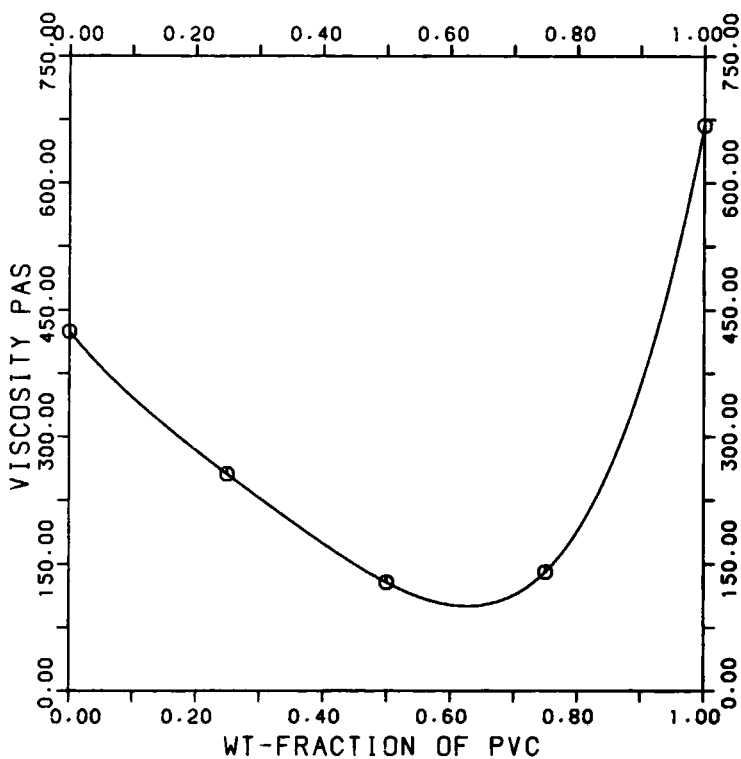


Fig. 4. The viscosity as a function of blend composition at constant shear stress (150 kPa).

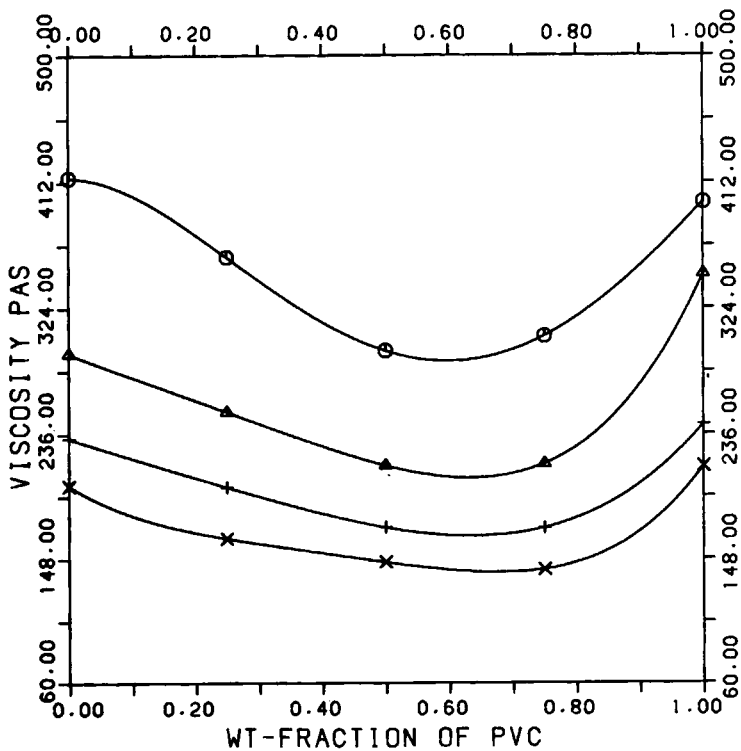
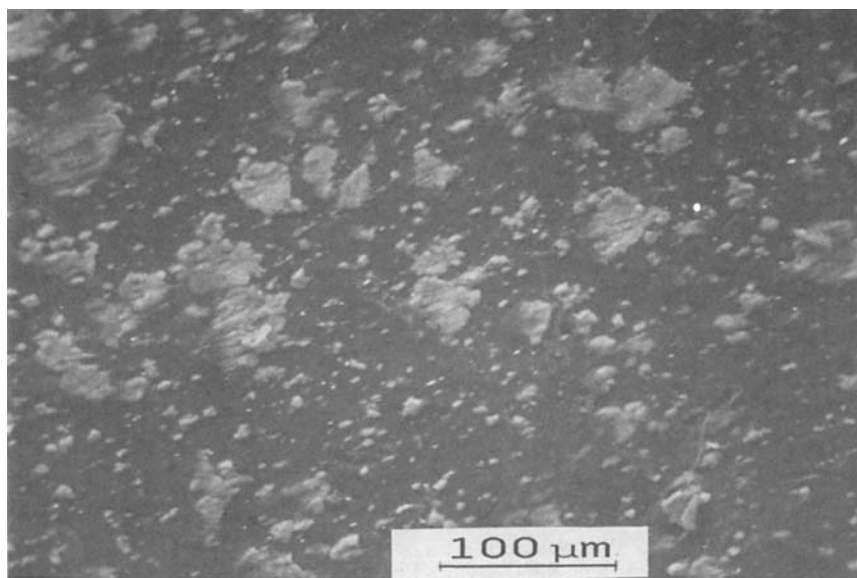
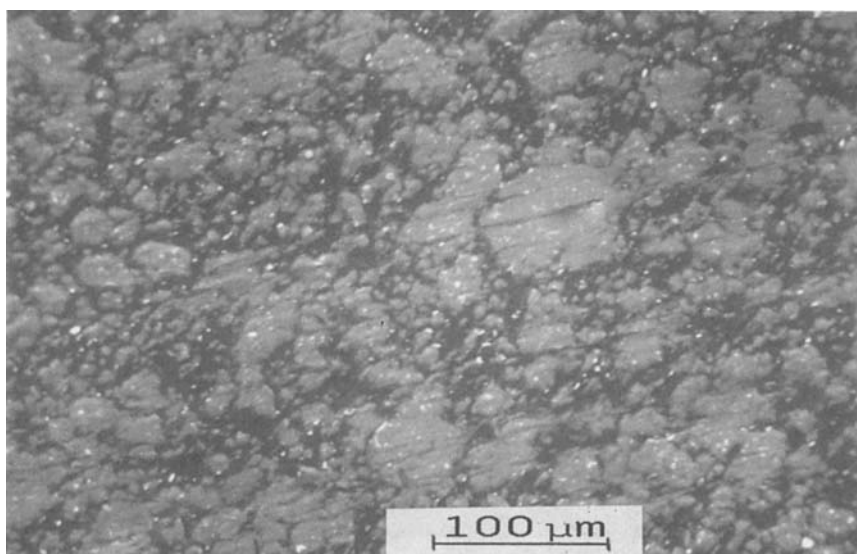


