

Chemorheological Study of Compatibilized Blends of Low-Density Polyethylene and Polydimethyl Siloxane Rubber

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ABSTRACT: Compatibilization of the blends of polydimethyl siloxane (PDMS) rubber and low-density polyethylene (LDPE) was achieved through reactive processing during extrusion in a Monsanto Processability Tester (MPT). The chemorheological characteristics of 50 : 50 LDPE : PDMS blends with varying proportions (0–8 wt %) of ethylene comethyl acrylate (EMA) were investigated at three different temperatures (170, 190, and 210°C) and four different shear rates (61.3, 122.6, 306.6, and 613.1 s⁻¹). It was found that EMA reacts with vinyl groups of PDMS rubber at a temper-

ature of 190°C during extrusion through the capillary of MPT, forming EMA-grafted-PDMS rubber (EMA-g-PDMS), which acts as the compatibilizer for the blend systems. The results are based on IR spectroscopy, melt rheology, and phase morphology of the blends. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2810–2817, 2003

Key words: compatibilization; blends; rheology; morphology; infrared spectroscopy

INTRODUCTION

In recent years blending techniques have been the focus of considerable attention and have been widely adopted in various polymer industries to overcome the disadvantages of individual polymers and to obtain the synergistic effect of end-use properties without following the tedious process of copolymerization. Only very few polymers form truly miscible blends, showing a single glass-transition temperature (T_g) and homogeneity at the molecular level (5–10 nm scale).¹ Almost all blends are immiscible; that is, they have a phase-separated morphology. Heterogeneous blends of technological importance are called “compatible,” and most of the commercial blends introduced recently are of this category. Thus, satisfactory physical and mechanical properties of the blends can be achieved by using a third component, known as a “compatibilizer,” which reduces the interfacial tension between the two phases, increases the surface area of the dispersed phase, promotes adhesion between the phase components, and stabilizes the dispersed phase morphology.¹

Polydimethyl siloxane (PDMS) has long been recognized as a rubber for both low- and high-temperature applications.² It has good insulating properties but, because of its high price, low mechanical properties,

and poor resistance to wear and tear, it requires considerable modifications³ by blending with different polymers. Here, a low-density polyethylene (LDPE) was chosen as the other material because of its low price, high mechanical properties, and high tear and wear resistance. However, blends of LDPE and PDMS rubber are not compatible because of the structural dissimilarity of blend constituents. Compatibilization is achieved by use of a third polymer, ethylene comethyl acrylate (EMA).

Previous investigators have already carried out a voluminous work in the field of compatibilization.^{4–15} However, not much attention has been paid to the study of processability of PDMS rubber and its blends. Recently, Santra et al.¹⁶ reported preliminary studies of the rheological behavior of blends of PDMS rubber and EMA copolymer. They also reported, with respect to physicomaterial properties, that the blends of PDMS and LDPE are incompatible throughout the composition range¹⁷ and that EMA acts as a very good compatibilizer for the blend system. In our present investigation we optimize the conditions for the *in situ* compatibilization of the blends through reactive processing by means of the Monsanto Processability Tester (MPT). This study deals with different parameters, such as melt viscosity, activation energy of flow, flow behavior index, die-swell, and also the level of compatibilizer concentration.

EXPERIMENTAL

Materials

LDPE (Indothane 20XL020; density, 919 kg m⁻³; melt flow index (MFI), 2.0 g/10 min; melting point, 112°C)

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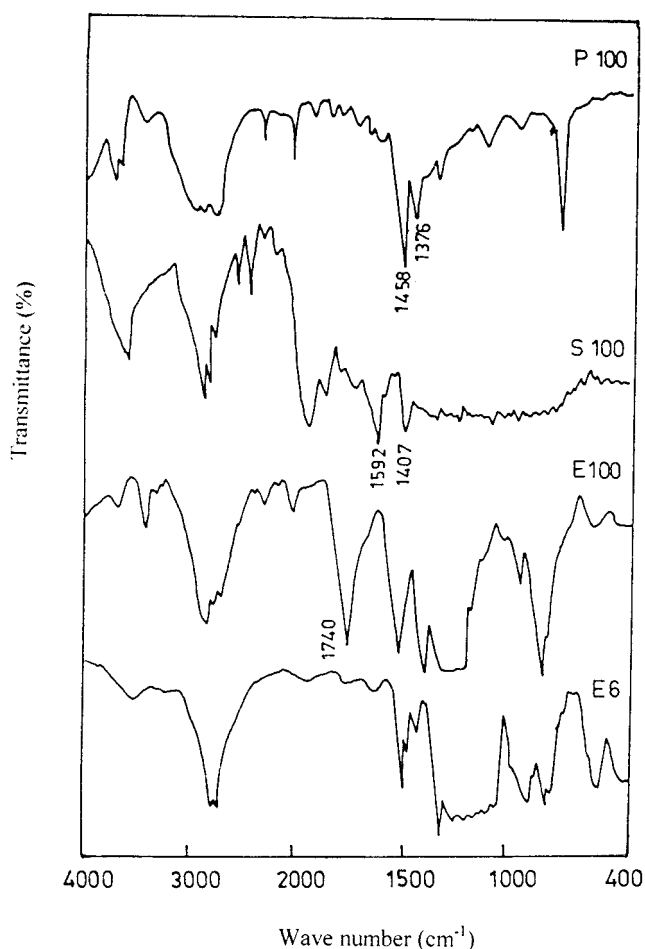


