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Determination of viscosities for alumina–polyethylene blends

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The rheology of different proportions of low-density polyethylene (LDPE) and low-density polyethylene wax (LDWAX) without and with alumina was studied and correlated to a model. The viscosities of the polymer blend (LDPE + LDWAX) were studied for various compositions of LDWAX at different temperatures. The Arrhenius plot of logarithmic viscosity and reciprocal temperature for the polymer blends is linear. The enthalpy of viscous flow, determined from the slope of the Arrhenius Plot, varies linearly as a function of the average molecular weight. It is thus possible to predict the viscosity of any intermediate composition of the polymer blend. The viscosities of alumina-polymer blends (AP blend) with 50 vol% of alumina, prepared by solvent method, were also studied as a function of temperature, at a shear rate of 1333.33 s^{-1}. The AP blends show a lower enthalpy of viscous flow compared to pure polymer blend because of the presence of stearic acid used as surfactant for alumina. The model developed in this study enables the prediction of viscosities of AP blends at any weight average molecular weight (M_w) of the main binder and temperature. © *2002 Kluwer Academic Publishers*

1. Introduction

The ceramic shape forming processes like injection molding [1, 2], fused deposition of ceramic (FDC) [3] etc. utilizes thermoplastic polymers as binders. The binder with ceramic should accomplish certain properties like desired viscosity, high green strength, and easy debinding [1, 2, 4, 5]. The viscosity of the binder is an important parameter, because a low viscosity of the binder in the ceramic blend leads to the segregation of the ceramic and the binder [2]. Higher viscosity will cause improper molding in case of injection molding and a very high backward force on the liquifier in FDC leading to the failure of the feed stock [6].

The desired viscosity of the binder can be achieved by varying the temperature or average molecular weight of the polymer. An increased temperature during operation can lead to degradation or evaporation of the polymer. This can lead to undesired, low green strength because of variation in the composition. The use of low molecular weight polymers in the binder can lead to low green strength at room temperature making the material handling difficult [1, 2].

The optimum operating temperature and the critical strength for handling the material is thus usually achieved by trial and error, which costs enormous time and resources. Reducing the time of development of suitable binder system for ceramic shape making process is critical. Thus models for the prediction of viscosities for a given average molecular weight binder, at any given temperature (above the glass transition of the polymer) are required.

LDPE is a thermoplastic polymer, frequently used as binder in injection molding and FDM of ceramics, with plasticizers [1, 2, 7, 8]. The existence of different grades of LDPE with different molecular weights leads to separate characterizations of rheology of LDPE for binder. Therefore, we have chosen LDPE as a main binder with LDWAX as a plasticizer to investigate AP blends. We have investigated the viscosity of LDPE and LDWAX blends with and without alumina as a function of temperature and developed a model to characterize the system. This model can predict the viscosity of the ceramic blends at any temperature and compositions of the polymer blend in the AP blend.

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2. Experimental

The molecular weight determination of LDPE and LDWAX (IPCL, India) was carried out using HPLC-GPC system (Water Inc.). This system consists of a high pressure pump (Waters 515), a refractive index detector (RI-2410) and three Styragel GPC columns in series maintained at high temperatures (90°C). Toluene was used as an eluent and pumped at a constant flow rate of 10^{-6} m^3/min. 0.2 mm^3 aliquots of the sample was dissolved in toluene and injected into the system. The refractive index was continuously monitored and the chromatograph of retention time and refractive index was obtained. This chromatograph was converted to the molecular weight distribution with a calibration curve.

The blending of base binder (LDPE) and the plasticizer (LDWAX) at different volume fraction of plasticizer (40 to 80% of LDWAX) was carried out by the solvent method, using toluene as solvent. A hot bath was used to maintain the temperature of the container containing LDPE, LDWAX and solvent at 100°C. A mechanical stirrer was used to mix the polymer in solvent medium. The stirring was continued until almost all the solvent was evaporated. The semisolid polymer blend was then transferred to an aluminum tray and degassed at 110°C at 0.145 MPa in a vacuum oven.