Fig. 5. The viscosity as a function of blend composition at constant shear rates. Shear rate: (○) 400; (Δ) 600; (+) 800; (×) 1000.

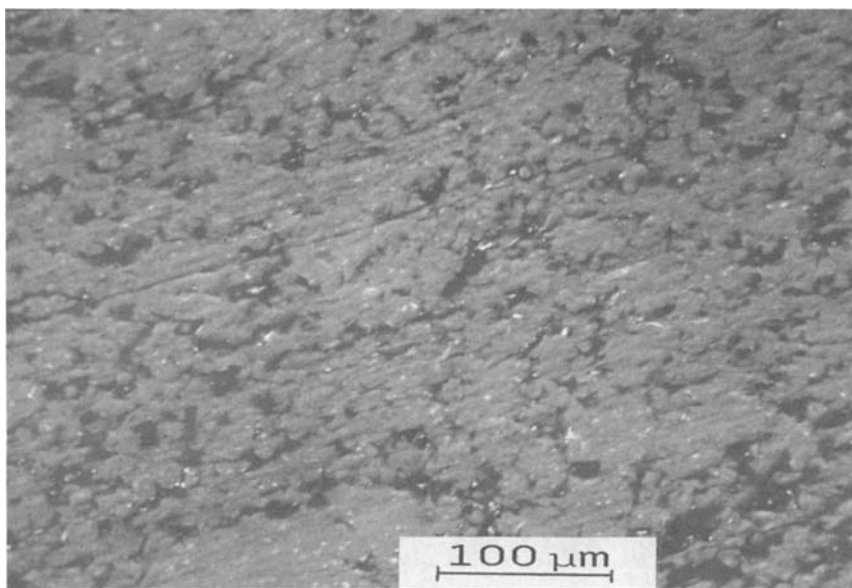


(a)



(b)

Fig. 6. SEM micrographs of polished surfaces of extrudate cross sections of LDPE/PVC blends: (a) 75/25; (b) 50/50; (c) 25/75.



