Extrudate Morphology of Blends of Plasticized Poly(vinyl Chloride) and Thermoplastic Copolyester Elastomer

INTRODUCTION

Properties of polymer blends are highly dependent on their morphology. During the last few years, several studies have been reported on the morphology of various polymer blends.[1-6] The phenomena of segregation, stratification, and phase inversion of heterogeneous polymer blends have been reported by various researchers.[7-12]

Blends of copolyester thermoplastic elastomer (hytrel 40D) and plasticized PVC combine the physical properties of hytrel and the excellent processing characteristics of PVC. These blends are popularly used in a variety of applications. Rheology, relationship between morphology and mechanical properties, failure behavior, compatibility, and radiation resistance of these blends have been studied[13-17] in this laboratory. However, no studies have been undertaken with respect to the extrudate morphology of these blends. Since these blends are used extensively in applications such as cables, tubes, and hoses, studies on the extrudate morphology of these blends become very important.

In this paper we report the results of our studies on the extrudate morphology of hytrel–PVC blends with special reference to the effect of blend ratios and extrusion shear rates.

EXPERIMENTAL

Details of the materials used in the present study are given in Table I. The mixes are denoted as H_{75}, H_{50}, and H_{25}, where the subscripts indicate the percentage of hytrel in the blend. The mixes were prepared in a Brabender Plasticorder (Model PLE 330), using a cam type mixer with a rotor speed of 80 rpm and the mixer chamber temperature set at 180°C. The mixed blend samples were extruded at a temperature of 190°C by using a capillary rheometer MCR 3210 attached to an Instron Universal Testing Machine (Model 1195). A capillary of length to diameter ratio (l_c/d_c) of 40 with an angle of entry of 90° was used. Details of capillary extrusion process were given in the earlier studies.[13]

The extrudates collected at shear rates of 122 s^{-1} and 1223 s^{-1} were fractured under liquid nitrogen. The hytrel phase was preferentially etched using chloroform. The samples were then dried at 40°C for about 48 h. The dried samples were sputter-coated with gold and examined by Philips 500 Model scanning electron microscope.

RESULTS AND DISCUSSION

Our earlier studies[13] on the rheological behavior of hytrel–PVC blends, and their constituent homopolymers have shown high viscosity of the hytrel phase as compared to PVC. The viscosity of the blends was found to increase with the increase of hytrel content. The viscosity of the blends extruded at the two shear rates is given in Table II.[13]

The major factors that determine the final morphology of the blends are component ratio, their melt viscosity, rate of shear during melt mixing, and the presence of other ingredients such as lubricants, extenders, plasticizers, and fillers. Danesi and Porter[6] have suggested that, for the same processing history, the composition of the blend and melt viscosity differences for the components determine the morphology. When the components have different melt viscosities, the morphology of the resultant blend depends on whether the minor component has a lower viscosity than the major one, and, if so, then this component will be finely dispersed. In contrast, the minor component will be coarsely dispersed in essentially spherical domains if its viscosity is higher than the major constituent. However, the morphology of hytrel–PVC blends shows some deviation from the expected trends. In this case, increase in proportion of one of the components does not cause any phase inversion in the system, as can be understood from the SEM photomicrographs.

TABLE I
Characteristics of the Materials Used

Property	Hytrel 40D[a]	PVC compound[b]
Chemical nature and composition	Random block copolymers of tetramethylene hard segments (4 GT units) and polyalkylene ether terephthalate soft segments (PTMG/T); the approximate wt % of hard segments is 33	Suspension polymerized poly(vinyl chloride) resin containing 60 phr dioctylphthalate plasticizer, 4 phr barium–cadmium stabilizer, and 2 phr barium stearate lubricant by weight; the compound was prepared by dry blending technique
Number average molecular weight of the raw polymer ($\overline{M}_n$)	25,000–30,000	64,000
Molecular weight distribution ($\overline{M}_w/\overline{M}_n$)	—	3
K value	—	65

[a] Hytrel 40D was obtained from E. I. Du Pont de Nemours and Co.
[b] PVC compound was received from National Organic Chemical Industries, Bombay.

