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Melt rheological behaviour of short sisal fibre reinforced polyethylene composites

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Abstract: This paper presents the melt rheological properties of short sisal fibre reinforced polyethylene (LDPE) composites. The rheological studies were carried out using a capillary rheometer. The effects of fibre length, fibre loading, fibre treatment, temperature and shear stress on melt viscosity and melt elasticity of the composite have been studied. Incorporation of sisal fibre into polyethylene results in an increase in melt viscosity and a decrease in melt elasticity. It is interesting to note that the fibre treatment, processing temperature, and shear rate have a significant influence on the rheological behaviour of polyethylene–sisal fibre composites. The morphology of the extrudates has been studied by optical and electron microscopy.

1 Introduction

Several cellulosic products and wastes such as shell flour, wood flour and pulp have been used as fillers in thermoplastics, primarily to achieve cost savings[1] and also to impart some desirable properties like decreasing shrinkage after moulding, increasing elastic modulus and creep resistance.[2] However, over the past decade, cellulosic fillers of a fibrous nature have been of greater interest as they would give composites with improved mechanical properties compared to those containing non-fibrous fillers.[3–5]

Incorporation of fillers in thermoplastics will increase their melt viscosity which may result in unusual rheological effects. White[6] and White and Tokita[7] have reported on the correlation between melt rheology and processing of polymers. Studies on the rheological behaviour of filled thermoplastics and its application in injection moulding have also been reported.[8,9] Melt rheological properties of short glass fibre filled thermoplastics and flow behaviour during moulding have been reported in detail.[10] Most of the data for short fibre filled thermoplastics, reported in the literature, have been obtained using a constant volume flow rate capillary rheometer. At low shear rates, the presence of fibres causes an appreciable increase in viscosity, but at a shear rate in the range of 10^4 to 10^5 s^{-1}, the viscosity values for the filled and unfilled material converge to a very similar value. Other observations that have been made are migration of fibres during shear flow, fibre alignment in the flow direction, and decrease in melt elastic properties such as die-swell and first normal stress differences.

Recently, sisal fibres have been successfully incorporated in elastomers and thermoplastics by Thomas and coworkers.[11–13] Processing characteristics and mechanical properties of the resulting composites have been reported.[11–13] Sisal fibre being quite different from fibres like glass with respect to dimensions and surface properties, the melt rheological characteristics of its composites may differ from those of glass fibre filled thermoplastics. In this paper we report the studies on the melt rheological behaviour of short sisal fibre reinforced polyethylene composites. The effects of fibre loading, fibre length, fibre treatment and temperature on the melt viscosity and melt elasticity parameters of the composite have been evaluated.

2 Experimental

2.1 Materials

Low density polyethylene (LDPE-Indothene 16MA400) obtained from the Indian Petrochemical Corporation Limited, Baroda, India, was used for

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the study. The properties of Indothene 16MA400 are given in Table 1.

Sisal fibre (Agave-Veracruz) was obtained from local sources. The fibres were used after washing thoroughly with water to remove dust and other extractables, and then drying in an air oven at 80–90°C for 4 h. The physical and mechanical properties of sisal fibres have been reported elsewhere.[14]

2.2 *Preparation of composites*

The oven-dried fibres were chopped into the required lengths before being mixed with the polymer. In the present study, composites of the polymer and the fibres were prepared by a solution mixing technique developed by our research group.[13] A viscous slurry of polyethylene was prepared by adding toluene to a melt of the polymer and the composites were prepared by solution mixing. The overall solution mixing was carried out in a fumehood using a stainless steel beaker. After thorough mixing, the composite was transferred into a tray and kept in a vacuum oven at 70°C for 24 h to remove the solvent completely. The solvent free composites were cut into small pieces and charged into a hand injection moulding machine (ram type) having a capacity of 100 cm^3. The chamber was electrically heated to 115 ± 5°C and the material was extruded in the form of rods having a diameter of 4 mm.