The glass transition temperature and enthalpy of transition for the polymer blends were determined by differential scanning calorimetry (DSC) at a heating rate of 5°C/min in air.

The viscosity of the blended polymer was determined in a Brookfield spindle viscometer (type DV-II) fitted with a thermostat. A number-32 spindle was used to measure the viscosity of the sample at different temperatures ranging from 110 to 200°C with 0.6 rpm.

The alumina polymer blend (AP blend) was made from A-16 grade alumina powder, milled with 2 wt% stearic acid in the toluene medium (acts as surfactant) and for one hour. The toluene was removed in a vacuum oven at 70°C and 0.145 MPa pressure. The surfactant treated alumina was then milled with equal volume of binder. The total binder content, which includes stearic acid (dispersed in alumina), LDPE and LDWAX were maintained at 50 vol%. The LDWAX content in the total binder system (excluding stearic acid) was varied from 40–70%. The amount of stearic acid was 1.06 vol% (2 wt% of alumina).

The viscosity of the AP blend was measured in a capillary rheometer (Shimadzu). The rheometer consists of 0.3 m barrel with a capillary tube of 1 mm diameter. The material is filled and compacted in the barrel and a controller (Chino Laxon) maintains the temperature of the barrel. At the desired temperature the compacted material was pushed through the capillary using a plunger connected to a load cell. The force exerted on the plunger was determined by the load cell, at a given speed of the plunger. The shear rate, shear stress and viscosity are determined based on the load and speed of the plunger.

3. Results and discussion

The number average molecular weight (M_n) of LDPE and LDWAX determined in HPLC-GPC system were 59000 and 2500 and the weight average molecular weights (M_w) were 341000 and 3000, respectively. Based on the experimentally determined average molecular weights of LDPE and LDWAX, the average molecular weights of intermediate compositions are calculated (Table I) based on standard formulae [9] mentioned below.

TABLE I The average molecular weights of LDPE, LDWAX and their blends

% of LDWAX	Identity	Molecular weight: Number average (M_n)	Molecular weight: Weight average (M_w)
0	LDPE	59000	341000
40	LDWAX 40%	5875	205800
50	LDWAX 50%	4795	172000
60	LDWAX 60%	4050	138200
70	LDWAX 70%	3500	104400
80	LDWAX 80%	3090	70600
100	LDWAX	2500	3000

$$M_n = \left(\sum N_i M_i\right) \Big/ \sum N_i \tag{1}$$

$$M_w = \left(\sum N_i M_i^2\right) \Big/ \sum (N_i M_i) \tag{2}$$

where N_i is the number of molecules of molecular weight M_i of ith component. The M_w varies linearly with the composition of LDWAX.

The Differential Scanning Calorimetric (DSC) study on LDPE showed that the melting temperature of LDPE was 108°C. LDWAX does not show any melting above room temperature. The DSC studies on different compositions does not show any change in glass transition, but showed a decreasing change in heat capacity (ΔC_p) with increasing LDWAX content, indicating melting at 108°C is mainly due to LDPE. As the LDPE content is decreased, the amount of energy needed to undergo transition decreases, but melting was observed at the temperature at which LDPE undergoes the transition. This indicates that the nature of individual polymer chains did not change after the blending process.

