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Composites of linear low density polyethylene and short sisal fibres: The effects of peroxide treatment

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Influence of sisal fibre content and different concentrations of dicumyl peroxide (DCP) on the thermal, mechanical and viscoelastic properties of short sisal fibre—linear low-density polyethylene (LLDPE) composites was investigated. Significant improvement of tensile strength was found after peroxide induced grafting between fibres and PE matrix. The stress relaxation measurements also suggest better stability upon prolonged loading of the samples prepared with 1% of DCP. It was shown, on the other hand, that higher DCP concentrations could have detrimental effects on the PE matrix, especially at low fibre contents. © *2004 Kluwer Academic Publishers*

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1. Introduction

Reinforcement of the polymer matrix using inorganic fibres is a widely used method for improving its properties. However, in recent years, cellulose based fibres are introduced as a possible replacement of synthetic materials [1–14]. The relatively high specific strength and stiffness of natural fibres, as well as their ability to withstand processing temperatures up to 230°C, make them very attractive as potential reinforcement for polyolefins [1]. Favourable properties, compared to conventional reinforcements, are also low price and the possibility to be burned. So far, enhanced moisture absorption and poor adhesion between hydrophilic fibres and the hydrophobic polymer matrix could be a disadvantage for their successful application. It is, however, believed that these problems can be overcome by treatment of the fibres with suitable chemicals [1–3].

Previous studies of Joseph *et al.* [3, 5] on low-density polyethylene—sisal fibre composites have shown that physical properties are significantly improved by chemical treatment of the fibres. It has been found that addition of a small amount of peroxides leads to the improvement of the tensile strength of the composite. In this paper a slightly modified approach was used, with linear low-density polyethylene (LLDPE) as the matrix. Besides the changes in the tensile properties, we also concentrated on the changes in thermal and viscoelastic properties of composites induced by an increase in sisal content and concentration of dicumyl peroxide (DCP), which is used as crosslinking agent because of the suitable decomposition temperature and low decomposition rate [3]. In order to investigate the effect of peroxide treatment on the degree of permanent deformation of composites during prolonged loading, a stress relaxation method was used.

2. Experimental

2.1. Materials

Sisal (*Agave sisalana*) fibre was obtained from the National Sisal Marketing Committee in Pietermaritzburg, South Africa. LLDPE was supplied in powder form by Sasol Polymers. It has a particle size of less than 600 μm, a melt flow index of 3.5 g/10 min, a weight-average molecular weight of 196000 g mol^{-1}, and a density of 938 kg m^{-3}. Dicumyl peroxide (DCP) supplied by Sigma Aldrich Co. Ltd., was used as the oxidizing agent.

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TABLE I List of the samples used in this study

LLDPE/DCP/sisal	LLDPE/DCP/sisal	LLDPE/DCP/sisal
50/0/50	49/1/50	47/3/50
60/0/40	59/1/40	57/3/40
70/0/30	69/1/30	67/3/30
80/0/20	79/1/20	77/3/20
90/0/10	89/1/10	87/3/10
100/0/0	99/1/00	97/3/00

2.2. Preparation of the composites

The sisal fibre was chopped into small pieces that fit in a CYCLOTEC 1093 sample mill for grinding. Ground fibres were soaked in petroleum ether at 40°C for 4 to 5 h, with regular shaking, washed thoroughly with warm distilled water and finally dried in a vacuum oven at 80°C. The size of the dried fibres was determined by optical microscopy and found to be 2.0 ± 0.3 mm in length and 130 ± 10 μm in diameter. Composites were prepared by mechanically mixing LLDPE, sisal and the corresponding amount of DCP (0, 1 and 3%) in a coffee mill for about 2 min. The samples were then melt pressed at 180°C into sheets with average dimensions 100 × 80 × 0.7 mm by using an AMS 10-ton (10^4 N) hot melt press. Table I outlines the samples prepared with different ratios of LLDPE-DCP-sisal of 20 g sample each.

2.3. Methods

Differential scanning calorimetry (DSC) analyses were performed in a Perkin–Elmer DSC7 thermal analyzer in a flowing nitrogen atmosphere. The samples, approximately 10 mg each, were heated from 25 to 180°C and maintained at this temperature for 5 min. They were then cooled to 25°C at a rate of 10°C min^{-1}, held at this temperature and reheated to 180°C at the same rate.

