Studies on the Polyblends of Poly(vinyl Chloride) with Various Methacrylate Copolymers, Melt Rheological Properties. II

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Synopsis

Studies have been made on the melt rheological properties of poly(vinyl chloride) (PVC) with copolymers of methyl methacrylate (MMA) and methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), and 2-ethyl hexyl acrylate (EHA) at a blending ratio of 80:20. Effect of blend composition on shear stress–shear rate, melt viscosity, melt elasticity, and extrudate distortion have been studied. A significant decrease in the melt viscosity is observed on incorporation of low T_g acrylate copolymers such as those with BA and EHA, thereby reducing the processing temperature. First normal stress and die swell ratio also decreases with an increase in the side chains of acrylate copolymer. PVC blended with P(MMA-co-BA) and P(MMA-co-EHA) is sensitive to both temperature and shear stress.

INTRODUCTION

Polymer blends are of considerable importance, as blending could provide a means for improving both mechanical properties as well as processability.[1] It is well known that poly(vinyl chloride) (PVC) is blended with rubbery polymers to improve its impact strength, thus making it suitable for rigid applications. Furthermore, the processing of PVC can be improved by the incorporation of additives like plasticizers and lubricants without which PVC cannot be processed easily.[2] Incorporation of a plasticizer increases the flexibility of PVC and also favorably affects its fusion and melt viscosity.[3] On the other hand, lubricants lower the processing temperature and hence improve its flow characteristics.[4] Besides these, the addition of a specialized polymer in relatively small quantities further improves the processing. These are mostly polyacrylate resins which when incorporated in small quantities act as processing aids and when added in an appreciable quantity can act as impact modifiers without detracting from the desirable properties of rigid PVC. The addition of copolymers of methyl methacrylate (MMA) and ethyl acrylate (EA) in a rigid PVC composition to reduce the incidence of processing defects associated with melt rupture have been reported by Gould and Player.[5] Rigid PVC melts are characterized by high viscosity, high pseudoplasticity, and their inability to sustain shear flow under accelerating stress without rupture. Copolymers of MMA and various acrylate monomers while improving the

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melt behavior also increase, the plasticization which is very important in polymer processing. Cogswell[6] has shown that high molecular weight acrylic polymers enhance the processability of PVC especially by increasing its extensibility and suppressing various defects. Similarly Bach and co-workers[7] have shown that ethylene vinyl acetate (KVA) copolymer reduces the melt viscosity of PVC. The physico-mechanical properties of polyblends of PVC and poly(MMA-co-acrylates) have been given in Part I of this article,[8] where a considerable improvement has been achieved in the impact strength of PVC on incorporation of these copolymers. The polymers synthesized and used were copolymers of MMA and (a) methyl acrylate (MA), (b) ethyl acrylate (EA), (c) butyl acrylate (BA), and (d) ethyl hexyl acrylate (EHA). The copolymers' compositions were MMA/acrylate 80 : 20 by weight. Blends of P(MMA-co-acrylate) copolymers and PVC in a 80 : 20 ratio by weight were prepared. The present study aims at determining the melt rheological properties of the blend system with a view toward understanding the processing behavior of modified PVC. The study is carried out on a piston type capillary rheometer. An attempt has been made to study the effect of different acrylate copolymers on various rheological parameters like shear stress, shear rate, melt viscosity, melt elasticity, and die swell. The effect of melt blending on melt fracture has been illustrated by extrudate distortion.

EXPERIMENTAL

Materials

Poly(vinyl chloride) with a viscosity average molecular weight (M_v) of 65,000 was supplied by M/s NOCIL Ltd., Bombay, India.

Synthesis of copolymers of MMA with methyl acrylate, ethyl acrylate, butyl acrylate, and 2-ethyl hexyl acrylate has been carried out as reported in Part I of this article.[8]

Octyl tin mercaptide (M/s ALA Chemicals) was used as a stabilizer for PVC.

All the copolymers had an intrinsic viscosity $(\eta)_0$ in the range of 0.24–0.28 dL g^{-1} using chloroform as a solvent. Exact value of M_v could not be found because of nonavailability of K and η_0 values for acrylate copolymers in the literature. However, homopolymer of MMA prepared has $\eta_0 = 0.24$ dL g^{-1} and, consequently, $M_v = 85500$, as calculated by equation $\eta_0 = KM^\alpha$.

Preparation of Polyblends

PVC/poly(MMA-co-acrylate) blends in 80 : 20 ratio were prepared by melt blending technique. The mixture of polymeric materials along with a heat stabilizer (octyl tin mercaptide) and lubricant (stearic acid) for PVC was mixed thoroughly and extruded in the form of strands by a single screw extruder with a barrel and die temperature of 165°C. Extruded strands were then chopped into granules in a granulator and the granules were used for further work.

Characterization Methods

Melt flow properties were measured on a piston type rheometer (Koka Flow Tester of Shimadzu Seisakushu Ltd.) using a circular die with an L/D ratio of 2, flat at the entrance region. In the Koka flow tester, the material is heated to the desired temperature in a cylindrical chamber to which a die is attached.

In one set of experiments, the pressure was kept constant and temperature was increased from a preset value below the glass transition temperature. This was then increased at a constant rate and the displacement of plunger noted as a function of temperature until fluid flow was attained. Such experiments provide an approximate measure of T_g and the minimum processing temperature. The plot of displacement vs. temperature is referred to as the plasticity curve.

In another set of experiments, the material is pushed through the die with a plunger at a constant pressure to extrude the material through the capillary, and the rate of output is determined. In other words, the shear stress is maintained at constant value and the shear rate measured. The pressure is varied in the range 10–110 kg/cm^2 to obtain shear stress vs. shear rate relationship. Experiments were carried out at three different temperatures, 190, 200, and 210°C. From these data the variation of melt viscosity η_{app} as a function of shear rate at various temperatures were determined. Furthermore, the variation of temperature at fixed shear rates were also determined. Die swell measurements were made by measuring the diameter of the strand extruded from the capillary (D_s) and comparing it to the diameter of the capillary (D).

