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Short Communication

Studies on the rheological behaviour of plasticized poly(vinyl chloride)–thermoplastic copolyester elastomer blends

Abstract: The rheological behaviour of plasticized poly(vinyl chloride) (PVC)–thermoplastic copolyester elastomer (HYTREL 40D) blends has been evaluated with specific reference to the effects of blend ratio and temperature on iscosity, flow behaviour index and die swell. The proortion of the thermoplastic rubber in the blend was found to have a profound influence on viscosity at higher shear stresses. The die swell of the extrudates was also found to decrease with increase in Hytrel content.

Nomenclature

A_p	Cross-sectional area of plunger (mm^2)
d_c	Diameter of capillary (mm)
d_e	Diameter of extrudate (mm)
F	Extrusion force (N)
l_c	Length of capillary (mm)
n'	Flow behaviour index defined by $d(\log \tau_w)/d(\log \dot{\gamma}_{wa})$
Q	Volume flow rate (mm^3 s^{-1})
$\dot{\gamma}_w$	Shear rate at wall (s^{-1})
$\dot{\gamma}_{wa}$	Apparent shear rate at wall (s^{-1}) $= 32\,Q/\pi d_c^3$
η	Shear viscosity (Ns m^{-2})
τ_w	Apparent shear stress at wall (Pa)
phr	Parts per hundred of resin
PVC	Poly(vinyl chloride)
rpm	Revolutions per minute

1 Introduction

Thermoplastic elastomers are materials which have properties of vulcanized rubbers but can be processed like thermoplastics. Such materials can be blends comprising rubber–plastic combinations or block copolymers consisting of a hard thermoplastic segment and a soft rubbery segment or those polymers which have specified stereo-regular structure and controlled extent of crystallinity.[1–6] The thermoplastic rubbery character of Hytrel is due to its two-phase domain structure where the crystalline phase serves as thermally reversible crosslinks and the amorphous phase contributes to the elastomeric character.[7] It has been reported[8, 9] that many of the commercial thermoplastic elastomers can be blended with different types of polymers so as to get optimum balance of physical and processing properties. The physical properties of these poly-blends are generally a compromise or may be superior to the properties of the individual constituent polymers.

Another reason for blending commercial thermoplastic elastomers is the cost–performance ratio. For example, an expensive polymer like Hytrel, whose property spectrum is much higher than is needed for a new application, may be blended with an inexpensive polymer like PVC, whose property spectrum is such that the resulting poly-blend has a cost–performance ratio that makes it very attractive for a given application.

It has been reported[10] that when Hytrel is added to a PVC system such that the plasticizer to vinyl ratio is kept constant, additional property improvements are observed. In addition to improving the low temperature flexibility, brittle point, heat distortion and abrasion resistance, the addition of Hytrel increases the tensile strength, modulus, elongation and tear strength of PVC. Since these materials can be processed in the same way as thermoplastics, rheological studies of these blends have become important in developing new processing equipment and dies necessary for the production of various types of extruded and injection-moulded parts.

The rheological behaviour of polymer blends and that of polymers containing gel and crosslinked particles have been studied by different research groups.[11–19] The effects of rubber particles, carbon black and non-black fillers on the flow properties of polymer melts have also been studied.[20–22] Various factors affecting the die swell, melt fracture and deformation of the extrudate have been reported by several authors.[23–27] Recently, Kuriakose and De[28] have studied the melt flow characteristics of natural rubber–polypropylene thermoplastic elastomer blends. Studies on the rheological behaviour of thermoplastic elastomer blends have become a subject of recent interest due to their growing commercial importance. In this paper, we report on the results of our rheological studies on plasticized poly(vinyl

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Table 1. Characteristics of the starting materials

Property	Hytrel 40D	PVC
Chemical nature and composition	Random block copolymers of tetramethylene glycol hard segments (4 GT units) and polyalkylene ether terephthalate soft segments (PTMG/T). The approximate wt % of hard segment 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.
Molecular weight distribution ($\bar{M}_w/\bar{M}_n$)	–	3[a]
K value	–	65[a]

[a] Values obtained from the supplier (NOCIL, India).

Table 2. Composition of Hytrel–PVC blends

Component	H_{100}	H_{75}	H_{60}	H_{50}	H_{40}	H_{25}	H_0
Hytrel 40D[a]	100	75	60	50	40	25	0
PVC[b]	0	25	40	50	60	75	100

[a] Hytrel 40D obtained from E. I. duPont de Nemours & Co., Delaware, USA.
[b] PVC received from NOCIL, India.

chloride) (PVC)-thermoplastic copolyester elastomer (Hytrel 40D) blends. The effects of blend ratio and temperature on viscosity, flow-behaviour index and extrudate swell have been studied.