The viscosity of the samples was measured in a range of temperatures (110 to 200°C). The viscosities of the polymer blends were measured at 0.6 rpm and show an exponential decrease in viscosity with increasing temperature. The viscosity decreases with decreasing average molecular weight (Fig. 1). This decrease can be attributed to the decreased interaction between long chain polymers. The relation between temperature and viscosity is given by the Arrhenius equation [10],

$$\eta = \eta_o \exp(-\Delta H_a/(RT)) \tag{3}$$

where η is the viscosity of the sample at absolute temperature T, η_o is a pre-exponential constant, R is the gas constant and ΔH_a is the enthalpy of viscous flow. The logarithmic viscosities of the blends vary linearly with the reciprocal temperature (Fig. 2) according to the Arrhenius equation. As shown in Fig. 2, the slopes of the curves decrease with increasing LDWAX content and the enthalpy of viscous flow can be determined from the slopes. Fig. 3 shows the variation of the enthalpy

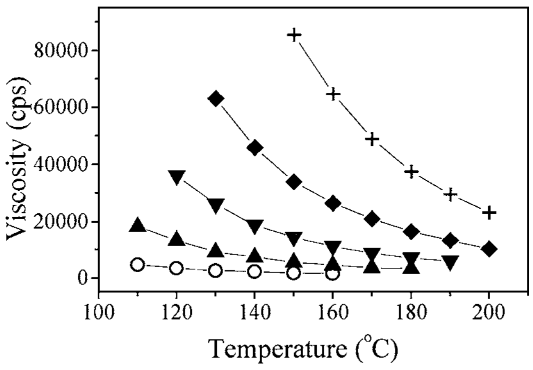

Figure 1 Variation in the viscosity of various M_w polymer blends as a function of temperature (○ LDWAX-80, ▲ LDWAX-70, ▼ LDWAX-60, ◆ LDWAX-50, + LDWAX-40).

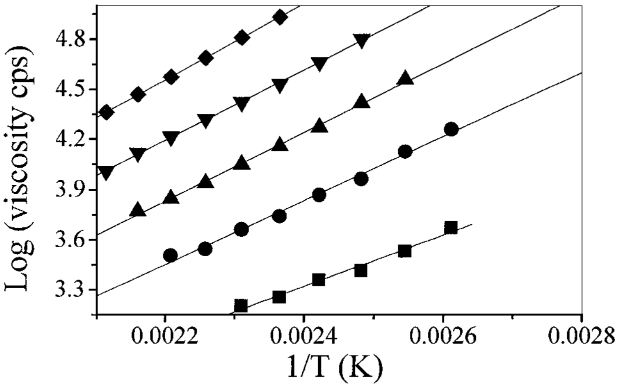

Figure 2 Arrhenius plot of the variation in the logarithmic viscosity of the polymer blend as a function of reciprocal temperature (■ LDWAX-80, ● LDWAX-70, ▲ LDWAX-60, ▼ LDWAX-50, ◆ LDWAX-40).

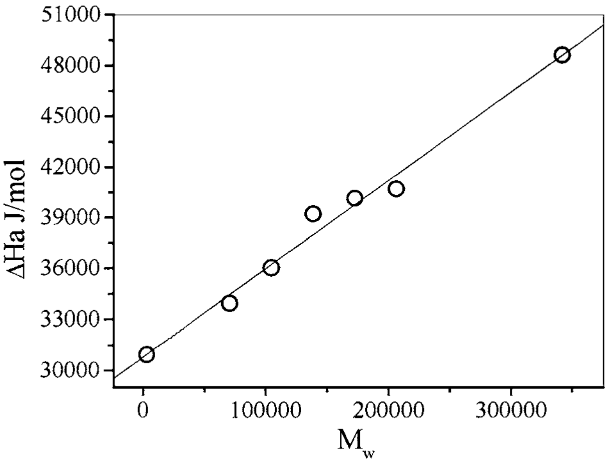

Figure 3 Variation in ΔH_a as a function of M_w of the polymer blend.