(c)

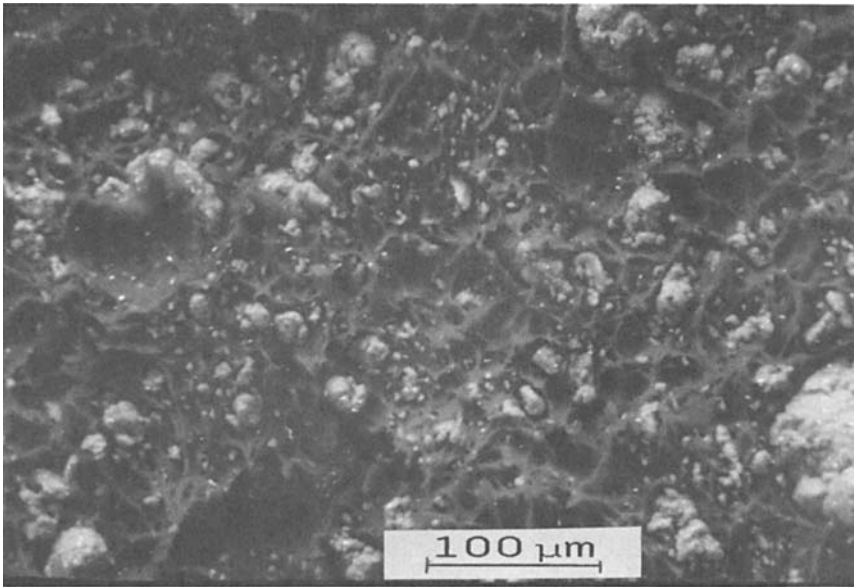
Fig. 6. (Continued from the previous page.)

has presented a viscosity minimum in a heterogeneous blend system attributable to the deformation of the discrete phase, when subjected to shear deformation.

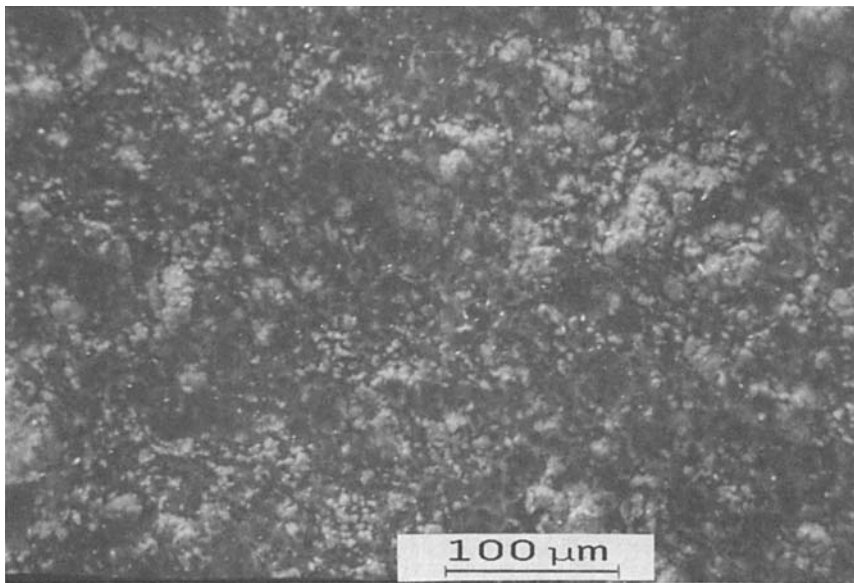
The LDPE/PVC blend system belongs to negative deviation blends as can be seen in Figures 4 and 5. There is a narrowing of the range of viscosities as the rate of shear increases. This has been reported to be typical for most NDB blends.³

Figure 6 gives SEM micrographs of ground and polished surfaces of the extrudate cross-sections. The straight lines in pictures are due to grinding. The white areas represent the PVC phase and the dark ones the LDPE phase. The cross sections of the extrudates fractured after freezing in liquid nitrogen are shown in Figure 7. The LDPE/PVC 75/25 and 50/50 blends exhibit a morphology consisting of large, irregular domains of PVC dispersed in the continuous LDPE matrix. The phase dimensions are in the range of 1–50 μm . There is little adhesion between LDPE and PVC phases. The boundaries of discrete and continuous phases have sharp interfaces. The morphology of the PVC-rich blend [Fig. 6(c) and 7 (c)], which gives a minimum in viscosity, is different from these two blends. No discrete domains are seen. It is obvious, however, that the LDPE phase remains as a continuous phase.

The die swell is defined as the ratio of the width of the extrudate at the extrusion temperature to that of the die. Figure 8 shows the plots of die swell ratio against shear stress. There are large differences in the die swell values of these blends compared to those of PE/PS and PE/PP blend systems reported in literature.^{14,15} The die swell is plotted against composition with shear rate as a parameter in Figure 9 and with shear stress as a parameter in Figure 10. The die swell values increase slightly with increases in the shear rate. This increase is most pronounced in the LDPE/PVC 25/75 blend. The die swell vs.