Figure 1 IR spectrograms of neat polymers and E_6 blend prepared by melt mixing in a Brabender at 140°C .

was supplied by Indian Petrochemicals (Vadodara, India). Polydimethyl siloxane rubber (Silastic WC-50; density, 1150 kg m^{-3} ; silica filler content, 30 wt %; brittle point, -39°C) was supplied by Dow-Corning (Midland, MI). Ethylene methyl acrylate copolymer (Optema TC-120) was obtained from Exxon Chemical (Bombay, India) having the following specifications: methyl acrylate content, 21%; melting point, 81°C ; MFI, 6.0 dg/min; and density, 940 kg m^{-3} .

Preparation of the blends

PDMS rubber and EMA were melt mixed in a Brabender plasticorder (Model PLE-300), with cam-type rotors at 140°C and 100 rpm rotor speed for 6 min and then LDPE was added and mixed for another 2 min. The molten mix was then sheeted out in a two-roll laboratory mill ($150 \times 300 \text{ mm}$). The sheet was cut into pieces and reprocessed in the plasticorder at 140°C for another 2 min and thereafter once again sheeted on the two-roll mill to ensure proper blending. The temperature was kept at 140°C to avoid any reaction of vinyl groups of PDMS rubber with EMA copolymer at this

stage. The aim of this stage was just to mix the blend constituents so that the sheet made from the molten mass could be fed to the MPT chamber without formation of any voids. The blends were coded as E_0 , E_4 , E_6 , E_8 , where subscripts denote the wt % of EMA in the 50 : 50 blend of LDPE and PDMS rubber, whereas E_{100} , P_{100} , and S_{100} indicate the neat EMA, LDPE, and PDMS rubber, respectively.

IR studies

Thin films ($\sim 0.1 \text{ mm}$ thick) of pure components and the blends were compression molded in a Moore press at 140°C . Infrared (IR) spectroscopic studies of the samples were performed with a Perkin-Elmer IR spectrophotometer (Model 843; Perkin Elmer Cetus Instruments, Norwalk, CT) in the wavenumber range of $4000\text{--}200 \text{ cm}^{-1}$.

Measurement of flow properties

The melt flow properties of the pure components and the blends were determined by means of a Monsanto Processability Tester (MPT; model no: 83077; Monsanto, St. Louis, MO), a high-pressure capillary rheometer at three different temperatures and shear rates, following the procedure recommended by the manufacturer.¹⁸ The capillary die used was 30 mm long, 1 mm in diameter, having L/D ratio of 30 : 1, with a conical entry having multiple cones of 45 and 60° .

SEM studies

Phase morphology of the blends was studied by examining the cryogenically fractured surfaces of extrudates after etching out of unmodified PDMS rubber with toluene for 48 h under a scanning electron microscope (model: Scan Cam Series-II). The solvent-extracted samples were dried in a vacuum oven at

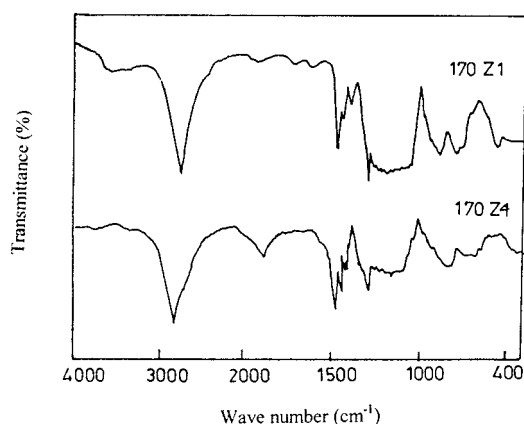


Figure 2 IR spectrograms of E_6 blend extruded from MPT at 170°C and at low ($Z_1 = 61.3 \text{ s}^{-1}$) and high ($Z_4 = 613.1 \text{ s}^{-1}$) shear rate.