2.3 *Melt rheological measurements*

The melt rheological measurements were carried out using a capillary rheometer attached to a Zwick UTM model 1474 and a capillary of length to diameter ratio (l_c/d_c) 40 with an angle of entry of 180°. The measurements were carried out at 115, 120, 125 and 135°C. The capillary used was made of tungsten carbide. The sample for testing 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 pre-selected speeds of the crosshead which varied from 0·5 to 50 mm min^{-1}. The height of the melt in the barrel before extrusion was kept the same in all the experiments and the machine was operated to give 10 different plunger speeds from lower to higher, with a single charge of the material. The forces corresponding to specific plunger speeds were recorded using a strip chart recorder assembly. The force and crosshead speed were converted into apparent shear stress (τ_{wa}), and shear rate (γ_w) at the wall by using the following equations involving geometry of the capillary and the plunger:

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

$$\gamma_w = \frac{3n'+1}{4n'} \cdot \frac{32Q}{\pi d_c^3} \qquad (2)$$

where F is the force applied to the plunger, A_p the cross-sectional area of the plunger, l_c and d_c the length and diameter of the capillary, respectively, and the factor $[(3n'+1)/4n']$ is the Rabinowitch correction applied to calculate the true shear rate at the wall from the apparent Newtonian shear rate at the wall:

$$\gamma_{wa} = \frac{32Q}{\pi d_c^3} \qquad (3)$$

where Q is the volume flow rate and n' the flow behaviour index.

$$n' = \frac{d(\log \tau_w)}{d(\log \gamma_{wa})} \qquad (4)$$

n' was obtained by regression analysis of the values of τ_w and γ_{wa} obtained from the experimental data.

The melt viscosity, η, was calculated as

$$\eta = \frac{\tau_w}{\gamma_w} \qquad (5)$$

The Bagley[15] correction for the pressure losses at the capillary was not applied because this correction factor becomes negligible for capillaries with high l_c/d_c ratios. No correction was also applied for the pressure drop in the barrel, although it becomes important at low values of n'.

2.4 *Melt elasticity*

The extrudates were carefully collected as they emerged from the capillary die, taking care to avoid

Table 1. Physical and mechanical properties of low density polyethylene (LDPE-Indothene 16MA400)

Melt flow index (g/10 min)	Density (g/cm^3)	Tensile strengh at break (kg/cm^2)	Elongation at break (%)	Modulus of elasticity (kg/cm^2)	Vicat softening point (°C)	Crystalline melting point (°C)
40	0·916	90	200	1 400	85	104

any deformation. The diameter of the extrudate was measured after 24 h of extrusion using a binocular stereomicroscope. The die-swell (D_1/D) was calculated as the ratio of the extrudate diameter D_1 to the capillary diameter D.

2.5 Extrudate morphology

The distortion and surface characteristics of the extrudates were studied using optical and electron microscopy. The extrudates were fractured under liquid nitrogen and the morphology of the extrudate cross-section was also studied using a scanning electron microscope.

3 Results and discussion

3.1 Effect of shear rate and fibre loading on viscosity

Melt viscosity versus shear rate plots of polyethylene and its composites containing 10, 20 and 30% by weight of short sisal fibre at a temperature of 130°C are shown in Fig. 1. The curves are typical of pseudoplastic materials, i.e., viscosity decreases with increasing shear rate. In general, the pseudoplastic behaviour can arise in either of the following two ways. (a) If a system of asymmetric molecules or particles which are randomly oriented or extensively entangled at rest is subjected to shear, the molecules tend to align themselves with their major axes in the direction of shear, and thereby points of entanglements are reduced; as a result the viscosity decreases. At very high shear rate the orientation may be complete, and near Newtonian behaviour may be observed. (b) In systems containing highly solvated molecules or particles where chemical interactions among polymer particles exist, the solvated layers may be sheared away by the increase of shear rate. This reduces the viscosity of the system. The curves in Fig. 1 can be represented by the Power law relation:[16]

$$\eta = K\gamma^{n-1} \tag{6}$$

where n is the Power law index and K, the consistency index.

In general the viscosity of composite increases with increasing fibre content and the increase is predominant at lower shear rates where fibre and polymer molecules are not completely oriented. The incorporation of fibre into the LDPE matrix increases the stiffness and modulus of the composite. The alignment of the polymer chain during extrusion becomes more restricted as fibre loading increases. Hence the viscosity increases with fibre loading. It is interesting to note that at high shear rates all the systems show a slight converging tendency. However, in the case of cellulose–polystyrene composites, Czarnecki and White[17] observed nearly the same viscosity at high shear rate. The low viscosity of the composites at high shear rates is an important factor in explaining the successful exploitation of these materials in injection moulding, since very little additional power will be required to mould the filled composites.[10]

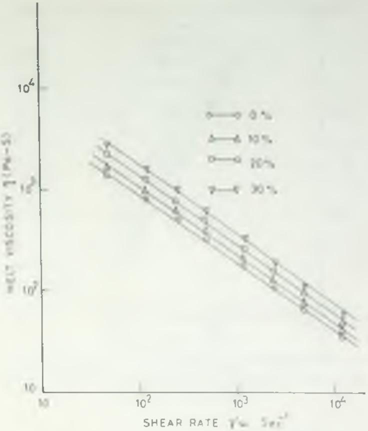


Fig. 1 Variation of melt viscosity (η) with shear rate (γ_w) of LDPE–sisal composites at a temperature of 130°C (average fibre length 5·8 mm).