Mechanical properties were investigated using a Hounsfield W5K tensile tester at a cross-head speed of 50 mm min^{-1}. At least five specimens were tested for each set of samples, and the mean values are reported.

The stress relaxation measurements were carried out on a Hounsfield H5KS tensile machine. Samples were stretched to a constant 1% strain at a crosshead speed of 50 mm min^{-1}. Decaying of the stress was monitored for 90 min. For both tensile and stress relaxation measurements, specimens were dumbbell shaped, with a cross-sectional area of 5 mm × 0.7 mm and a gauge length of 25 mm.

The morphological aspects of the sisal-PE interfaces at fracture surfaces were observed by scanning electron microscopy (Jeol 6400 WINSEM model at 5 keV).

Water absorption was determined according to the following procedure: Samples were weighed and placed in distilled water. They were taken out of the water at regular intervals, dried by blotting and weighed, then returned into the distilled water, which was changed every day. Percentage moisture uptake was calculated according to the equation:

$$\text{mass}\% = [(W_{\text{w}} - W_{\text{d}})/W_{\text{d}}] \times 100,$$

where mass% is the total moisture uptake, while W_{d} is the initial sample weight and W_{w} the weight of the sample after immersion in water.

3. Results and discussion

3.1. Calorimetry

DSC heating curves of uncrosslinked PE and PE-sisal fibre composites are shown in Fig. 1. As expected, the magnitude of the melting peak decreases with increasing sisal content, since only PE contributes to the crystallinity. Composites melt-pressed in the presence of DCP show similar behaviour. In order to check the influence of the sisal content and oxidising agent on the melting behaviour of the composites, the melting enthalpies and melting temperatures are plotted vs. sisal

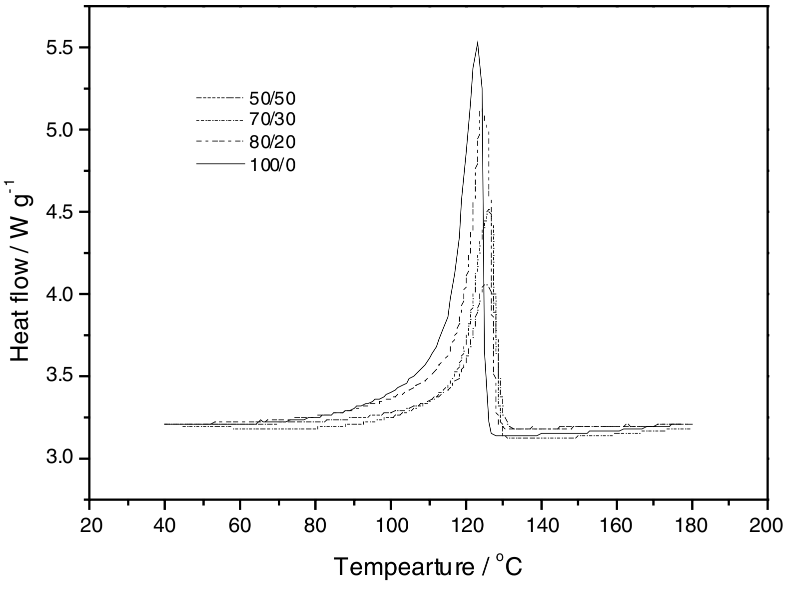

Figure 1 DSC heating curves of LLDPE and LLDPE/sisal fibre composites (0% DCP).