2 Experimental

2.1 Preparation of the blends

Details of the materials used in the present study are given in Table 1. Formulations of the mixes are given in Table 2. The mixes are denoted by suffixes H_{100}, H_{75}, H_{60}, H_{50}, H_{40}, H_{25} and H_0 corresponding to the percentage of Hytrel in the blend. The mixes were prepared in a Brabender Plasti-Corder 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 total mixing time was 7 min in all cases. In preparing the blends, Hytrel was melted in the mixer for 1 min and then PVC was added and the blend was allowed to mix for 5 min. The blend was taken out and sheeted through a laboratory mill at 2 mm nip setting. The sheeted-out material was cut into small pieces, again mixed in the plasti-corder at 180°C for 1 min and finally sheeted-out in the mill to obtain uniform dispersion. Specimens of dimensions 5·0 × 5·0 × 2·5 mm were cut from the sheets and used for melt flow measurements.

2.2 Rheological measurements

The rheological measurements were carried out 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 4 with an angle of entry of 90°C was used for this study so as to minimize the capillary end effects. The sample was placed inside the barrel of the extrusion assembly and forced down into the capillary with the plunger attached to the moving crosshead. After a warming-up period of 5 min the melt was extruded through the capillary at preselected speeds of the crosshead which varied from 0·5 to 500 mm min^{-1}. The melt height in the barrel before extrusion was kept the same in all experiments and the machine was operated to give ten different plunger speeds, with a single charge of the material. Force corresponding to specific plunger speeds was recorded using a strip chart recorder. The force and crosshead speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at the wall using the following equations involving the geometry of the capillary and the plunger:[29]

$$\tau_w = \frac{F}{4A_p(l_c/d_c)} \tag{1}$$

$$\dot{\gamma}_w = \left(\frac{3n'+1}{4n'}\right)\frac{32Q}{\pi d_c^3} = \left(\frac{3n'+1}{4n'}\right)\dot{\gamma}_{wa} \tag{2}$$

The flow behaviour index n' was determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from the experimental data. The shear viscosity η was calculated from τ_w and $\dot{\gamma}_w$.

2.3 Swell measurements

The extrudate emerging from the capillary was collected, taking maximum care to avoid any further deformation. The diameter of the extrudate was measured at several points using a microscope fitted with a micrometer. The diameter was measured at several intervals of time and it was noticed that there was no change in diameter after 24 h. The values after 24 h were recorded as those at equilibrium extrudate diameter, d_e. The swelling index was calculated as the ratio of the diameter of the extrudate to that of the capillary.

3 Results and discussion

3.1 Effect of blend ratio and shear stress on viscosity

The effects of blend ratio and shear stress on viscosity of thermoplastic Hytrel–PVC blends at temperatures of 180°, 190° and 200°C are shown in Figs 1, 2 and 3 respectively. At lower shear stresses, H_{100} and H_{75} approach constant shear viscosity at all the temperatures studied. At higher shear stresses, Hytrel shows higher viscosity than PVC, and the blend viscosities increase with increasing proportion of Hytrel. This behaviour is found at all temperatures. At the lowest shear stresses measured and at temperatures of 180° and 190°C, H_{25}, H_{40}, H_{50} and H_{60} exhibit higher viscosity than Hytrel but H_{75} and H_0 show lower viscosity. Moreover, it is also noted that at these shear stresses, the blend viscosities do not show any regular change with increasing proportion of Hytrel. At 200°C, even though Hytrel shows higher viscosity compared to blends, the blend viscosities do not show uniform variation with changing proportions of Hytrel. This is evident from the lower viscosity of H_{75} compared to those of H_{25}, H_{40}, H_{50} and H_{60}.

3.2 Effect of temperature on viscosity

The effect of temperature on the viscosity of the blends at two different shear rates is shown in Fig. 4. In general, at all shear rates, the viscosity decreases with increase of temperature from 170° to 200°C and the decrease is more pronounced for pure PVC and blends containing higher proportions of PVC, particularly at low shear.

3.3 Effect of temperature and blend ratio on flow behaviour index n′

The effect of temperature and blend ratio on flow behaviour index n' is presented by histograms in Fig. 5. In general n' increases with increase of temperature except for the blend H_{50} which shows a lower value of n' at 190° and 200°C than at 180°C. Moreover, values of n' do not show a regular change with varying blend composition.