3.2 Effect of shear stress and fibre loading on viscosity

Figure 2 shows the melt viscosity versus shear stress plots of LDPE–sisal composite having different fibre loadings. In all cases melt viscosity decreased with increasing shear stress due to the orientation of the fibre and polymer molecule in the extrusion direction.

Many authors[17–21] have reported that filled polymer systems exhibit yield stress due to the interparticle network formation which becomes quite strong with very fine particulate fillers at high filler loadings and at low shear rates. However, in the present work we have not observed any yield value. This may be due to lack of strong interaction between fibres as well as between fibre and polymer. Since the length of the fibres used in this study is less than 6 mm, it is expected that physical entanglement among the fibres normally observed in fibre composites is practically absent in this case. The absence of yield value has already been reported in the case of glass and cellulose fibre filled systems.[22–24]

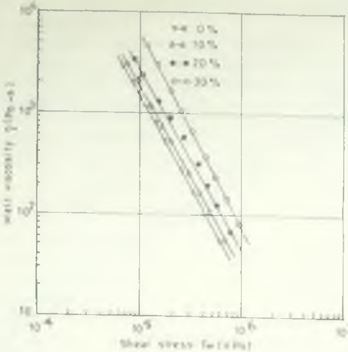


Fig. 2 Variation of melt viscosity (η) with shear stress (τ_w) of LDPE–sisal composites at a temperature of 120°C (average fibre length 5·8 mm).

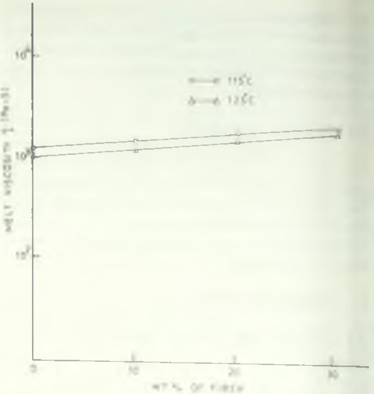


Fig. 3 Variation of melt viscosity (η) with fibre wt% at two different temperatures and at a shear rate of 83 s^{-1}

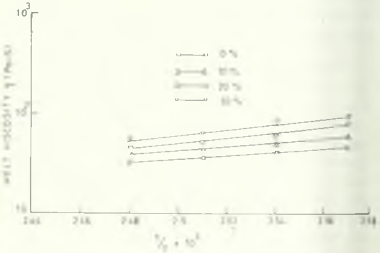


Fig. 4 Arrhenius plots of the melt viscosity (η) vs $1/T$ for LDPE–sisal fibre composites at a constant shear rate of 83 s^{-1}.

3.3 Effect of temperature on viscosity

Figure 3 shows the variation of melt viscosity at two temperatures with fibre loading at a shear rate of 83 s^{-1}. Melt viscosity decreased with increasing temperature. Generally, the viscosity decreases in a polymer melt with increase in temperature since molecular motion is accelerated at higher temperatures due to the availability of greater free volume.

Figure 4 shows the semi-logarithmic Arrhenius plot of the melt viscosity data ($\log \eta$ vs $1/T$) for LDPE–sisal fibre composites at a constant shear rate of 83 s^{-1} for different fibre concentrations.

Flow activation energy values were calculated from the slopes of the above plot and are presented in Fig. 5. The flow activation energy of a polymer melt evaluated in the non-Newtonian region at a constant shear rate is important in understanding its temperature dependence. According to published data the higher the flow activation energy, the more temperature sensitive is the melt. In the case of sisal–LDPE composites, it is seen that the melt viscosity of the composite is more temperature sensitive than that of the unfilled LDPE as evidenced by higher ΔE values of the composites. The flow of the short fibre composites is dependent upon the quantity of fibre present and the fibre length, besides temperature and rate of shear. The presence of fibre restricts molecular mobility under shear. With increase in temperature, the viscosity is reduced and the alignment of the fibres in the direction of flow becomes easier at the same rate of shear. This effect will be prominent in composites containing a higher quantity of fibre, since their viscosity is higher. Hence the composites containing a higher loading of fibre become more temperature sensitive.