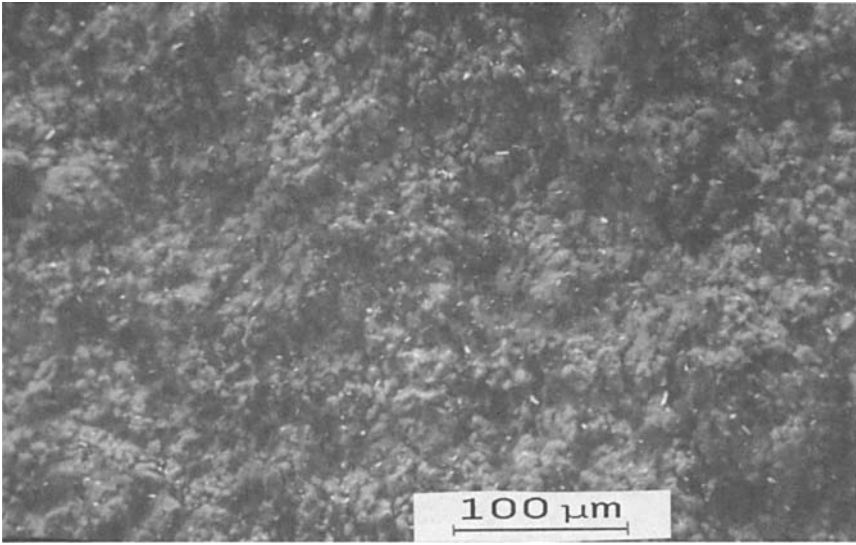


(a)



(b)

Fig. 7. SEM micrographs of cross sections of LDPE/PVC blends, extrudates fractured at liquid nitrogen: (a) 75/25; (b) 50/50; (c) 25/75.



(c)

Fig. 7. (Continued from the previous page.)

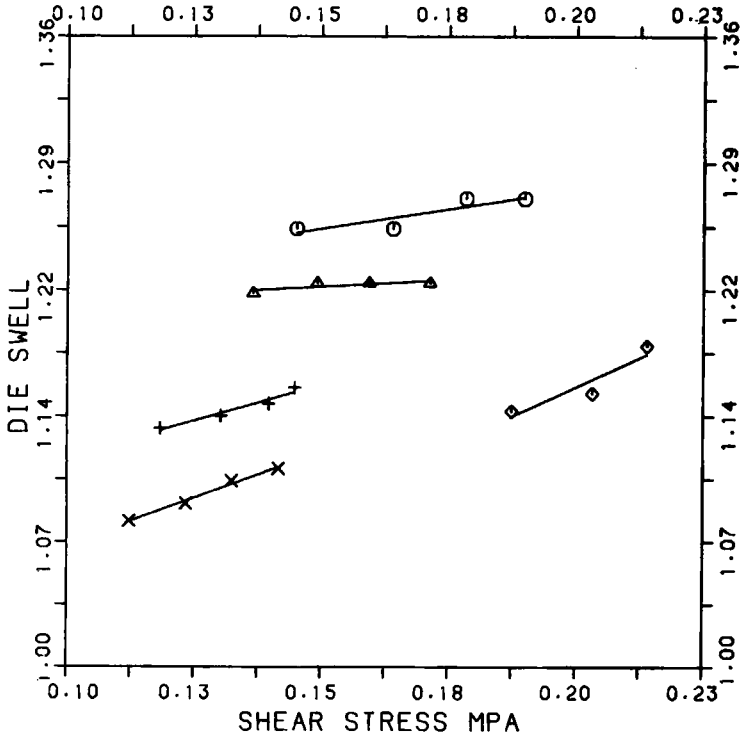


Fig. 8. The die swell ratio as a function of shear stress. LDPE/PVC: (⊙) 100/0; (△) 75/25; (+) 50/50; (×) 25/75; (◇) 0/100.