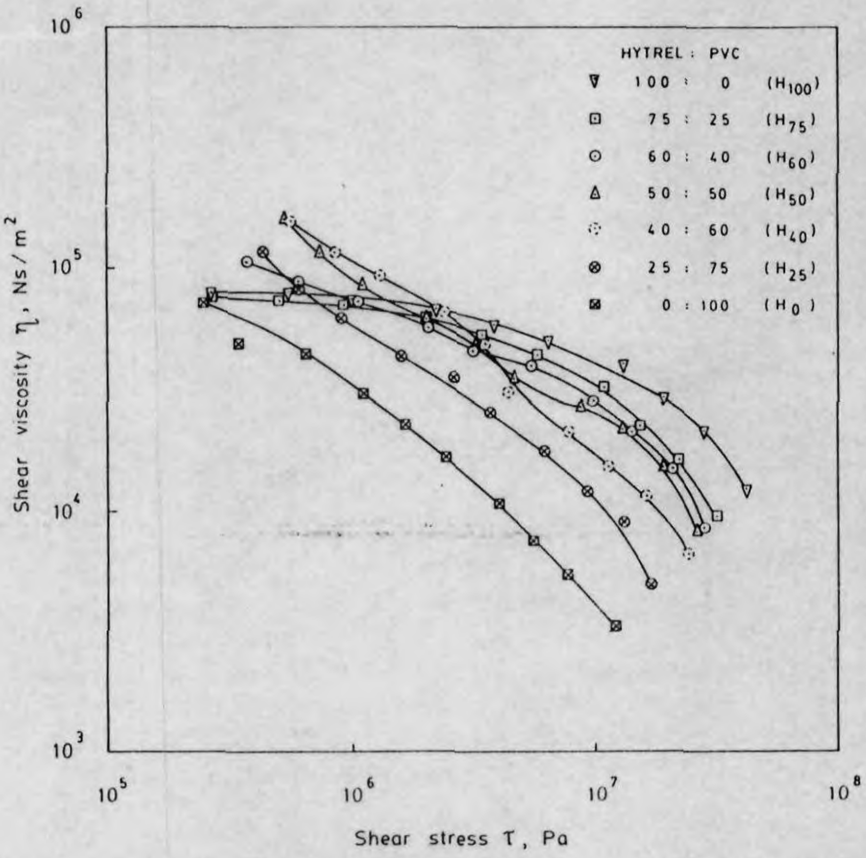

Fig. 1 Viscosity-shear stress plots showing effect of blend ratio in Hytrel-PVC blends at 180°C.

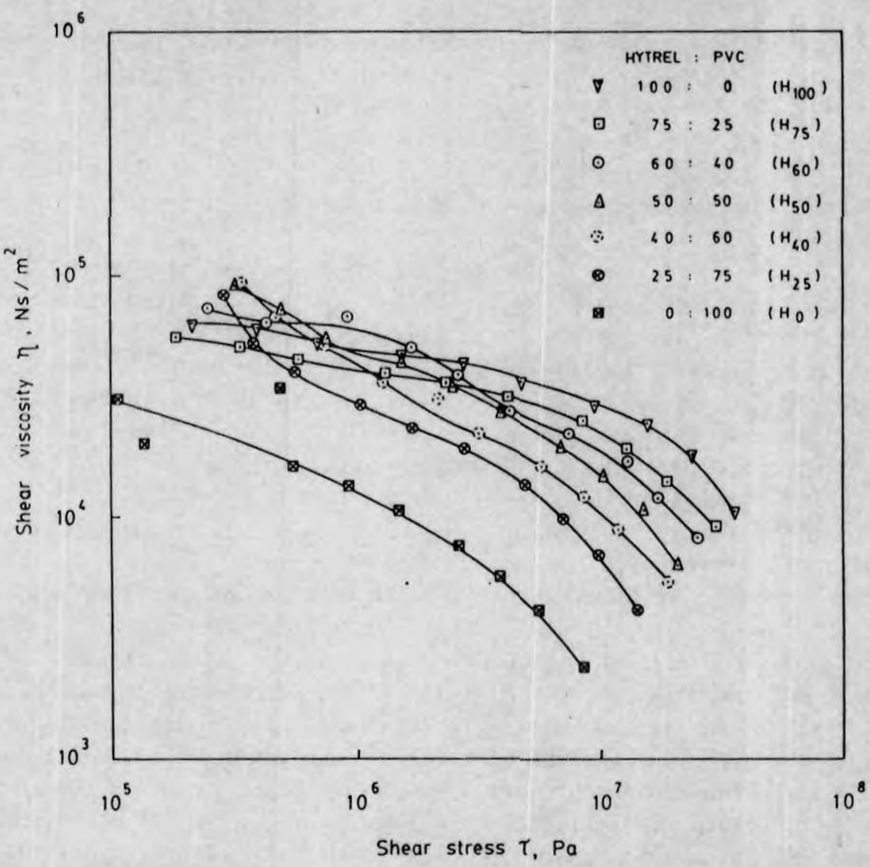

Fig. 2 Viscosity-shear stress plots showing effect of blend ratio in Hytrel-PVC blends at 190°C.