RESULTS

Plasticity Curves

Plasticity curves represent the temperature dependence of plunger displacement at constant temperature. For a proper range of study, the plasticity curves were obtained using 30 kg/cm^2 pressure. The speed of the recorder chart has been kept 1 in./min. These curves indicate the different rates of increase of temperature and also the time dependence of various flow. It is obvious that these factors are dependent on the composition of a particular material. Plasticity curves of PVC and PVC/P(MMA-co-acrylate) blends are shown in Figure 1.

The typical plasticity curve obtained can have distinct regions and can be indicated by points ABCDE.[9] From A to B, there is practically no movement of the plunger, and the material is in glassy state. However, at B there is a slight downward movement of the plunger, which roughly corresponds to the glass transition temperature (T_g). This has been referred as T_1, which goes on decreasing with an increase in the size of the side chain of the acrylic copolymer. From B to C is the transition from glassy state to rubbery state of the polymer. This temperature has been referred as T_2. From C to D there is a steady state and the material absorbs heat and finally at point D (T_3) onwards there is a continuous downward movement of the plunger and material starts extruding at die orifice. This particular temperature is known as flow temperature or processing temperature. At point E there is a fast rate
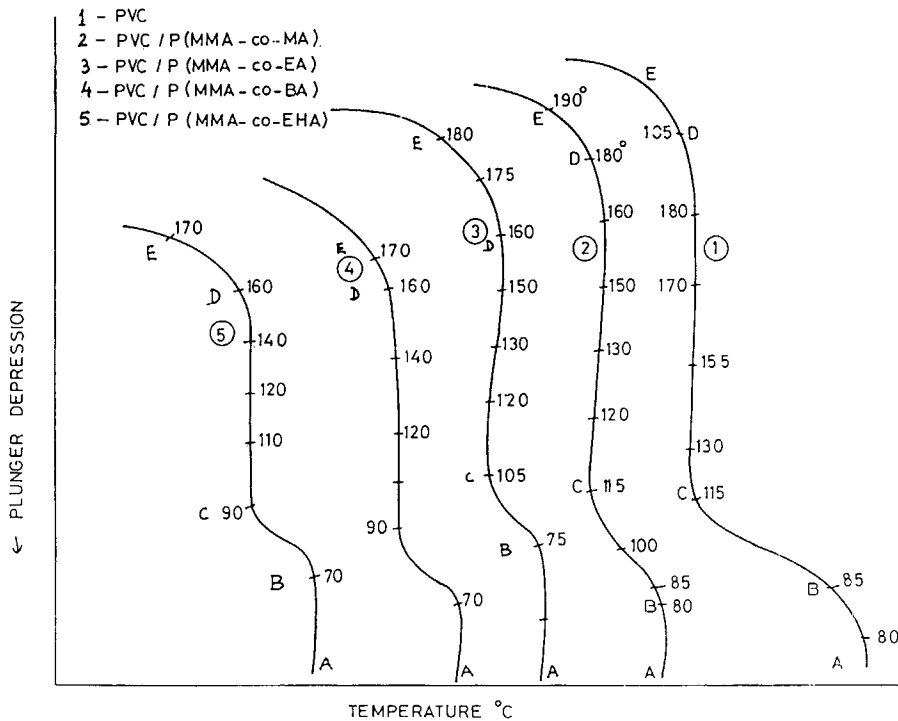
Fig. 1.   Plasticity curves of PVC and PVC/P(MMA-co-acrylate) blends.

of the flow polymer. Values of three temperatures T_1, T_2, and T_3 are given in Table I for various PVC/Polyacrylate blend compositions.

Shear Stress–Shear Rate Curves

From the data at constant temperature and varying pressure, the shear stress–shear rate relationships was determined for these blends. The apparent shear stress $\tau_{w\,app}$ was calculated from the following expression at constant L/R ratio of the die:

$$\tau_{w\,app} = \Delta P / 2 L / R$$

where P is the pressure difference between the entrance and exit of the die, L the length of capillary, and R the radius. The shear rate $\dot{\gamma}_{app}$ was calculated

TABLE I
Values of T_1, T_2, and T_3 for Various PVC Blends

Sample	T_1 (°C)	T_2 (°C)	T_3 (°C)
PVC	85	115	185
PVC/P(MMA-co-MA)	85	110	185
PVC/P(MMA-co-EA)	75	105	175
PVC/P(MMA-co-BA)	70	90	165
PVC/P(MMA-co-EHA)	70	90	160

from the expression:

$$\dot{\gamma}_{app} = 4Q/\pi R^3$$

where Q is the flow rate. The apparent melt viscosity η_{app} was calculated according to Poiseuille equation:

$$\eta_{app} = \tau_{w\,app}/\dot{\gamma}_{app}$$

Plots of shear stress $\ln \tau_{w\,app}$ vs. shear rate $\ln \dot{\gamma}_{app}$ at the three different temperatures 190, 200, and 210°C are shown in Figure 2. The linearity of these curves over the entire range studied confirms the validity of power law relationship:

$$\tau_{w\,app} = k\dot{\gamma}_{app}^{n}$$

where K is a constant and n is the power law exponent. The slope of these curves gives the values of n to be less than 1 as listed in Table II. These values show that PVC and its blends are pseudoplastic in nature as is the case with most of polymeric melts.