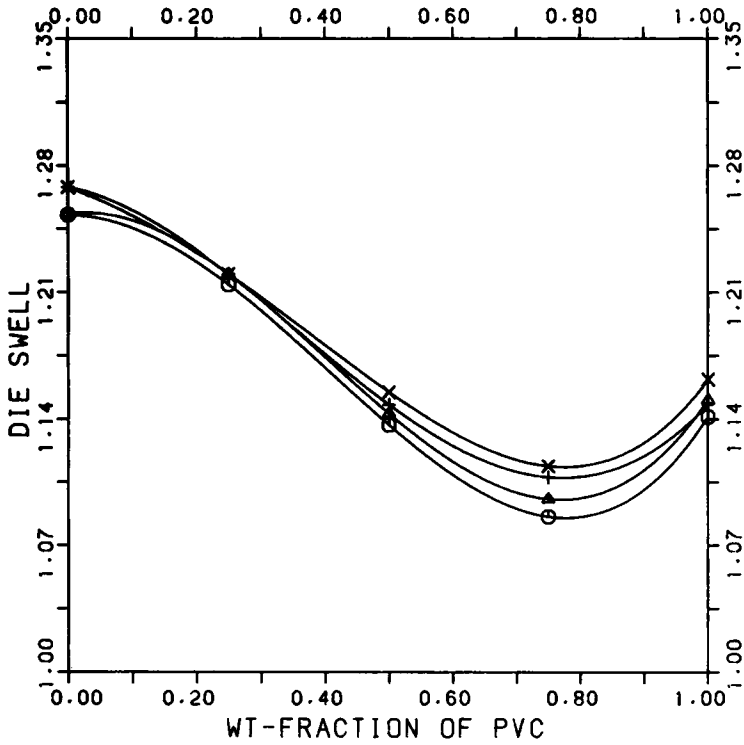


Fig. 9. The die swell ratio as a function of blend composition at constant shear rates. Shear rate (1/s): (○) 400; (△) 600; (+) 800; (×) 1000.

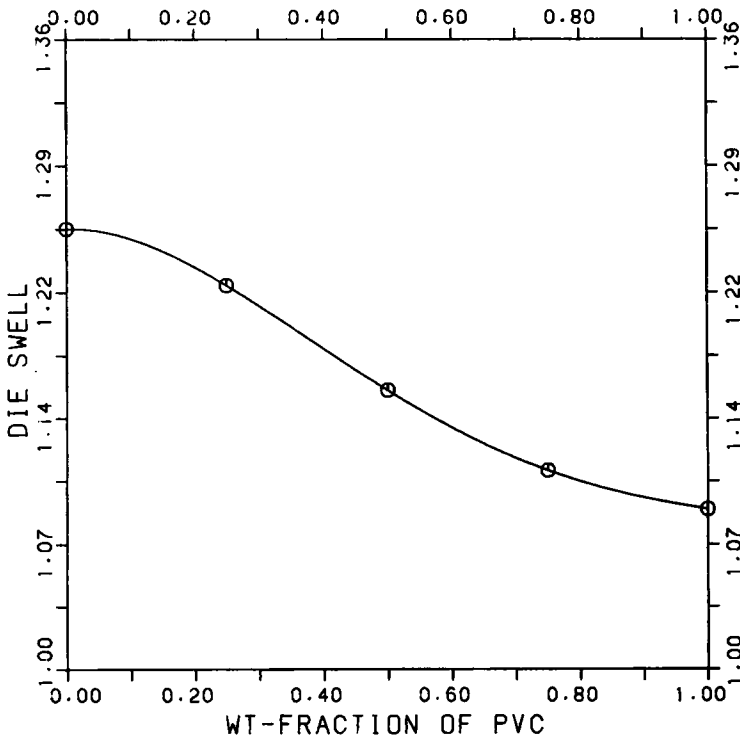


Fig. 10. The die swell ratio as a function of blend composition at constant shear stress (150 kPa).

composition exhibits a minimum at a blending ratio of about 70 wt % PVC, plotted at constant shear rate, but the curve is *S*-shaped at constant shear stress.

The die swell is related with the melt elasticity of polymers. The maxima/minima in die swell have been found to correspond to maxima/minima in principal normal stress difference.¹⁰ Utracki¹² has postulated that, in blends where there is very little interaction between the phases and the viscosity shows a negative deviation rule, the first normal stress difference shows the positive deviation from the log-additivity rule. Han¹⁰ has also reported that the trend of viscosity behavior of many blend systems is almost opposite to that of elasticity behavior, i.e., normal stress effect. The data of the LDPE/PVC blends is consistent with these results. The dependences of viscosity and elasticity on composition (Figs. 4 and 10) show different trends when plotted with shear stress as a parameter (though there is no maximum in the die swell corresponding to a minimum in the viscosity). Instead, the respective dependences of viscosity and elasticity when plotted with shear rate as a parameter (Figs. 5 and 9) are observed to be very similar. Now you have to bear in mind that the LDPE/PVC blend system consists of two phases and the shear rate at the interface between the phases may be discontinuous as noted earlier.

The ultrasonic velocity vs blend composition is plotted in Figure 11 with shear rate as a parameter and in Figure 12 with shear stress as a parameter. This dependence shows the same trend whether shear rate or shear stress is used.