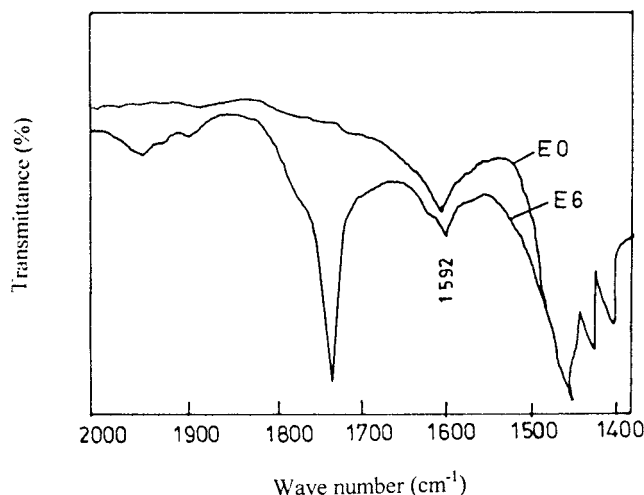


Figure 3 IR spectrograms of E_6 blend extruded from MPT at 190°C .

70°C for 12 h and cooled to room temperature in a desiccator. Subsequently, the etched surfaces were sputter coated with gold for facilitating scanning under the SEM at a 0° tilt angle.

RESULTS AND DISCUSSION

Mechanism of action of EMA copolymer by IR study

Infrared spectrograms of neat polymers and the E_6 blend prepared by melt mixing in a Brabender at 140°C are shown in Figure 1. The IR spectrum of LDPE (P_{100}) shows a rocking vibration of $-\text{CH}_2-$ at 1458 cm^{-1} and methyl branching at 1376 cm^{-1} , indicating the presence of minor chain branching in LDPE. The IR spectrum of PDMS rubber (S_{100}) shows the presence of vinyl groups attached to the silicone atom, as evidenced from $\text{C}=\text{C}$ stretching at 1592 cm^{-1} and in-plane vibration of the vinyl group ($-\text{CH}=\text{CH}_2$) at 1407 cm^{-1} . The IR spectrum of EMA copolymer (E_{100}) reveals the presence of ester groups from the strong peak at 1740 cm^{-1} . However, the IR spectrum of the blend containing 6 wt % of EMA (E_6), prepared by melt mixing in a Brabender at 140°C and 100 rpm rotor

speed, shows no extra peaks except those of LDPE, PDMS, and EMA. This provides ample evidence that there is no specific interaction or chemical reaction during melt processing.

Moreover, the IR spectrum (Fig. 2) of the E_6 blend extruded at 170°C shows no specific interaction either at low (Zone 1) or high (Zone 4) shear rates. The IR spectrum (Fig. 3) of the E_6 blend extruded at 190°C , however, shows a reduction in the $\text{C}=\text{C}$ stretching peak at 1592 cm^{-1} , indicating that a part of the vinyl group was used in the reaction with EMA during extrusion. The absorbance ratio Ar ($Ar = A_{1592}/A_{1458}$, where A_{1592} and A_{1458} are absorbance at 1592 and 1458 cm^{-1} , respectively), according to the ASTM D 3677 method, also shows a decrease with respect to the E_0 blend. The Ar value for the E_0 blend was 1.1879 and that for the E_6 blend was 0.1235; thus, there is reduction in the absorbance ratio of $\text{C}=\text{C}$ for the terblend of about 89.6%. This strongly supports an interaction by chemical bond formation between PDMS and EMA copolymer.