Activation Energy for Viscous Flow

The viscosity of a polymer decreases as the temperature increases. Over a small region of temperature variation, the temperature dependence of viscos-
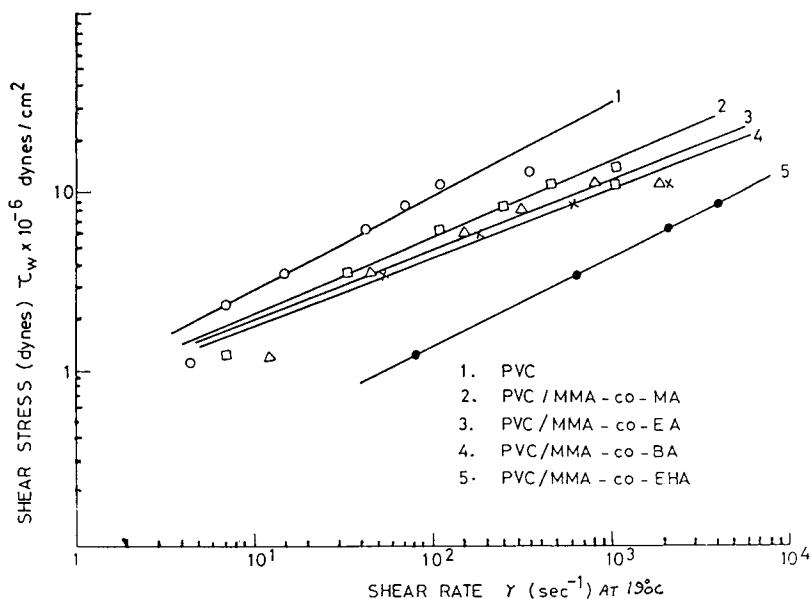

Fig. 2. Plot of shear stress $\tau_{w\,app}$ vs. shear rate $\dot{\gamma}_{app}$ of PVC and PVC/P(MMA-co-acrylate) blends at 190°C.

TABLE II
Values of Power Law Exponent (η) for Various Blend Composition

Sample	Power law exponent n		
	190°C	200°C	210°C
PVC	0.53	0.509	0.80
PVC/P(MMA-co-MA)	0.44	0.44	0.72
PVC/P(MMA-co-EA)	0.46	0.46	0.62
PVC/P(MMA-co-BA)	0.48	0.62	0.62
PVC/P(MMA-co-EHA)	0.53	—	—

ity can be represented by the equation

$$\eta_{\text{app}} = A \exp^{-E/RT}$$

where A is a constant, E the activation energy, R the gas constant, and T the absolute temperature. A plot of η_{app} against $1/T$ gives an Arrhenius plot (Fig. 3).

Melt Viscosity

Rigid PVC possesses a very high melt viscosity which is greatly reduced by the addition of acrylate copolymers.[2] Variation of η_{app} with shear rate of PVC and PVC/P(MMA-co-acrylate) blends at 80:20 ratio at 190°C is shown in
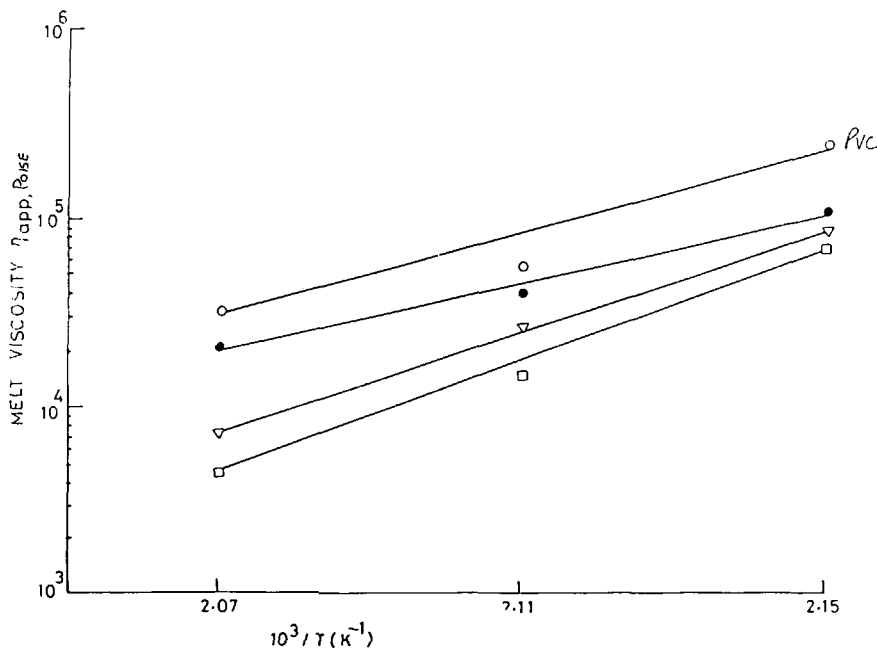

Fig. 3.   Arrhenius plot of melt viscosity vs. temperature of PVC and PVC/P(MMA-co-acrylate) blends at $\tau_{w\,\text{app}} = 3.67 \times 10$ dyn/cm. (○) PVC; (●) PVC/P(MMA-co-MA); (▽) PVC/P(MMA-co-EA); and (□) PVC/P(MMA-co-BA).
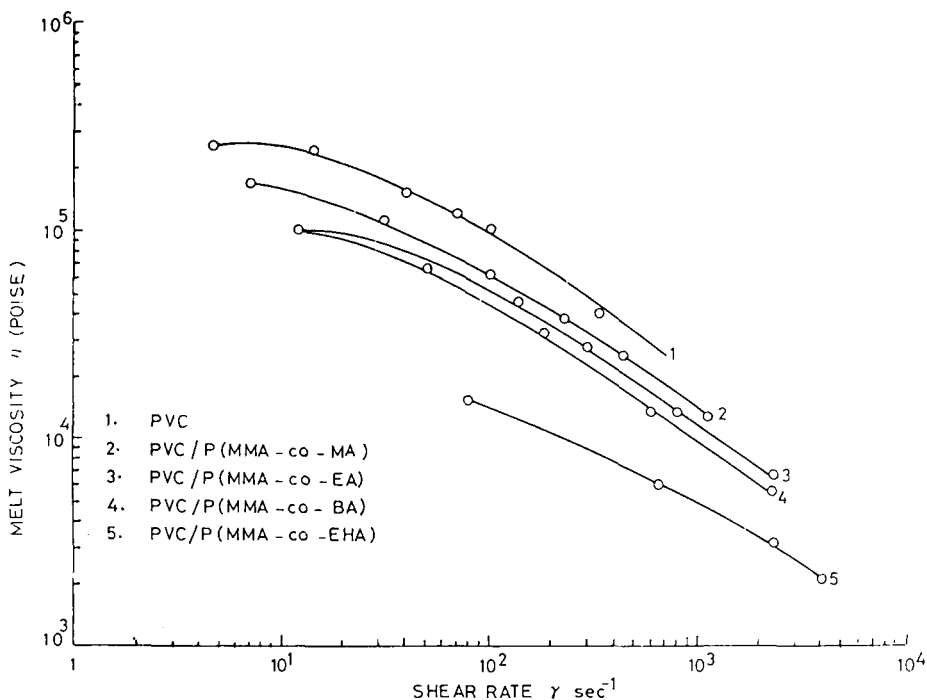
Fig. 4.   Plot of melt viscosity vs. shear rate of PVC/P(MMA-co-acrylate) blends at 190°C.