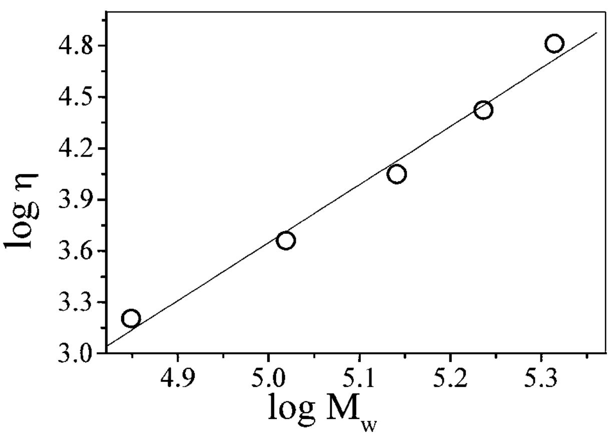

Figure 4 Log-log plot of Viscosity and M_w at 160°C is linear with a slope of 3.4.

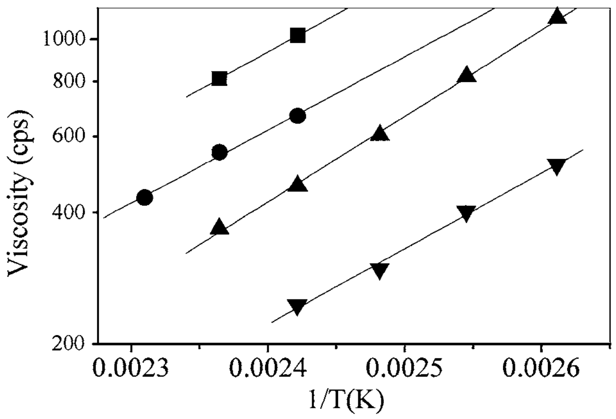

Figure 5 Arrhenius plot of logarithmic viscosity with reciprocal temperature of AP blend at various composition of the polymer blend (■ AP-40, ● AP-50, ▲ AP-60, ▼ AP-70).

of viscous flow as a function of M_w at various temperatures. The enthalpy of viscous flow varies linearly with the average molecular weight and is similar to the relationship determined by Yamaguchi and Abe [10].

Though the enthalpy of viscous flow for particular intermediate M_w can be determined from Fig. 3, one can not predict the viscosity of the blend because η_o is unknown. To eliminate η_o, the viscosity of the particular M_w at a given temperature needs to be determined. It is however, possible to predict the viscosity for a given M_w at a particular temperature, because the log-log plot of viscosity and the M_w is linear with slope of 3.4 [12]. To verify this relationship, we have determined the viscosities of the blends at various M_w at 160°C. Fig. 4 shows the log-log plot of viscosity and M_w with a slope of 3.4. Therefore, Equation 1 can be rewritten as,

$$(\eta_{160}/\eta_o) = \exp[(\Delta H_a/(RT)) - (\Delta H_a/(433\,R))] \quad (4)$$

If one is interested in determining the viscosity of a particular blend of LDPE and LDWAX, then the M_w of the blend is first determined. The enthalpy of various flow (ΔH_a) is then determined at the desired temperature for this M_w. Using the values of ΔH_a and η_{160} ($=M_w^{3.4}$) in Equation 4, η_T at any desired temperature can be determined.

The ceramic polymer blends with LDWAX 40, 50, 60 and 70% in the binder were abbreviated as AP-40,

TABLE II The ratio of viscosity of the polymer blend and AP blend for various temperatures. (The viscosity of polymer blend is measured at rpm 0.6 and AP blend at shear rate 1333.33)

	110°C	120°C	130°C	140°C	150°C	160°C
LDWAX 40%	–	–	–	102.6	105	–
LDWAX 50%	–	–	–	68.66	61.6	66.9
LDWAX 60%	39.1	44.1	43.4	40.5	39.2	–
LDWAX 70%	35.3	33.3	31	30.2	–	–

TABLE III Comparative table of viscosities of experimental and calculated results