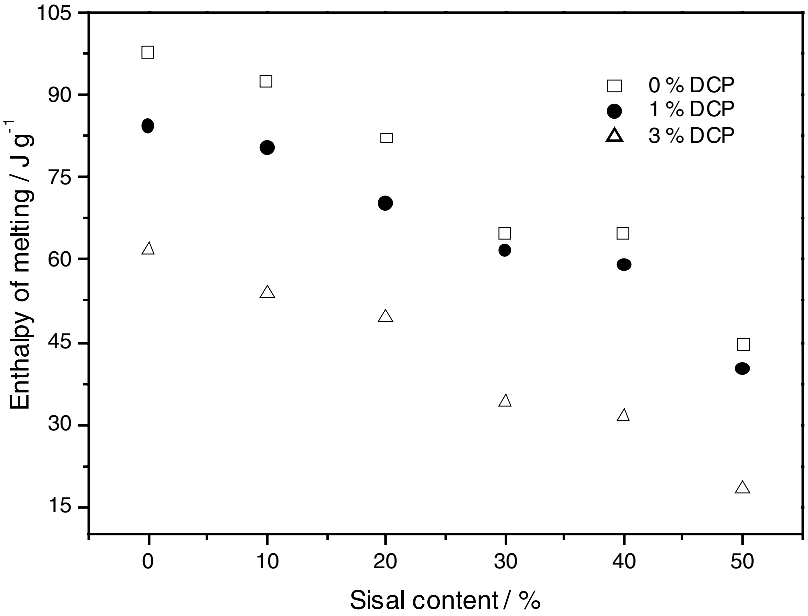

Figure 2 Variation of melting enthalpies with an increase in sisal content for LLDPE and LLDPE/sisal fibre composites at different DCP concentrations.

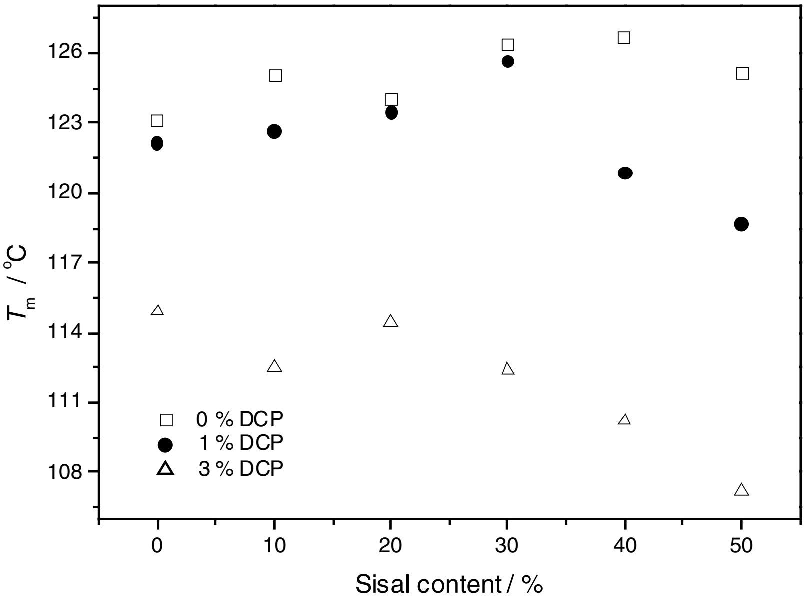

Figure 3 Variation of melting temperatures with an increase in sisal content for LLDPE and LLDPE/sisal fibre composites at different DCP concentrations.

content in Figs 2 and 3. It can be seen in Fig. 2 that the melting enthalpies decrease with an increase in both the concentration of DCP and the amount of fibre in the composite. It seems, however, that the main trend of decrease in crystallinity with increasing sisal content is not affected by chemical treatment. On the other hand, the chemical reactions induced by peroxide radicals will change the functional dependence of the melting temperatures (taken as the melting peak maximum) on the sisal content (Fig. 3). While melting temperatures (T_m) of untreated composites increase with increasing amount of sisal fibre, samples with 3% of DCP show the opposite behaviour. The presence of the sisal fibres in the untreated composite obviously favours lamellar thickening, probably as a result of reduced mobility of the PE chains. Regardless of the amount of sisal in the composite, introduction of DCP leads to a decrease in the melting temperature due to crosslinking of the matrix as well as grafting of PE chains to the fibres suggested in a previous study [3]. Fig. 3 also shows that samples with 3% of DCP have the lowest melting temperature because the degree of crosslinking increases with DCP concentration. However, since DCP decomposition induces both crosslinking and grafting, it is presently not clear how they affect the properties of the composite that determine the functional dependence of the melting temperature on the sisal content. As can be seen in Fig. 3, the melting temperature of the sample with 3% DCP steadily decreases with increasing amount of sisal, while in the sample with 1% DCP it increases for low sisal amounts (<30%), after which it starts to decrease. Further investigations are necessary to clarify this behaviour.