In a single-phase melt, the ultrasonic velocity can be expressed as

$$c = (K/\rho)^{1/2} \quad (7)$$

where K is the bulk modulus and ρ is the density.^{16,17} K is a function of temperature T and pressure p . On the other hand, K is related to the melt viscosity η . The variation in density with the extrusion variables is small compared with variations in K in the single-phase system. One can therefore write^{16,17}

$$c = f(T, p) \quad (8)$$

$$c = g(\eta, p) \quad (9)$$

In two-phase blend systems, an extra variable, a blend composition has to be included in the eqs. (8) and (9). Both the melt density and viscosity depend on the relative contents of each phase.

Piché¹⁸ has reported that the ultrasonic velocity is linearly correlated to the density in polyethylenes in the solid state. Considering PE as a composite material (crystalline regions are embedded in an amorphous matrix), he uses theoretical models of multiphase materials for the elastic modulus and proposes that the relationship between the velocity and density simply reflects the interdependence that exists between the modulus and crystallinity.

The density of the LDPE/PVC blends increases almost linearly with an increasing weight fraction of PVC. The composition dependence of the ultra-

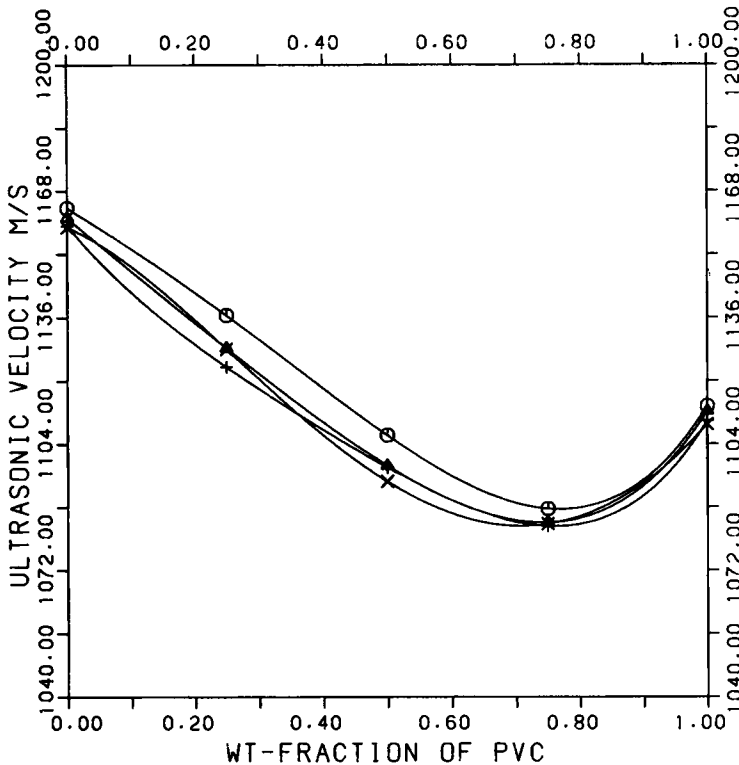


Fig. 11. The ultrasonic velocity as a function of blend composition at constant shear rates. Shear rate (1/s): (○) 400; (△) 600; (+) 800; (×) 1000.

sonic velocity was not found to be linearly increasing in these melt blends (Figs. 11 and 12). The bulk modulus, and hence the ultrasonic velocity, depend on temperature, pressure, and viscosity of the melt, as stated before. The variation of the ultrasonic velocity with temperatures and pressures used in the extrusion was small, as can be seen in Figure 11, where the values of ultrasonic velocity at a certain blend ratio correspond to different temperature and pressure conditions. Thus, the factors most effecting the behavior of the ultrasonic velocity with the blend composition are melt viscosity and melt elasticity. The curves of the ultrasonic velocity vs. the weight fraction of PVC follow very closely those of the die swell (Figs. 9 and 11). The viscosity behavior is also qualitatively similar (Figs. 4 and 5).

Several researchers have used ultrasonic velocity measurements in the studies of polymer blend compatibility in solutions^{19,20} and in solid phase.^{20,21} They have noticed that in the blends having distinct two-phase morphology the curves of ultrasonic velocity vs. composition are S-shaped, indicating a region of phase inversion. For compatible and semicompatible systems essentially linear plots have been obtained. The behavior of solution viscosity vs. composition has been similar to that of ultrasonic velocity. In the LDPE/PVC blends, the essentially linear decrease in the ultrasonic velocity for the compositions to 60 wt % of PVC arises, because the morphology of the blends in this region remains similar: the discrete PVC-phase existing in the continu-