Flow behavior of the blends

On the basis of plunger speed, barrel diameter, capillary length, and diameter, the apparent shear rate and shear stress were calculated following the procedure described elsewhere.¹⁸ The true shear rate was calculated by applying Rabinowitsch correction.¹⁸ Bagley's correction for the shear stress was neglected, given that the capillary used was with a multiple conical entry and a high L/D ratio. The viscosity was calculated as the ratio of shear stress to the true shear rate. The power law equation was applied to describe the rheological behavior of the system. The flow behavior index n and consistency index K were calculated using a linear regression analysis. The n and K values are reported in Table I. The system shows a pseudoplastic nature ($n < 1$). The flow behavior index increases with an increase in the concentration of EMA copolymer and also with temperature, indicating a marginal reduction in the pseudoplastic character of the blends. The pseudoplasticity of a system is a consequence of capacity of the polymer molecules to orient them in

TABLE I
Flow Behavior Index (n) and Consistency Index (K) of the Blends and the Pure Components at Different Temperatures

Sample code	n			K ($\text{kPa} \cdot \text{s}^n$)		
	170°C	190°C	210°C	170°C	190°C	210°C
E_0	0.3267	0.3458	0.3732	61.9592	61.7179	61.5921
E_4	0.3388	0.3534	0.3753	19.6450	19.1240	18.3751
E_6	0.3430	0.3554	0.3779	18.7231	17.1461	14.5634
E_8	0.3497	0.3699	0.3882	17.0390	13.3976	10.7157
E_{100}	0.5307	0.5574	0.5679	3.4347	3.2089	2.6809
P_{100}	0.3856	0.5036	0.5859	14.2417	5.4465	2.6042
S_{100}	0.1015	0.2364	0.2926	79.3835	32.1847	22.8748

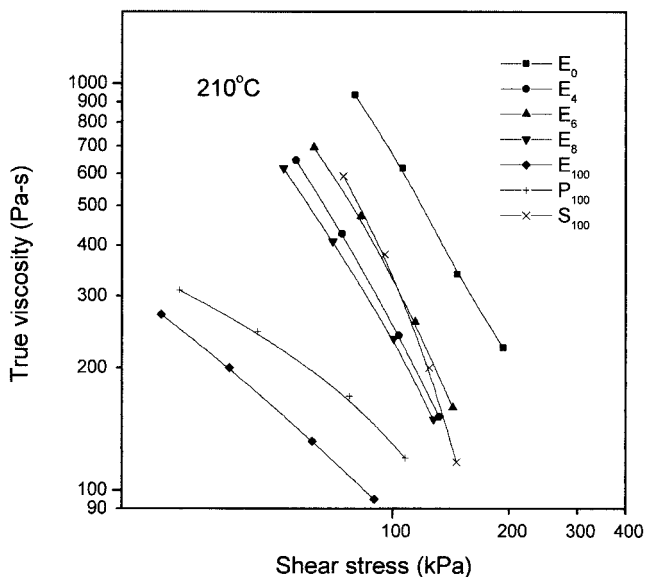


Figure 4 Flow curves of the different blends at 210°C.

the direction of the flow. The increase in temperature increases the molecular vibration and, therefore, the chance of orientation of molecules is reduced. Moreover, EMA reacts in the backbone of PDMS and gives EMA-g-PDMS rubber. The interaction between the grafted EMA chain and main chain may reduce the possibility of chain orientation. Thus, with an increase in both temperature and EMA concentration the n value increases.

The consistency index (K) decreases with temperature as well as with EMA concentration. The consistency index represents the viscosity at unit shear rate. With an increase in temperature, the extent of grafting of EMA increases and the free volume of the system increases; thus the K value decreases.

Melt viscosity

The melt viscosity of the neat components and 50 : 50 blends of PDMS and LDPE, containing different proportions of EMA at 210°C, are shown in Figure 4. The melt viscosity decreases with increase in shear rate, showing the shear thinning nature of the blends. The melt viscosity of E_{100} is the minimum and that of E_0 is the maximum. The maximum value for melt viscosity of E_0 may be explained by the fact that the PDMS rubber used for this investigation contains about 30 wt % of inherent silica filler, which may promote physical entanglement with the crystalline zone of LDPE, thereby increasing LDPE-PDMS rubber interaction and, in turn, the melt viscosity. At lower concentrations of EMA there may be very little or practically no grafting reaction between EMA and PDMS rubber. Therefore, EMA acts only as a plasticizer, thus reducing the viscosity.

From Figure 5 it can be seen that the viscosity of the blend generally decreases with the addition of EMA. The rate of decrease in viscosity is much higher at low concentration of EMA (up to 4 wt %) and then remains more or less constant with a further increase in EMA concentration, particularly at low temperatures (170°C). At higher temperatures (190 and 210°C), the viscosity increases between 4 and 6 wt % of EMA and then decreases, giving a maximum increase at 6 wt % of EMA.