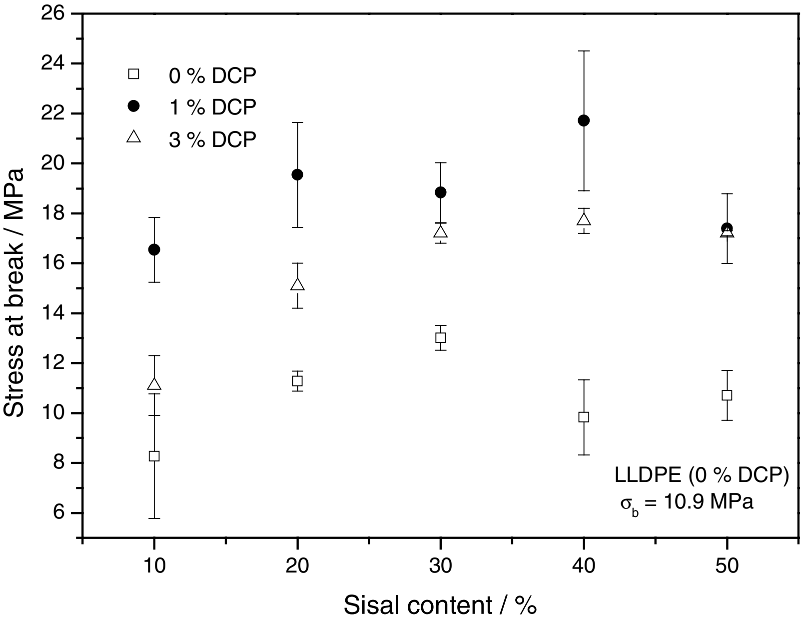

Figure 4 Stress at break vs. sisal content for untreated (0% DCP) and peroxide treated composites (1 and 3% DCP).

3.2. Mechanical properties

Fig. 4 depicts the tensile strength of the composites as a function of the sisal content. After introduction of the fibres the material becomes stronger, which is manifested by an increase in the tensile strength with increasing amount of sisal, regardless of the presence of DCP (Fig. 4). However, because of the improved interaction between the matrix and fibres, composites prepared with DCP show higher tensile strength values for a given PE-sisal composition. It can also be seen that above 40% of sisal fibre, the tensile strength of the pure composite starts to decrease. This is the result of the poor wetting of the fibres by the matrix, which is especially manifested at high fibre concentrations. Obviously, grafting between the PE chains and the fibres induced by DCP, improves stability of the material at high sisal loadings. This conclusion is supported by the SEM micrographs of the fracture surface of untreated and DCP treated composites with 30% fibre (Figs 5 and 6). It can be seen that in the untreated composites the fibres are pulled out from the matrix during tensile failure, whereas in the samples treated with 3% DCP, the fibres mostly undergo delamination. Although grafting improves the interaction between the