3.4 Flow behaviour index (n')

Values of flow behaviour index as a function of fibre weight per cent at a temperature of 120°C are shown in Fig. 6. Non-Newtonian pseudoplastic fluids have values of n' below 1. Therefore, a high value of n' indicates a low pseudoplastic or non-Newtonian nature of the system. For all systems, n' values are less than unity, indicating the pseudoplastic nature of the composites. The degree of pseudoplasticity of the composites increases with increase of fibre loading, as evidenced by lower n' values of the com-

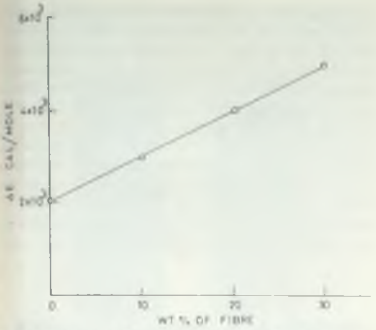


Fig. 5 Variation of flow activation energy ΔE with fibre wt% (average fibre length 5·8 mm)

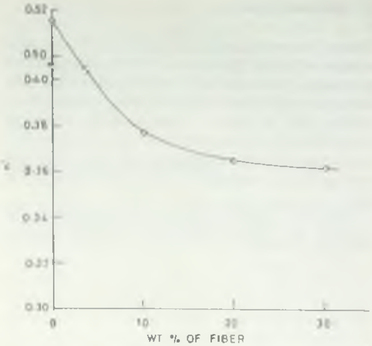


Fig. 6 Plot of flow behaviour index (n') with wt% of fibre at a temperature of 120°C.

posites. This observation further supports the fact that the presence of fibre restricts molecular mobility, and the orientation of the fibre in the direction of flow becomes more difficult as the fibre content is increased.

3.5 *Effect of fibre length on viscosity*

Figure 7 shows the effect of fibre length on the melt viscosity of LDPE–sisal fibre composite. It was difficult to study the flow behaviour of composites containing fibres having a length beyond 6 mm. At low shear rates, viscosity increases only marginally with fibre length, but at higher shear rates the increase is predominant. The increase in viscosity with the increase of fibre length is due to the fact that it is difficult for fibres having higher lengths to become oriented in the direction of flow.

At lower shear rates of 8 s^{-1} and 16 s^{-1} the alignment and distribution of fibres in the composite do not change to any appreciable level and hence the effect of fibre length in increasing the viscosity is only marginal. But at higher rates of shear both fibre alignment and fibre distribution can occur simultaneously. Fibres having shorter lengths become more easily aligned and distributed than those having higher lengths. As a result of this, composites containing fibres of shorter length show much lower viscosity than those having fibres of higher length, at higher shear rates.

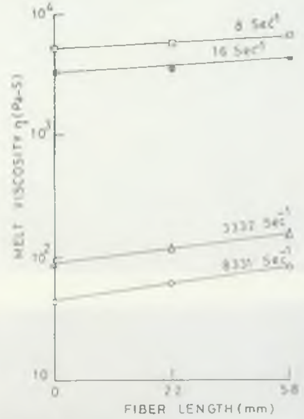


Fig. 7 Melt viscosity (η) vs fibre length of LDPE–sisal fibre composites for different shear rates.

3.6 *Effect of fibre treatment on viscosity*

Figure 8a shows the effect of fibre treatment on the rheological properties of LDPE–sisal composites. Isocyanate treated composites showed slightly higher viscosity than the untreated composites. This may be due to better fibre matrix adhesion as is evident from the tensile fracture surface of untreated (Fig. 8b) and isocyanate treated (Fig. 8c) composites. It may be noticed that the treated fibre surface contains polyethylene fragments due to the improved interaction between the polymer and the fibre.

3.7 Die-swell ratio

Figure 9 shows the variation of die-swell ratio as a function of weight per cent of fibre loading at two shear rates. It is seen that die-swell values decreased sharply by addition of 10% of fibre followed by a levelling off at higher fibre loading. Die-swell increased with increase of shear rate. Chan *et al.*[24] have reported that incorporation of fibres causes a very significant reduction in die-swell of the parent melt.