With the increase in temperature the viscosity further decreases, giving a steeper decline in blend viscosity. As the concentration of EMA is increased (>4%), the extent of grafting reaction increases and becomes maximum at around 6 wt % of EMA. Thus at 6 wt % of EMA almost all the vinyl groups of PDMS rubber have been reacted with α -carbon of EMA to form EMA-g-PDMS rubber, which acts as the compatibilizer for the blend system. With further increase (>6 wt %) in EMA proportion in the blend system, there will be no grafting reaction because of the lack of vinyl groups contributed by PDMS rubber. The unreacted EMA will thus again act as a plasticizer for the blend system, thereby decreasing its melt viscosity; thus, the E_8 blend shows lower viscosity than that of the E_6 blend.

The experimental viscosity values were compared with values calculated using the log-additivity equation¹

$$\log \eta_{\text{blend}} = \sum w_i \log \eta_i \quad (1)$$

where w_i and η_i are the weight fraction and melt viscosity of the i th component in the blend. These

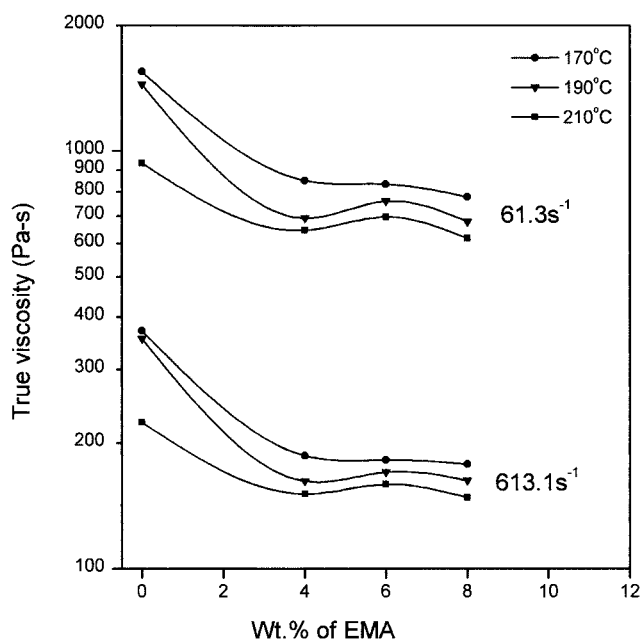


Figure 5 Plot of melt viscosity versus wt % of EMA at two different shear rates (61.3 and 613.1 s^{-1}).

TABLE II
Experimental and Theoretical True Viscosity of the Blends and the Pure Components

Sample code	170°C		190°C		210°C	
	log η_{theo}	log η_{expt}	log η_{theo}	log η_{expt}	log η_{theo}	log η_{expt}
E ₀	2.8164	3.1913	2.7107	3.1610	2.6314	2.9714
	2.6413	3.0411	2.5464	3.0012	2.4859	2.7912
	2.4062	2.7708	2.3313	2.7614	2.2663	2.5304
	2.1812	2.5701	2.1359	2.5507	2.0757	2.3512
E ₄	2.8077	2.9302	2.7034	2.8311	2.6237	2.8103
	2.6362	2.7412	2.5412	2.6704	2.4788	2.6313
	2.4033	2.4808	2.3274	2.4109	2.2608	2.3805
	2.1811	2.2706	2.1338	2.2112	2.0720	2.1812
E ₆	2.8036	2.9210	2.6999	2.8803	2.6200	2.8414
	2.6338	2.7402	2.5387	2.7004	2.4755	2.6713
	2.4019	2.4813	2.3256	2.4412	2.2582	2.4121
	2.1811	2.2605	2.1328	2.2315	2.0703	2.2014
E ₈	2.7996	2.8902	2.6966	2.8302	2.6165	2.7913
	2.6316	2.7213	2.5363	2.6614	2.4723	2.6116
	2.4006	2.4514	2.3238	2.4115	2.2557	2.3721
	2.1811	2.2513	2.1318	2.2113	2.0686	2.1712
E ₁₀₀		2.5908		2.5209		2.4315
		2.5103		2.4107		2.3019
		2.3304		2.2309		2.1234
		2.1807		2.0811		1.9802
P ₁₀₀		2.8115		2.6411		2.4915
		2.6312		2.5016		2.3909
		2.3813		2.3213		2.2314
		2.1911		2.1404		2.0805
S ₁₀₀		2.8212		2.7802		2.7712
		2.6513		2.5912		2.5809
		2.4311		2.3412		2.3012
		2.1712		2.1314		2.0709

experimental values have been found to be always higher than those calculated, giving positively deviating blends (Table II). This also indicates a strong interaction between the blend constituents.