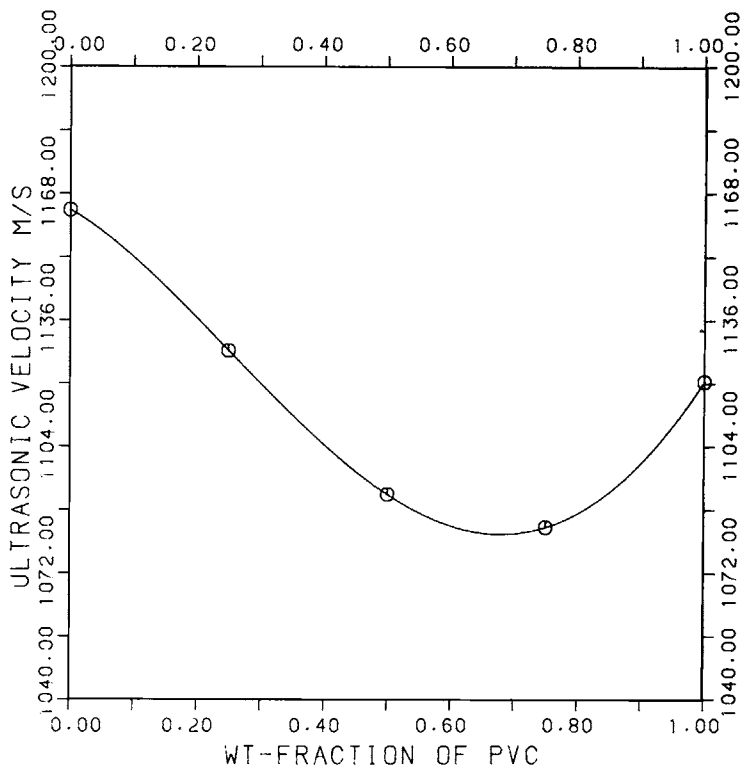


Fig. 12. The ultrasonic velocity as a function of blend composition at constant shear stress (150 kPa).

ous LDPE matrix (Figs. 6 and 7). A minimum in the ultrasonic velocity corresponds to a different blend morphology, [Figs. 6(c) and 7(c)] than that found in blends with below 60 wt % PVC. No phase inversion is found in these blends.

The tensile strength, tensile modulus and elongation at break are plotted against PVC content in Figures 13, 14, and 15, respectively. The tensile strength decreases smoothly as the PVC content increases, reaching a minimum at 70 wt % of PVC. The elongation at break drops very drastically from the values of pure components on the additions of small amounts of the other component. The tensile modulus of blends is equal to or higher than that of pure LDPE. PVC weakens the LDPE matrix but also makes it more rigid. It is noted that mechanical properties of a blend consisting of two incompatible polymers are often lower than those of the individual polymers because of poor interfacial adhesion between phases and poor stress transfer.²² It can be said, however, that the blending of plasticized PVC to LDPE does not result in a significant deterioration of tensile properties.

In summary, the blends of LDPE and plasticized PVC are two-phase systems, where the interactions between phases are weak. The incompatibility of phases is a maximum at compositions of about 70 wt % PVC. The melt viscosity, die swell, and mechanical properties show a minimum in this range. The surfaces of high PVC content extrudates (i.e., 70 wt % or higher) appears

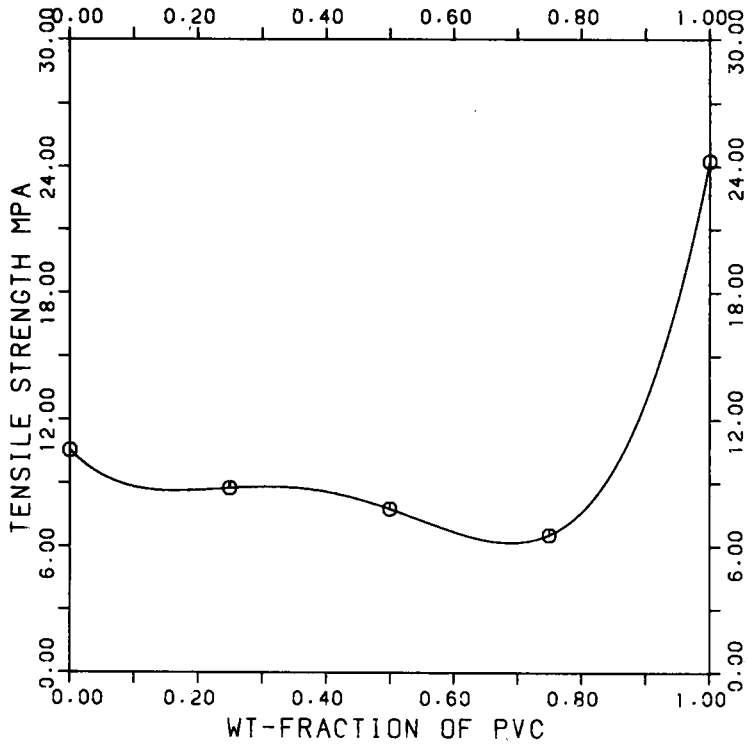


Fig. 13. The tensile strength as a function of blend composition.