When the molten polymer flows through the capillary, the polymer molecules undergo orientation under the applied shear force.[25] As the melt comes out of the die, reorientation and recovery of the molecule occurs. This leads to the phenomenon of die-swell. In the case of short fibre composites, orientation of both polymer molecules and fibres takes place during flow through the capillary. On emerging from the capillary the composite tries to retract by the recoiling effect of the polymer chains. The fibres, being non-elastic, exert little retractive force. The unequal retractive forces experienced by the two components of the composite can lead to redistribution of the fibres. Since the molecules at the periphery undergo maximum deformation, the

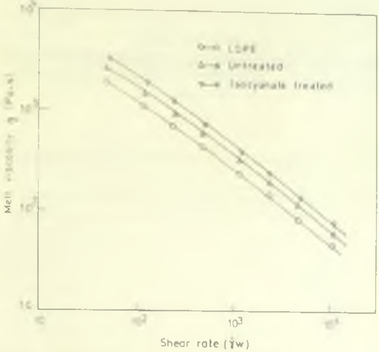


Fig. 8a Melt viscosity (η) vs shear rate ($\dot{\gamma}_w$) of LDPE–sisal fibre composites for different fibre treatments. Original magnification ×600.

Fig. 8b SEM photomicrograph of tensile fracture surface of untreated sisal–LDPE composites. Original magnification ×600.

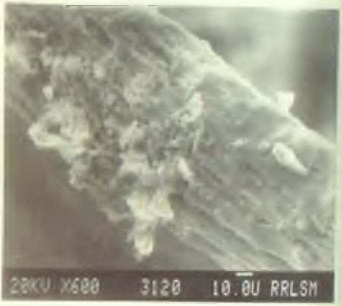


Fig. 8c SEM photomicrograph of tensile fracture surface of isocyanate treated sisal–LDPE composites.

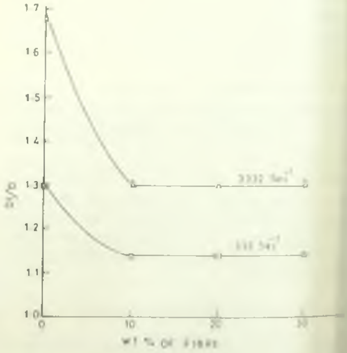


Fig. 9 Variation of die-swell ratio with wt% of fibre at a temperature of 115°C.

retractive forces on these molecules will also be higher. This leads to migration of the fibres to the periphery of the extrudate. Thus the reorientation and migration of the fibres take place at the expense of the retractive forces, which is mainly responsible for the die-swell, resulting in reduced swell of the short fibre composites.

3.8 Extrudate characteristics

Figure 10 is an optical photograph of the extrudates at two different shear rates. It is seen that the extrudates of unfilled LDPE showed maximum deformation and non-uniformity in diameter. This is associated with the melt fracture where the shear stress exceeded the strength of the melt. The deformation of the extrudates increased with the increase of shear rate. Addition of sisal fibre substantially reduced the distortion of the extrudates.

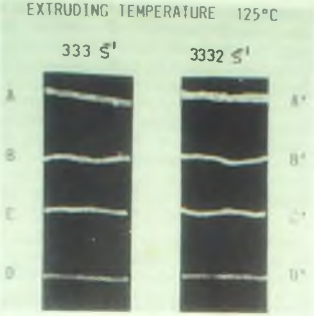


Fig. 10 Optical photomicrographs of the extrudates at two different shear rates. A, B, C and D indicate the wt% fibre, viz. 0, 10, 20 and 30% respectively.