Figure 4. As can be seen, η_{app} decreases when the number of carbon atoms in the side chain of the acrylate comonomer increases at a particular shear rate.

A plot of $\ln \eta_{app}$ vs. $\ln \dot\gamma_{app}$ at three different temperatures for various PVC/coacrylate blends is shown in Figure 5. It can be observed that, for a given material, viscosities stay constant at low shear rates up to a certain value of shear rate and then decrease as shear rate is increased further. PVC/P(MMA-co-acrylate) blends follow the power law equation as observed. Substituting

$$\eta_{app} = \tau_{w\,app}/\dot\gamma_{app}$$

the power law becomes

$$\eta_{app} = k^{\dot\gamma_{app}(n-1)}$$

Variation of melt viscosity with blend composition at 190°C at constant shear stress is shown in Figure 6. It is observed that PVC has highest melt viscosity which goes on decreasing when acrylate copolymers are incorporated. The decrease is steady from P(MMA-co-MA) to P(MMA-co-EHA). Hence these polyblends can be processed at a lower temperature and shear stress as compared to PVC alone.

Die Swell and Melt Elasticity

The swelling of an extrudate on emerging from a capillary is typical of non-Newtonian viscoelastic fluids and is related to their elastic properties. Die
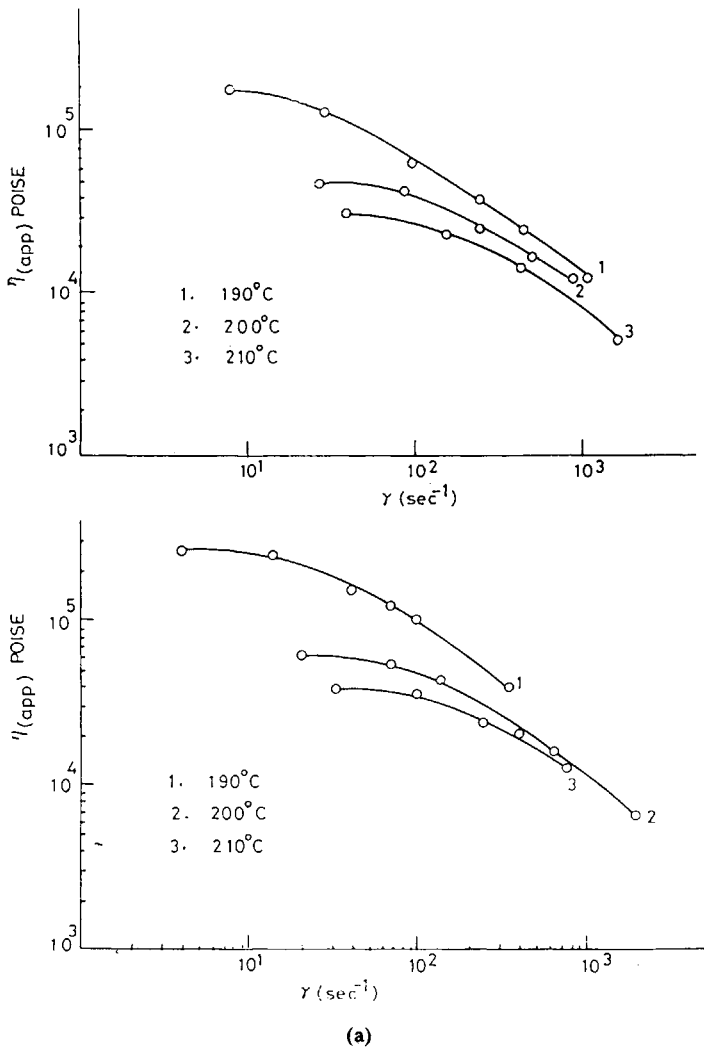
Fig. 5. (a) Plot of melt viscosity η_{app} vs. shear rate $\dot{\gamma}_{app}$ at three different temperatures. Top: PVC/P(MMA-co-MA). Bottom: PVC. (b) Plot of melt viscosity η_{app} vs. shear rate $\dot{\gamma}_{app}$ at three different temperatures. Top: PVC/P(MMA-co-BA). Bottom: PVC/P(MMA-co-EA).

swell ratio has been defined by the ratio of the completely relaxed extrudate diameter D_s to the capillary diameter D.[10]

It can be seen from Table III that the value of D_s/D increases with the shear rate. This is because the recoverable elastic energy put into the melt while flowing in the capillary increases as shear rate is increased.

Plots of the die swell ratio as a function of blend composition at a constant shear stress are shown in Figure 7.