TABLE II
Viscosity of the Samples at 190°C

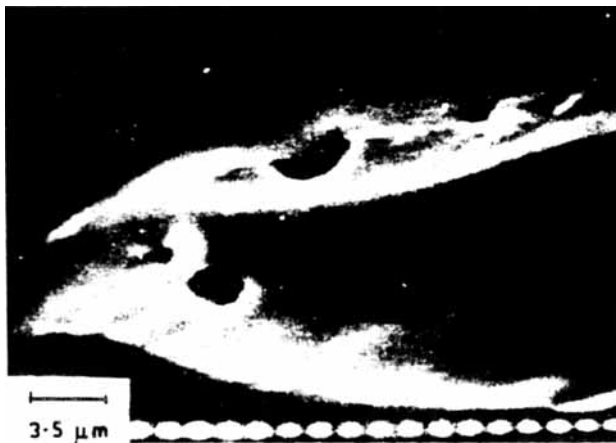| Shear rate (s^{-1})	Viscosity (N s/m²) × 10⁴				
	Hytrel	H_{75}	H_{50}	H_{25}	PVC
122	3.65	3.19	2.78	1.95	1.07
1223	1.82	1.49	0.69	0.60	0.40

Fig. 1(a). Morphology of H_{25} extruded at a shear rate of 122 s^{-1} showing the core region.

Fig. 1(b).   Morphology of H_{25} extruded at a shear rate of 122 s^{-1} showing the periphery region.

Fig. 1(c).   Morphology of H_{25} extruded at a shear rate of 1223 s^{-1} showing the core region.

Fig. 1(d).   Morphology of H_{25} extruded at a shear rate of 1223 s^{-1} showing the periphery region.

Fig. 2(a). Morphology of H_{50} extruded at a shear rate of 122 s^{-1} showing the core region.

Figure 1(a) shows the core region of the extrudate of H_{25} extruded at 122 s^{-1}. The black holes indicate the position of hytrel domains removed during etching. It is clear that hytrel phase is dispersed as domains in the continuous PVC matrix. The domain size is approximately 1.83 μm. The average domain size has been measured from the SEM photomicrographs and given in Figure 4. The periphery of the extrudate [Fig. 1(b)] shows only fewer hytrel domains, indicating its poor concentration at this region. At higher shear rates (1223 s^{-1}) the size of the particles has been considerably reduced as evident from the core region of the extrudate as shown in Figure 1(c). The sheath of the same extrudate [Fig. 1(d)] shows a lesser number of hytrel domains, indicating phase separation. On increasing the proportion of hytrel, the domain size also increases (Fig. 4). This is evident from the SEM photomicrograph of the core region of H_{50} [Fig. 2(a)] extruded at 122 s^{-1}. The average domain size has increased from 1.83 to 2.47 μm. The periphery region of the extrudate [Fig. 2(b)] contains fewer hytrel domains showing phase separation. At higher shear rates (1223 s^{-1}), the extrudate [Fig. 2(c)] shows smaller hytrel domains (0.82 μm). The corresponding periphery region of the extrudate [Fig. 2(d)] clearly indicates the absence of hytrel domains.

A further increase in the proportion of hytrel to 75% increases the particle size considerably (Fig. 4). This can be seen from the photomicrograph of the core region of H_{75} [Fig. 3(a)]. The particle size has increased to 5.79 μm. The periphery region of the extrudate [Fig. 3(b)] is richer in PVC. At higher shear rates the particle size has reduced to 1.53 μm [Fig. 3(c)]. Figure 3(d)
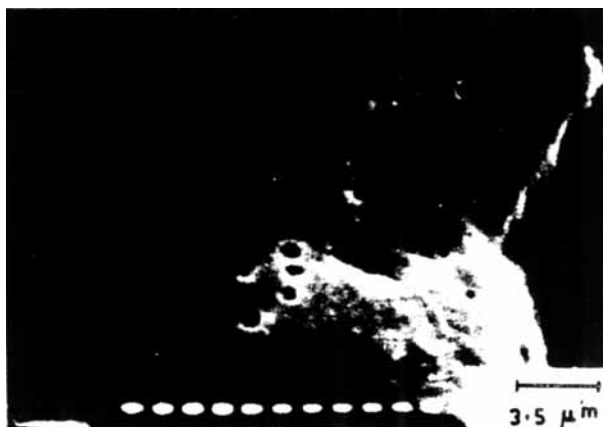

Fig. 2(b). Morphology of H_{50} extruded at a shear rate of 122 s^{-1} showing the periphery region.
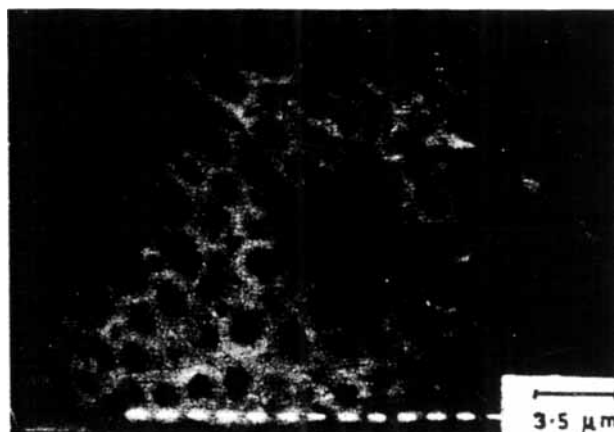
Fig. 2(c). Morphology of H_{50} extruded at a shear rate of 1223 s^{-1} showing the core region.