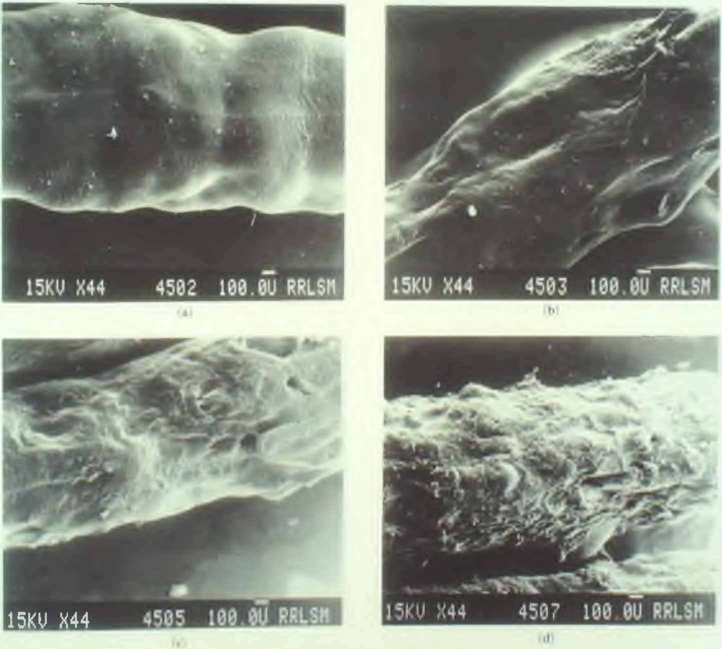


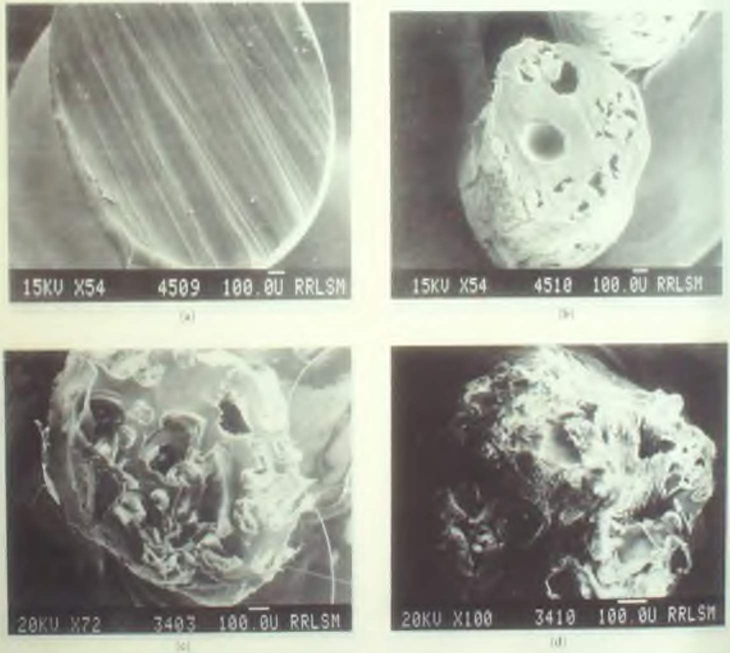
Fig. 11 SEM photomicrograph of the surface of the extrudate with fibre content (a) 0%, (b) 10%, (c) 20% and (d) 30%. Original magnification ×44.

Figures 11(a)–(d) show the surface morphology of the extrudate at a shear rate of $333\ s^{-1}$ and a temperature of 125°C for different fibre loadings, viz. 0, 10, 20 and 30 wt%, respectively. It is clear from these figures that surface discontinuity increased with fibre concentration. This again implies that the addition of fibre into the polymer creates discontinuity in the matrix. The surface discontinuity is associated with the migration of the fibre towards the periphery of the extrudate (see below). As compared to LDPE, the decrease in melt elasticity of the fibre composites is attributed to this phenomenon, which in consequence causes discontinuity in stress transfer for elastic recovery or deformation.

Figures 12(a)–(d) show the extrudate cross-section morphology of LDPE–sisal fibre composites at three different fibre loadings, viz. 0, 10, 20 and 30 wt%, respectively. From these figures, it can be seen that the fibres are well oriented along the direction of extrusion. It is interesting to note that the fibres are concentrated more at the periphery of the extrudate. As discussed earlier, the unequal retractive forces experienced by the components in the composite (elastic polymer matrix and non-elastic fibre) result in the redistribution of the fibre and its consequent migration to the periphery of the extrudate. Migration phenomenon in fibre composites has been reported by many researchers.[26-31]

4 Conclusion

The rheological behaviour of LDPE–sisal composites has been investigated. These composites exhibit pseudoplastic behaviour and can be represented by the Power law equation. At any given temperature the value of the flow behaviour index decreases with increasing sisal fibre content. This suggests that fibre filled composites are more



(a) (b) (c) (d)

Fig. 12 SEM photomicrograph of the cross-section of the extrudate with fibre content (a) 0%, (b) 10%, (c) 20% and (d) 30%. Original magnifications × 54, × 54, × 72 and × 100, respectively.

pseudoplastic than pure LDPE. Increasing fibre loading increases the shear viscosity of the system. The activation energy of the flow of composites increases with increasing concentration of sisal fibre. Die-swell ratio decreases with increasing fibre concentration. Addition of sisal fibre to LDPE decreases the extrudate distortion. However, sisal fibre creates discontinuity in the polymer matrix which was evident from the SEM photomicrographs. The SEM studies on the cross-sectional morphology of the extrudates indicated that fibres are concentrated more at the periphery of the extrudate.

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