Activation energy of flow

The activation energy of viscous flow was calculated by using an Arrhenius-type equation¹⁹:

$$\eta = Ae^{E/RT} \quad (2)$$

where η is the melt viscosity, A is the preexponential factor, E is the activation energy, T is the absolute temperature, and R is the molar gas constant.

The plots of activation energy of flow (calculated from the slope of straight-line plots of log melt viscosity against the reciprocal of temperature; figures not shown) against the EMA proportion in 50 : 50 LDPE : PDMS are shown in Figure 6. The activation energy of flow decreases with an increase in the proportion of

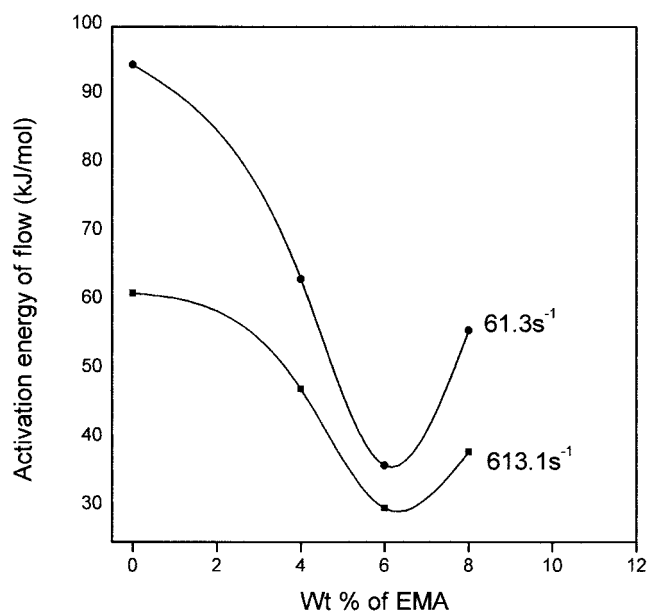


Figure 6 Plot of activation energy of flow versus wt % of EMA in the blends.

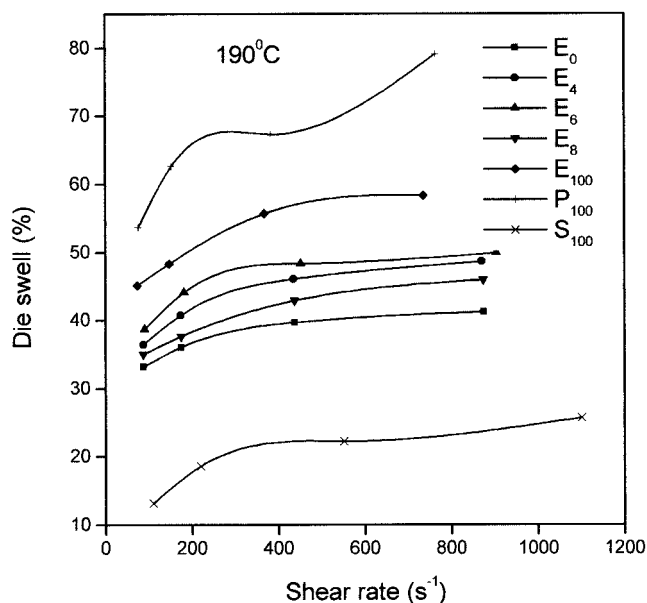


Figure 7 Variation of die swell with shear rate for different blends at 190°C.

EMA up to 6% and then increases, giving a minimum value at 6 wt % of EMA copolymer and thus indicating easy processability. It is probably attributable to the change in phase morphology of the system, which changes from a two-phase to a cocontinuous nature (discussed later), resulting in a uniform stress distribution in the system. For EMA concentrations higher and lower than 6 wt %, the system shows a two-phase morphology, resulting in stress concentration around the discrete domains and, therefore, requires higher energy to flow. The activation energy of flow is considerably reduced at higher rate of shear because of the pseudoplastic nature of the system, which reduces the viscosity at higher shear rates.

Die-swell characteristics

The die swell increases with increase in shear rate (Fig. 7) and decreases with temperature (Fig. 8). Figure 9 shows the variation of die swell with wt % of EMA at two shear rates (61.3 and 613.1 s^{-1}). Die swell was found to increase initially with wt % of EMA and then decrease, showing a maximum value at 6 wt % of EMA.