Fig. 2(d). Morphology of H_{50} extruded at a shear rate of 1223 s^{-1} showing the periphery region.

showing the periphery region of H_{75} reveals the stratification of the extrudate as observed in other blend ratios.

The present morphological investigations yield four important observations.

1. The absence of phase inversion in the system as evident from the discrete nature of the hytrel phase in all the blend ratios studied.

2. The increase of hytrel domain size with the increasing proportion of the hytrel phase.

3. Stratification of the extrudate with hytrel as the core region and PVC forming the sheath.

4. Decrease of hytrel domain size with increasing shear rates.

The absence of phase inversion in the hytrel–PVC blend is associated with the high viscosity of hytrel phase as compared to PVC (Table II).[14] The high viscosity component (hytrel) is dispersed as domains in the low viscosity continuous PVC matrix over the entire range of blend ratios studied (that is, up to 75% hytrel). The increase of hytrel domain size with increasing proportion of the hytrel phase is due to diffusion and recombination or coalescence of the dispersed particles. The occurrence of coalescence at higher concentrations of one of the components has been reported by some authors.[5,18] Heikens and Barentsen[18] have reported the similar observations in the case of polyethylene–polystyrene blends, which they explained on the basis of coalescence. The stratification of the extrudates is associated with the migration of the lower viscosity PVC component to the surface of the extrudate forming a sheath around the high viscosity hytrel phase. The phenomenon of stratification during the extrusion of polymer blends have been
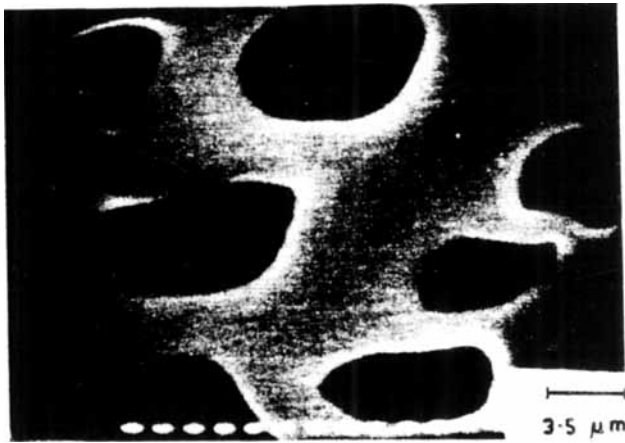
Fig. 3(a). Morphology of H_{75} extruded at a shear rate of 122 s^{-1} showing the core region.

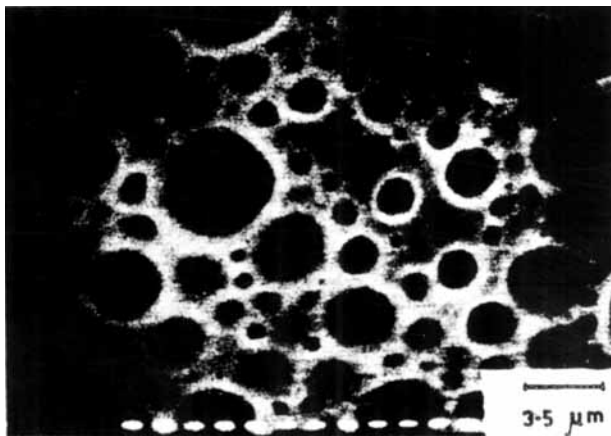Fig. 3(b). Morphology of H_{75} extruded at a shear rate of 122 s^{-1} showing the periphery region.

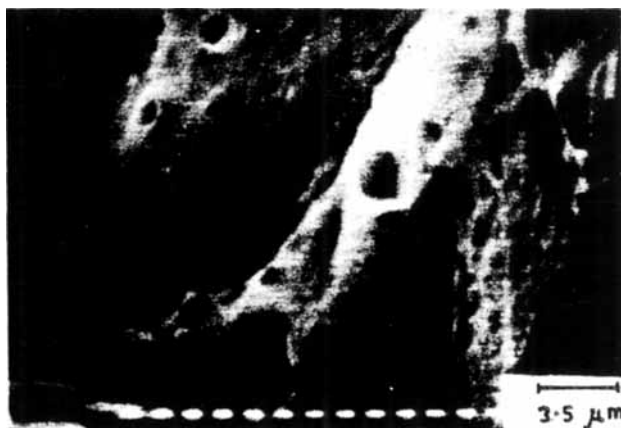Fig. 3(c). Morphology of H_{75} extruded at a shear rate of 1223 s^{-1} showing the core region.