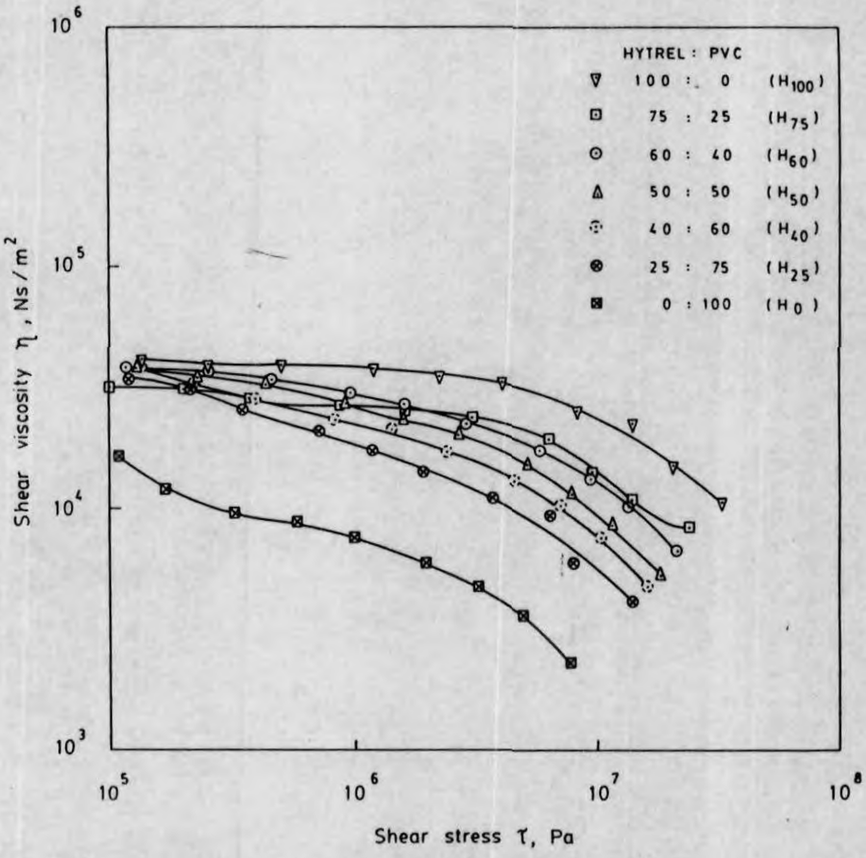

Fig. 3 Viscosity-shear stress plots showing effect of blend ratio in Hytrel-PVC blends at 200°C.