	110°C		120°C		130°C		140°C		150°C		160°C		
Sample code	Exptl.	**Cal.**	Exptl.	**Cal.**	Exptl.	**Cal.**	Exptl.	**Cal.**	Exptl.	**Cal.**	Exptl.	**Cal.**	Ar. % error
AP-40	–	–	–	–	–	–	1018	**958**	812	**722**	–	–	*−8.5*
AP-50	–	–	–	–	–	–	667	**717**	550	**548**	433	**422**	*3.3*
AP-60	1112	**1231**	819	**911**	601	**682**	461	**518**	367	**399**	–	–	*11.3*
AP-70	515	**553**	402	**416**	297	**315**	245	**243**	199	**189**	–	–	*4.5*

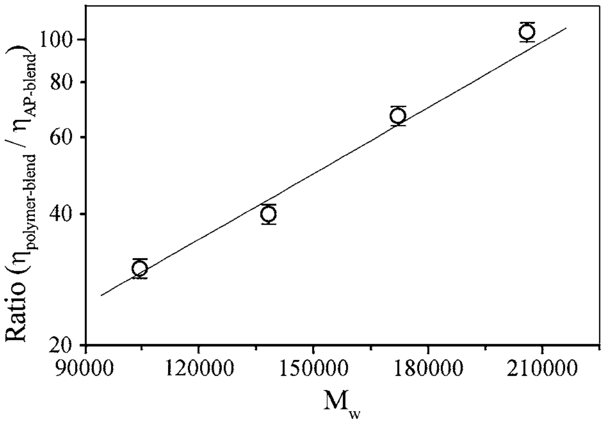

Figure 6 The ratio of ($\eta_{\text{polymer-blend}}/\eta_{\text{AP-blend}}$) and M_w of the polymer blend.

AP-50, AP-60 and AP-70. The viscosities of AP blends were measured as a function of temperature at a shear rate of 1333.33 s^{-1}. The Arrhenius plot of log viscosity and reciprocal temperature is shown in Fig. 5. Though the variation is linear, the slope is less than the slope for AP blends than polymer blends, indicating that the enthalpy of viscous flow is less in AP blends. This may be due to stearic acid acting as a plastisicer.

The proper prediction of viscosities of ceramic blends is very important. In order to achieve this, we conducted a series of experiments for AP blends with the alumina content constant at 50 vol% and polymer at 50 vol%. This ratio was chosen based on the utility of the ratio in industry. The LDWAX content in the polymer blend (binder) was varied and the viscosities of the ceramic blend were determined. Table II shows the ratio of viscosity of polymer blend and AP blend, where in the ratio for a particular composition (LDWAX percentage in binder) is constant at any given temperature. Table II clearly indicates that, at a particular LDWAX%, the ratio of the viscosities of the polymer blend to the ceramic blend is constant (within experimental error). Further, the ratio of the viscosities of the polymer blend and AP blend can be determined for any given composition of polymer blend. For a given composition of the polymer blend, the M_w can be determined and the ratio of viscosities can be determined (Fig. 6).

Since the viscosity of the polymer blend can be estimated at any temperature and any composition by the procedure outlined earlier, the viscosity of the AP blend can also be predicted at any composition of the polymer blend and at any temperature. Utilizing this procedure, we predicted the viscosities of the AP blends. Table III shows the predicted and experimental values of viscosity of AP blends. It is clear from the table that the model prediction reasonably matches with the experimental values. Since the ratio of the viscosities is independent of temperature, the same procedure can be applied to any temperature in the range investigated in this study. This modeling process can also be adopted to realistic binder systems which can include other polyolefins, plasticizers and tackifiers etc.

4. Conclusion

A series of experiments were conducted to determine the rheological properties of polymer blends (LDPE + LDWAX) and AP blends (polymer + alumina). The viscosities were determined as a function of compositions and temperatures. The enthalpy of viscous flow varies linearly as a function of the average molecular weight. The AP blends show lesser enthalpy of viscous flow compared to pure polymer blend. A model was developed to predict the viscosities of these blends. The model was able to predict the viscosity of the AP blend at any polymer blend composition and at any given temperature.

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