PVC has a lower die swell ratio as compared to PVC/P(MMA-co-MA) and PVC/P(MMA-co-MA) blends. However, there is a significant decrease in the die swell ration in case of PVC/P(MMA-co-BA) and PVC/P(MMA-co-EHA) blend.
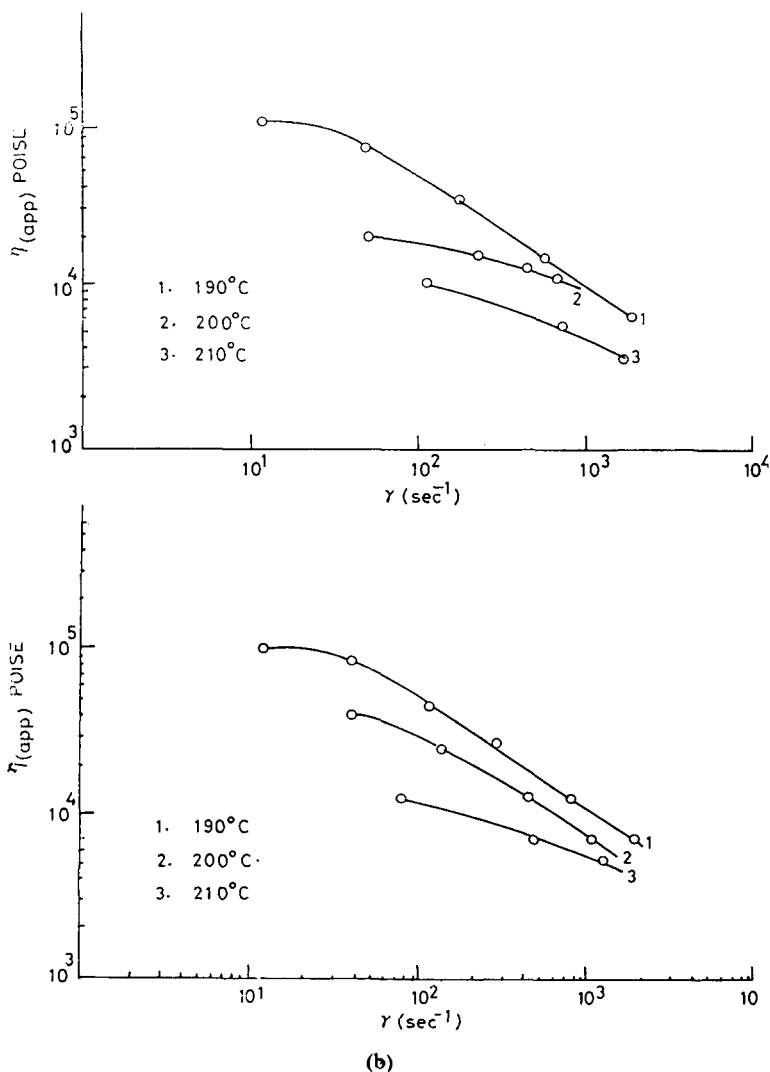
(b)

Fig. 5.   (*Continued from the previous page.*)

A plot of die swell ratio vs. temperature of various blend compositions at a constant shear stress presented in Figure 8 reveals that for PVC and PVC/P(MMA-co-MA) blend the die swell ratio shows a definite increase. In case of PVC/P(MMA-co-EA), there is a sudden increase and then decrease while in case of PVC/P(MMA-co-BA) there is a regular decrease in the die swell as the temperature is increased. The measurement of the die swell ratio is correlated with normal stress functions. Bagley, Giassley, and Tanner have summarized theoretical expression which related first normal stress difference $(\tau_{11} - \tau_{22})$ to die swell ratio. Here the values are reported according to Tanner's equation[11]

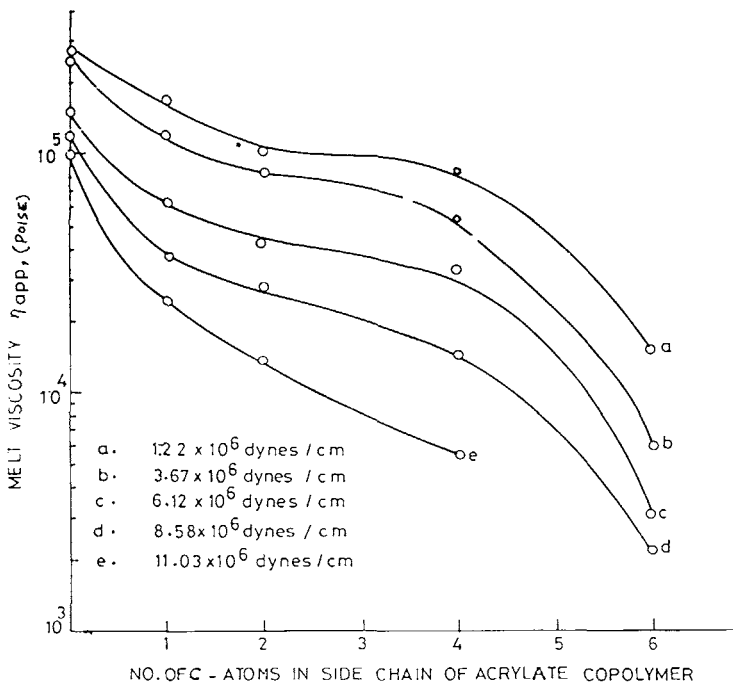$$\tau_{11} - \tau_{22} = 2\tau_{w_{app}}\left[2(D_s/D)^6 - 2\right]^{1/2}$$

Fig. 6. Plot of melt viscosity vs. number of carbon atoms in side chain of acrylate copolymer at constant shear stress.

The expression is used with the assumption that the material obeys Hooke's law. Other parameters calculated are:

$$S_R = \tau_{w_{app}}/G \quad \text{or} \quad G = \tau_{w_{app}}/S_R$$

$$S_R = \tau_{11} - \tau_{22}/\tau_{w_{app}}$$

where S_R is the recoverable shear strain and G is the apparent shear modulus.

Plots of first normal stress difference vs. shear rate for PVC and PVC-co-acrylate blends are given in Figure 9. It can be seen that there is an increase in the first normal stress difference as shear rate increases, indicating a decrease in melt elasticity.

Variation of die swell ratio and first normal stress at different shear stress of various PVC coacrylate blends is given in Table III.

Figure 10 shows a plot of first normal stress difference vs. blend composition at constant shear stress. PVC has got maximum first normal stress difference which goes on decreasing when the number of C atoms in the acrylate copolymer increases. However, at lower shear stress, the first normal stress difference shows a small increase in case of PVC blends containing methyl and ethyl acrylate.