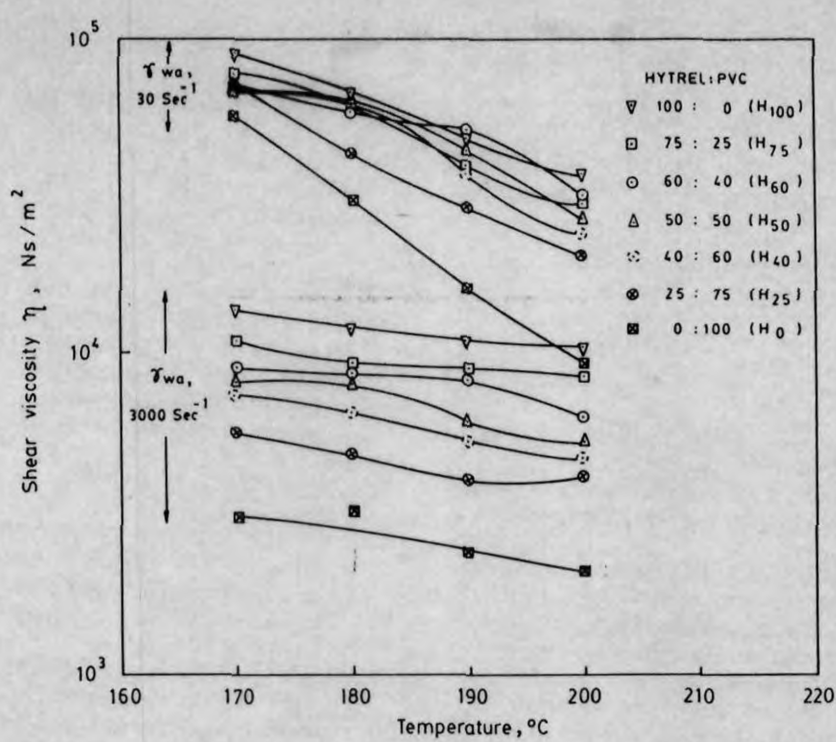

Fig. 4 Viscosity-temperature plots showing effect of temperature on Hytrel-PVC blends at different shear rates.

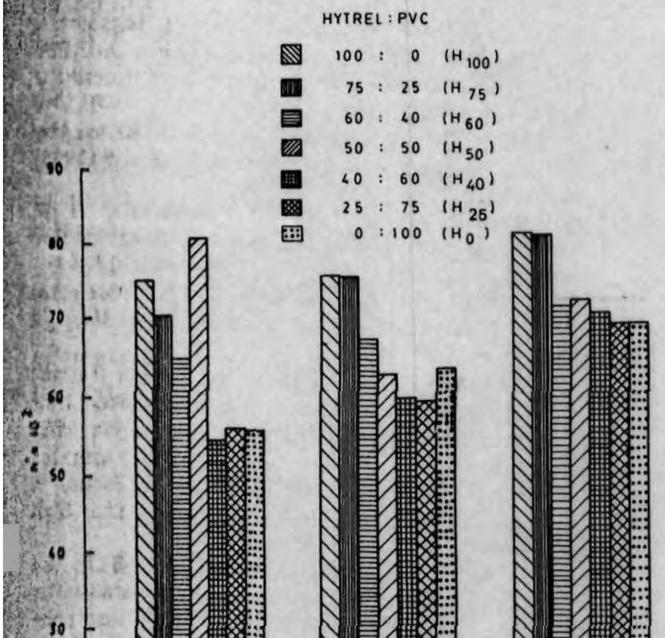

Fig. 5 Effect of temperature and blend ratio on flow behaviour index of Hytrel–PVC blends.

3.4 *Effect of shear rate and blend ratio on swelling index*

Figure 6 shows the die swell values of the system at two different shear rates at a temperature of 190°C. In general, the die swell values increase with increase

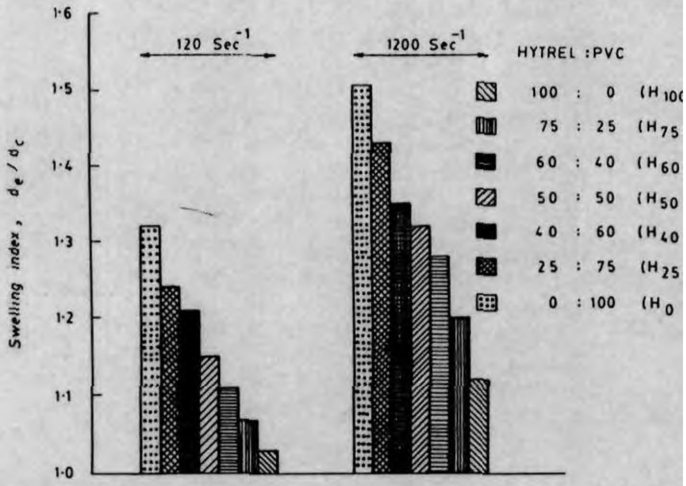

Fig. 6 Effect of blend ratio and shear rate on swelling index of Hytrel–PVC blends at 190°C.

in shear rate. At both shear rates under study, PVC shows the maximum die swell and Hytrel shows the least. As expected, the die swell values of the blends gradually decrease with increasing proportion of Hytrel. This is attributed to the high tensile set and lower elastic recovery of Hytrel compared to PVC.[30]

Summary and conclusions

The following conclusions can be drawn from the preceding discussion:

(1) Thermoplastic Hytrel–PVC blends can be processed like thermoplastics, as the viscosity at

higher shear stresses is intermediate between those of Hytrel and PVC.

(2) In the thermoplastic Hytrel–PVC blends, the increase in viscosity with increase in Hytrel content is predominant only at higher shear stresses.

(3) The die swell of the extrudates decreases with increasing Hytrel content.

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