Fig. 3(d).   Morphology of H_{75} extruded at a shear rate of 1223 s^{-1} showing the periphery region.

reported earlier.[6,8-12,19-22] Danesi and Porter[6] have studied the influence of extrusion speed on the stratification of EPDM/PP blends. They observed increased quantity of the lower melt viscosity polymer at the surface of the extrudate. Yu and Han,[19] Southern and Ballman,[20] and Lee and White[8,9] have studied the factors affecting the interface distortion in the two-phase flow of polymer melts. The conclusion of each of these studies were that differences in shear viscosity between the two melts lead to interface distortion, with the lower viscosity melt encapsulating the high viscosity melt. MacLean[21] and Everage[22] have suggested that the reason for encapsulation of high viscosity fluids by lower viscosity fluids during conduit flow is due to the tendency of multiphase system to take on a phase configuration, giving the lowest rate of viscous dissipation.
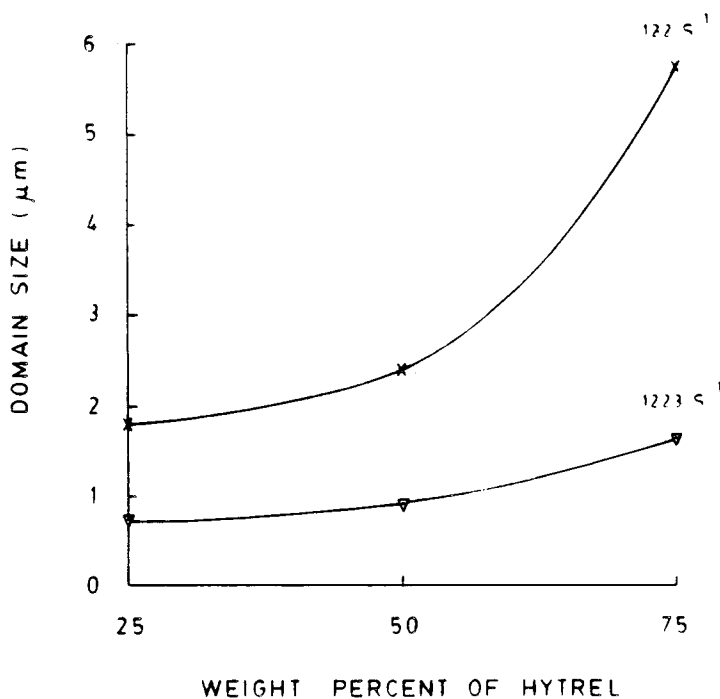

WEIGHT   PERCENT   OF   HYTREL

Fig. 4.   Effect of wt % of hytrel on hytrel domain size.
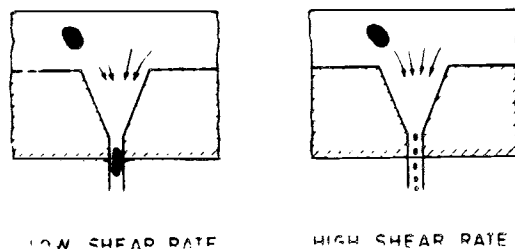
ᴵᴼᴺ SHEAR RATE   HIGH SHEAR RATE

Fig. 5. Morphological changes of hytrel domains during extrusion.

Finally, the decrease of particle size with the increase of shear rate is due to the fact that during extrusion the dispersed hytrel domains are elongated at the entrance of the capillary under the action of the shear force, resulting in the deformation and consequent breakdown of the hytrel particles as shown in Figure 5.[23]

CONCLUSIONS

Extrudate morphology of hytrel–PVC blends has been studied with special reference to the effect of blend ratio and extrusion shear rate. It is observed that hytrel phase, due to its high viscosity as compared to PVC, was dispersed as domains in the continuous PVC matrix over the entire ranges of blend ratios studied. The size of the hytrel domains was found to increase with the increase of hytrel content due to diffusion and recombination of the domains. At higher shear forces, the domains were broken down into smaller ones. The stratification of the extrudate with hytrel forming the core and PVC as the sheath was also observed at lower and higher shear rates.

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