A slight increase is also observed from methyl to ethyl acrylate, although it does not seem of any significance. It can be overall inferred that decrease in first normal stress difference from PVC to PVC/poly(MMA-co-EHA) blend; however, the change is remarkable from PVC/P(MMA-co-EA) to

TABLE III
Values of Melt Elasticity Parameters of PVC and PVC/P(MMA-co-Acrylate) Blends
at Different Shear Rates and 190°C

Sample	Shear rate $\dot{\gamma}_{app}$ (s^{-1})	Shear stress $\tau_{app} \times 10^{-6}$ (dyn/cm^2)	D_s/D	$\tau_{11} - \tau_{22}$ $(dyn/cm^2 \times 10^7)$	Recoverable strain S_R	Apparent shear modulus $G \times 10^5$ (dyn/cm^2)
PVC	4.87	1.2	1.30	0.67	2.79	4.3
	14.25	3.5	1.40	2.5	3.57	10.0
	40.72	6.1	1.60	6.7	5.58	10.98
	69.23	8.5	1.64	10.3	6.05	14.04
	101.82	11.0	1.54	13.3	6.04	18.21
PVC/	7.12	1.2	1.38	0.82	3.41	3.51
P(MMA-co-	32.58	3.5	1.42	2.73	3.90	8.77
MA)	101.82	6.1	1.46	5.08	4.23	14.42
	234.18	8.5	1.46	7.08	4.16	20.43
	448.0	11.0	1.46	9.16	4.16	26.44
PVC/	12.21	1.2	1.42	0.91	3.79	3.16
P(MMA-co-	42.76	3.5	1.52	3.42	4.88	7.72
EA)	142.54	6.1	1.54	6.06	5.05	12.07
	305.40	8.5	1.50	7.7	4.5	18.88
	814.50	11.0	1.48	9.59	4.3	25.58
PVC/	12.21	1.2	1.28	0.62	2.58	4.65
P(MMA-	52.94	3.5	1.42	2.73	3.9	8.97
co-BA)	183.27	6.1	1.32	3.59	2.99	20.40
	590.00	8.5	1.32	5.02	2.95	28.81
	2036.00	11.0	1.32	6.44	2.92	37.67
PVC/	79.41	1.2	1.26	0.58	2.41	4.97
P(MMA-	631.28	3.5	1.26	1.70	2.42	14.46
co-EHA)	2036.0	6.1	1.32	3.5	2.91	20.96
	4072.8	8.5	1.30	4.7	2.76	30.79

PVC/P(MMA-co-BA) blend. This can be attributed to the presence of long chain and low T_g acrylate copolymer, where segmental mobility of the polymer chains starts at lower temperature and consequently the flow of the material is facilitated at lower temperature.

At any shear rate, the recoverable shear strain (S_R) decreases and shear modulus (G) increases from PVC to PVC/P(MMA-co-EHA) blends.

Melt Fracture

At a critical value of shear rate and shear stress, the polymer extrudate becomes rough and distorted. This is known as melt fracture. In case of PVC the melt fracture takes place at high shear stress and high temperature as shown in Figure 11. At high temperature (210°C) the extrudate distortion starts at much less shear stress. The melt fracture is considerably reduced in PVC/P(MMA-co-MA) blend and is comparable to PVC. However, since there is a decrease in melt viscosity, it can be processed at a lower temperature and can withstand higher shear stress. In the case of PVC/P(MMA-co-EA), the extrudate is smooth at 190°C and lower shear rates, but increase of tempera-
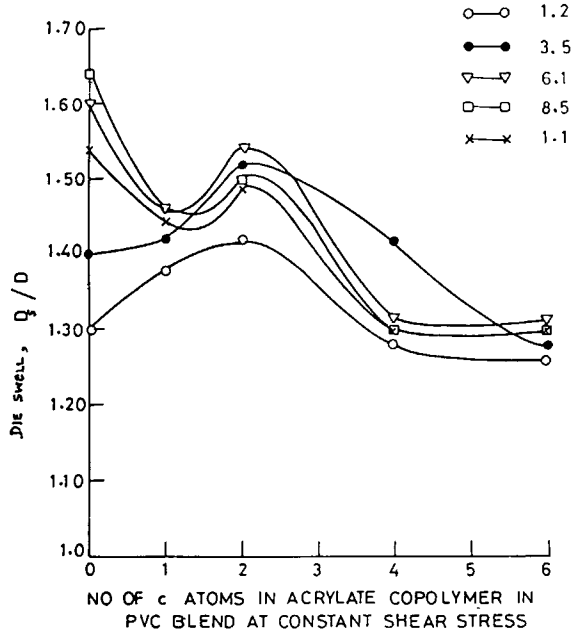
Fig. 7. Plot of die swell ratio vs. number of carbon atoms in acrylate copolymers of PVC/P(MMA-co-acrylate) blends at constant shear stress and temperature (190°C).
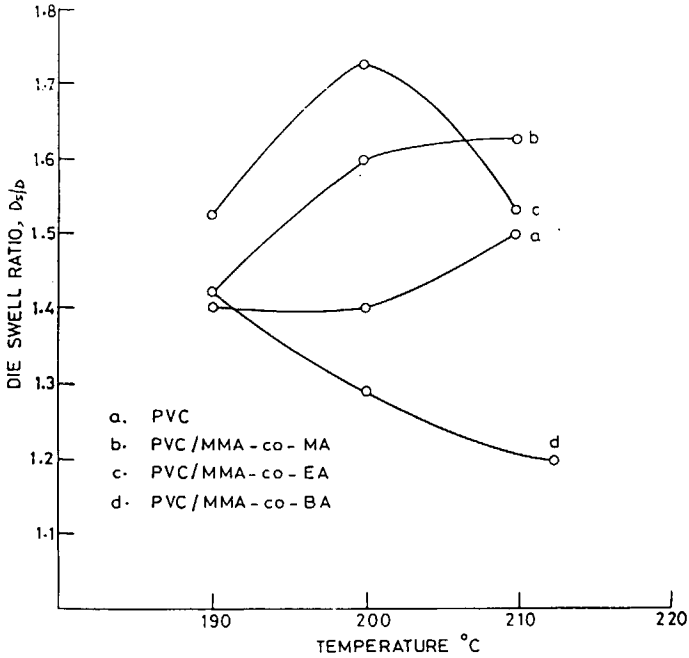