The increase in die swell with increasing shear rate may be attributed to the considerable increase in the recoverable elastic energy of the system at higher shear rates. The increase in temperature increases the mobility of the polymer chain, which reduces the capacity of polymer molecules to store the elastic energy and, hence, there is a reduction in the die swell values.^{20–22} Die swell at 6 wt % of EMA is maximum at any shear rate, implying that optimum compatibilization leads to a physically entangled structure of a

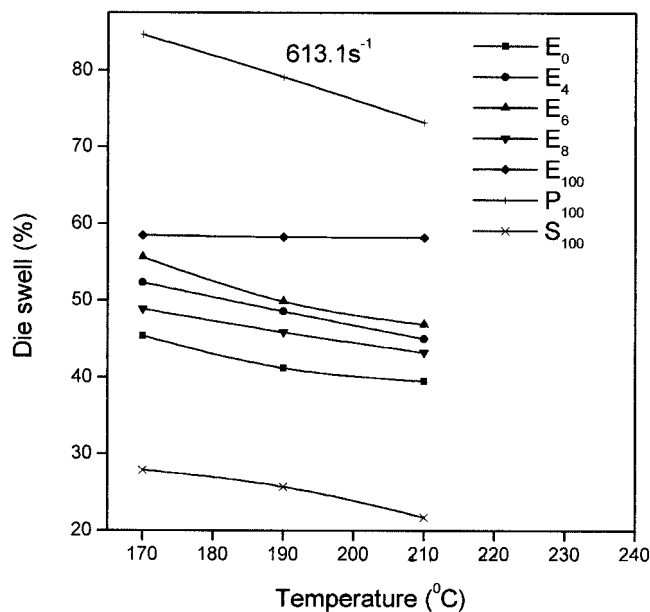


Figure 8 Variation of die swell with temperature at a constant shear rate of 613.1 s^{-1} .

three-dimensional network, which obstructs the chains to move past one another. Beyond 6 wt % of the compatibilizer (i.e., 8 wt % of EMA copolymer), it acts as a plasticizer, thereby decreasing the number of entanglements and consequently the die swell. Jansen et al.²³ and George et al.²⁴ showed that die swell decreases regularly with wt % of compatibilizer. However, EMA compatibilized blends show abnormal behavior on die swell, which was thoroughly explained in our earlier communication.²⁵

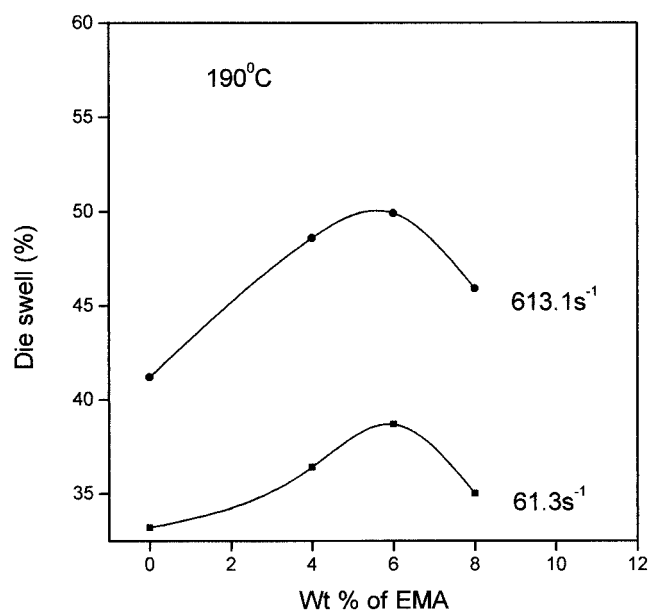


Figure 9 Variation of die swell with wt % of EMA at two different shear rates at a temperature of 190°C.