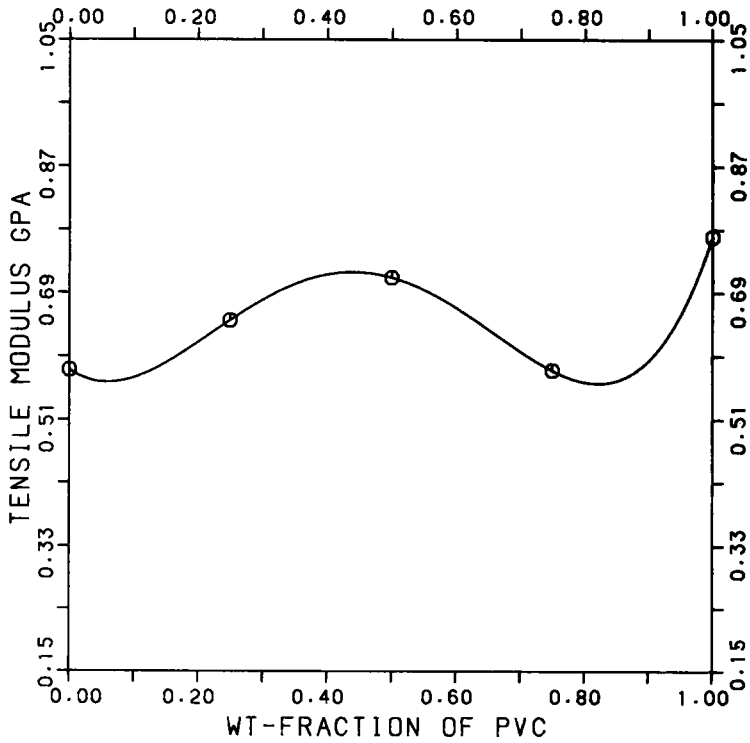


Fig. 14. The tensile modulus as a function of blend composition.

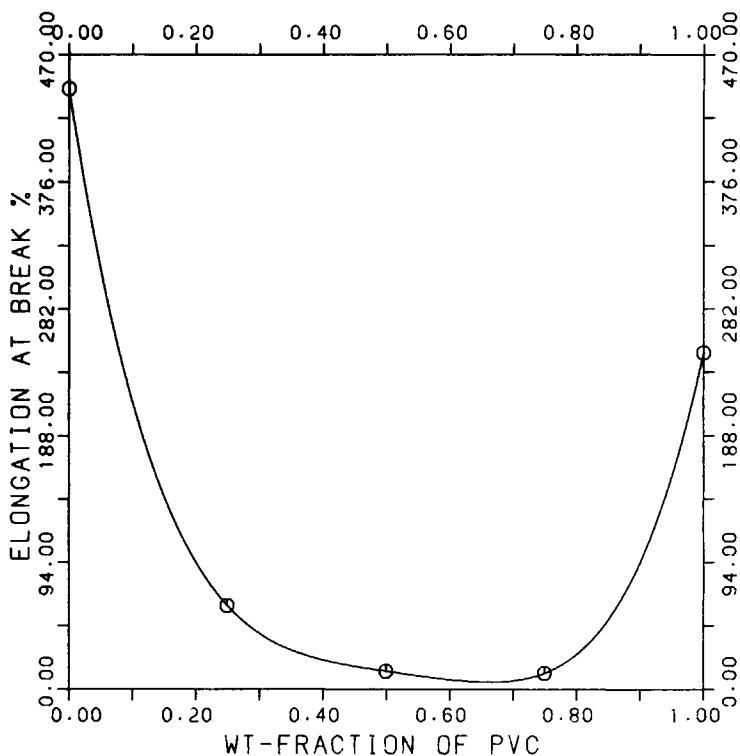


Fig. 15. The elongation at break as a function of blend composition.

rougher than the smooth and glossy appearance in smaller PVC content extrudates. The rheology and morphology of blends is reflected in the behavior of the ultrasonic velocity in the melt state. The compatibility of polymers may be characterized by ultrasonic techniques in addition to other more sophisticated techniques.

The present study indicates that wastes of LDPE and plasticized PVC can be utilized as blends, if an effective separation process is not available or is too expensive.

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