Fig. 8. Plot showing die swell ratio vs. temperature of PVC and PVC/P(MMA-co-acrylate) blends.
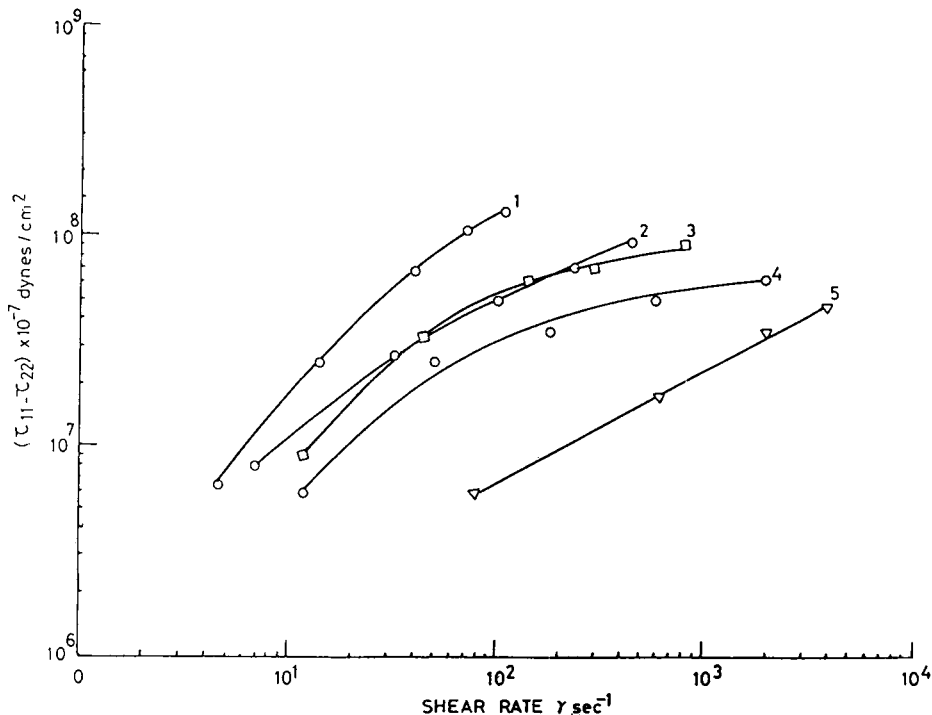
Fig. 9. Plot showing first normal stress difference vs. shear rate of PVC and PVC/P(MMA-co-acrylate) blends at 190°C. 1. PVC; 2. PVC/P(MMA-co-MA); 3. PVC/P(MMA-co-EA); 4. PVC/P(MMA-co-BA); and 5. PVC/P(MMA-co-EHA).
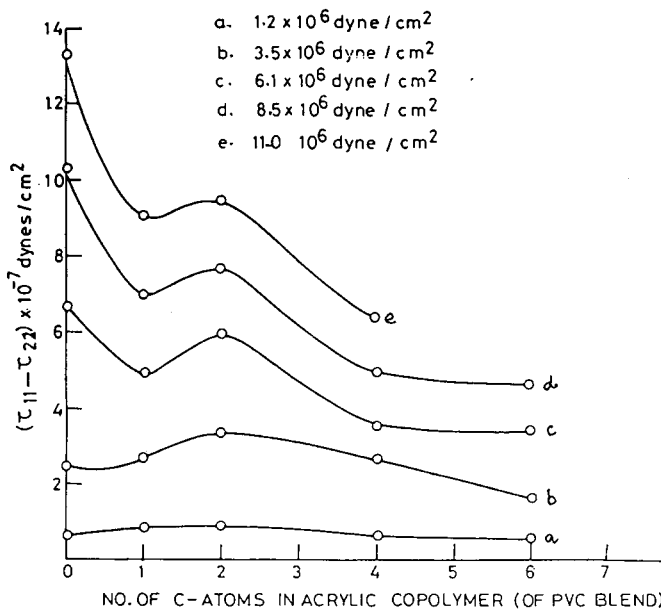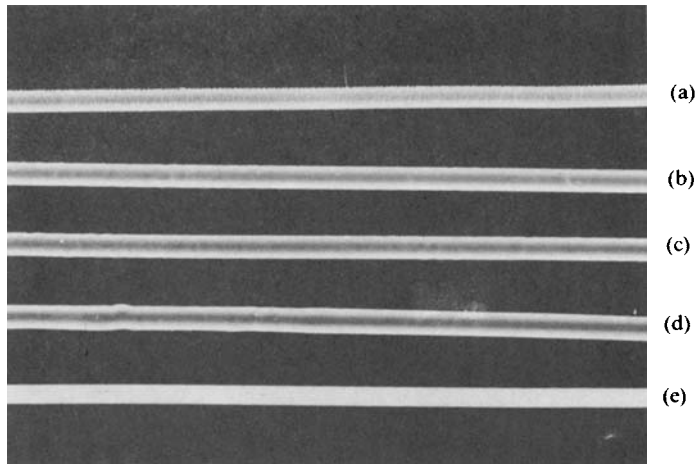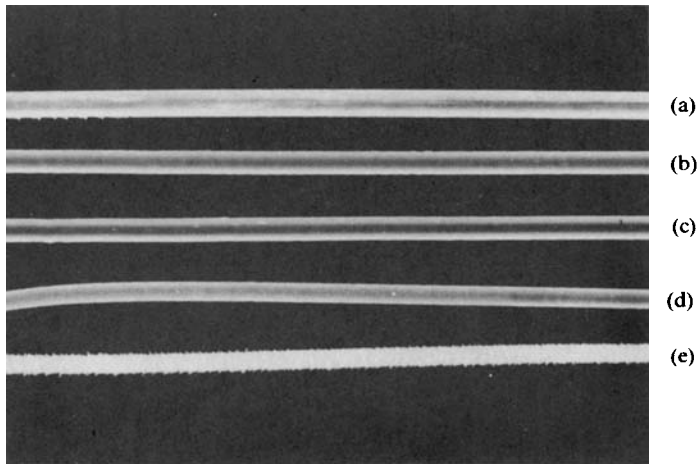

Fig. 10. Plot of first normal stress difference vs. number of carbon atoms in acrylate copolymers in PVC/P(MMA-co-acrylate) blends at constant shear stress.