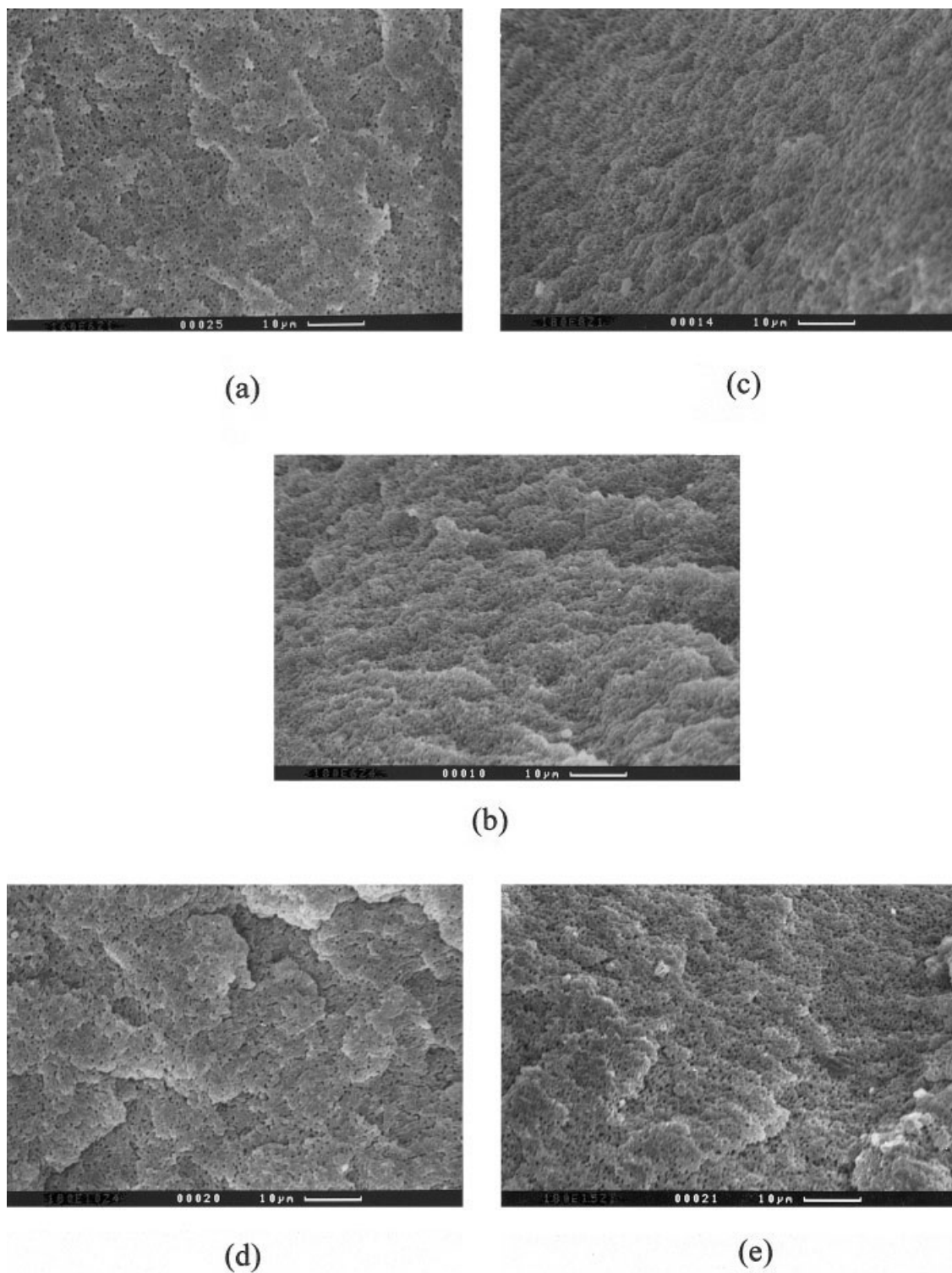


Figure 10 SEM micrographs of fractured surfaces of the extrudates of the blends at a shear rate of 613.1 s^{-1} : (a) E_6 blend at 170°C , (b) E_6 blend at 190°C , (c) E_6 blend at 210°C , (d) E_4 blend at 190°C , and (e) E_8 blend at 190°C .

Phase morphology

The phase morphology was studied by SEM at different temperatures of blending and with various loadings of EMA. It is observed from the SEM photomi-

crographs that at a lower temperature (i.e., 170°C), the E_6 blend is characterized by a dispersed domain structure [Fig. 10(a)], whereas the domain size decreases at higher temperatures (190 and 210°C), indicating an almost cocontinuous phase morphology [Fig. 10(b)

and (c), respectively]. Figure 10(d) and (e) show the SEM photomicrographs of E_4 and E_8 blends at 190°C, respectively. It is clear from these figures that the domain size of the dispersed phase is higher than that of the E_6 blend. Thus at the optimum level of compatibilizer and above 170°C better phase morphology is observed.

CONCLUSIONS

1. The viscosity of the blend without compatibilizer is higher than the viscosity of either parent because of the polymer–filler interaction.
2. The addition of a small amount of compatibilizer produces blends whose viscosity is close to, but slightly higher than, that predicted by the logarithmic additivity rule.
3. Flow behavior index (n) increases both with EMA proportion and temperature but the consistency index (K) shows the reverse trend.
4. Activation energy of flow is minimum at 6 wt % proportion of EMA copolymer in the blend (E_6).

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