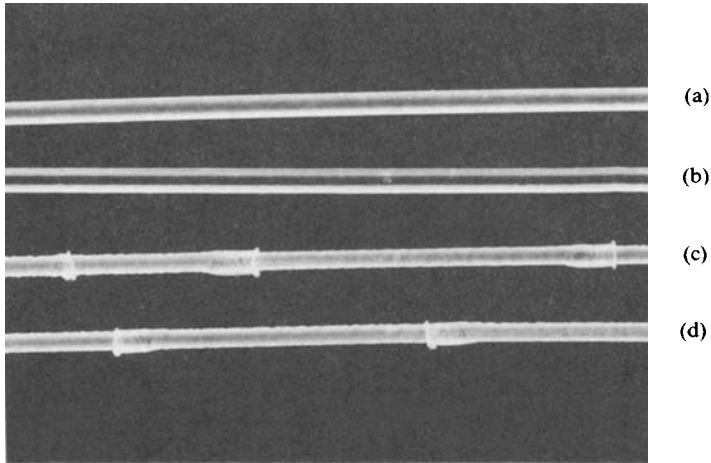$\tau_{w_{app}} = 3.0 \times 10^6$ dynes/cm^2; temp. 190°C.

(a)

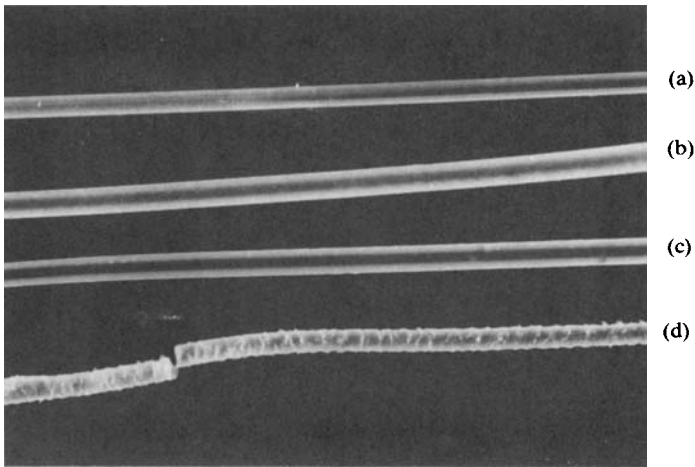$\tau_{w_{app}} = 11.0 \times 10^6$ dynes/cm^2; temp. −190°C.

(b)

Fig. 11. Extrudate behavior of PVC and PVC/P(MMA-co-acrylate) blends. (a) PVC; (b) PVC/P(MMA-co-MA); (c) PVC/PMMA-co-EA); (d) PVC/P(MMA-co-BA); (e) PVC/P(MMA-co-EHA).

(a)

(b)

(c)

(d)

$\tau_{w_{app}}$ = 6.5 × 10^6 dynes/cm^2; temp. 200°C.

(c)

(a)

(b)

(c)

(d)

$\tau_{w_{app}}$ = 6.5 × 10^6 dynes/cm^2; temp. 210°C.

(d)

Fig. 11.   (*Continued from the previous page.*)

ture makes the material highly vulnerable to extrudate distortion. A similar phenomenon is observed in PVC/P(MMA-co-BA), where the extrudate surface is highly distorted even at moderate shear stresses when the temperature is increased. However, in the case of PVC/P(MMA-co-EHA), the extrudate distortion is observed even at 190°C beyond a level of shear stress and so much so that it is unable to withstand any shear stress beyond 190°C. This blend composition is sensitive to both temperature and shear stress. However, it has very low melt viscosity and needs to be processed to fairly low temperature and pressure as compared to PVC.

DISCUSSION

Incorporation of acrylate copolymers makes the melt flow behavior of PVC easier. As can be seen from the plasticity curves, when there is a downward movement of the plunger corresponding to glass transition temperature, the role of particular co-acrylate is significant. The T_g goes on decreasing when the length of the side chain of acrylate copolymer increases. The highest glass transition temperature is shown in case of PVC/P(MMA-co-MA) and lowest in PVC/P(MMA-co-EA). The glass transition data determined by TMA has been presented in Part I of this paper. Processing temperature is also reduced in a similar way.

Variation of melt viscosity with blend composition shows maximum melt viscosity of PVC at any given shear stress which goes on decreasing with the increase in the size of the side chain of the methacrylate copolymer. Introduction of methacrylate copolymers reduces the interaction between PVC chains, which in the process increases the free volume of the system so that PVC matrix becomes softer and more flexible. This reduces the melt viscosity of PVC by facilitating flow. With increase in the length of the side chain, the interstitial space should increase, resulting in better flow. This also indicates that even small quantities of long chain esters are able to make significant changes in flow characteristics.

The plot of shear stress vs. shear rate suggests linearity over the entire range of study. However, there is a slight shift in the slope in the case of PVC/P(MMA-co-EHA) blend. Similarly extrudate distortion observed in this particular blend at a temperature of 190°C can be attributed to low compatibility of PVC with P(MMA-co-EHA). PVC has a solubility parameter $\delta = 9.42$ and those of P(MMA-co-EHA), P(MMA-co-EA), and P(MMA-co-EHA) are 9.38, 9.54, and 9.26, respectively. P(MMA-co-EHA) $\delta = 9.02$, which is low as compared to other acrylate copolymers. Hence there are chances that because of less compatibility the final polyblend becomes more sensitive to shear stress and temperatures.

The sensitivity to shear stress and temperature and less compatibility of PVC/P(MMA-co-EHA) makes this material vulnerable to melt fracture also.

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