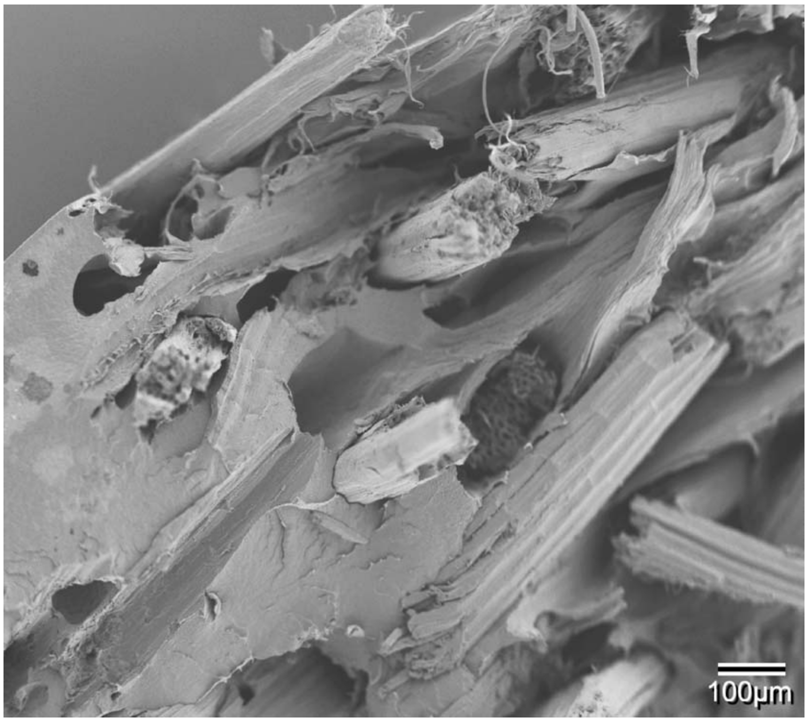

Figure 5 SEM micrograph of the tensile fracture surface of the untreated sisal-PE composites (30% of fibre loading) showing poor interaction between matrix and fibres.

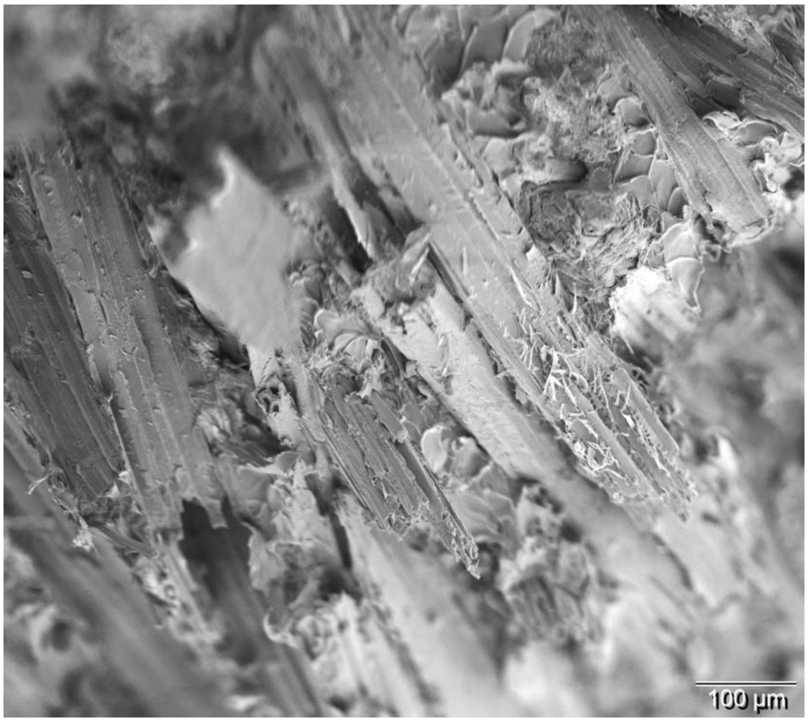

Figure 6 SEM micrograph of the tensile fracture surface of DCP treated sisal-PE composites (30% of fibre loading and 3% of DCP) showing delamination of the fibres during failure.

phases, Fig. 6 suggests that it cannot suppress tearing within the fibre itself and this aspect should get special consideration in future studies. Nevertheless, as already concluded from Fig. 4, DCP treatment improves the material properties, because the tensile strength value of about 20 MPa for the composite with 30% sisal and 1% DCP is about 100% higher than that of the pure matrix. This is in agreement with previous results of Joseph *et al.* [3] on randomly oriented sisal fibre-LDPE composites. However, these authors have used fibres with average length of 5.8 mm and a different method of sample preparation, and the comparison should be made with some restriction. It should also be noticed that composites with 3% DCP show lower tensile strength values than those with 1%, for one specific sisal concentration. Melt pressing of the sheets in the presence of higher DCP concentrations induces besides crosslinking, significant degradation of the matrix, which consequently reduces tensile strength.

Elongation at break of the composites is, of course, low and it decreases with increase in sisal content (Fig. 7). It can also be seen in Fig. 7 that the combined effects of crosslinking and grafting lead to an increase in the elongation at break. At low sisal contents, when the effects of crosslinking are more pronounced, elongation at break is significantly higher then in the pure composite. Further increase in sisal content reduces elongation at break, but still to values that are higher than those of the untreated material. Similar results are also obtained for the composites with alkali treated sisal fibres [3].

Fig. 8 shows the elastic modulus of the pure and DCP treated composites plotted vs. sisal content. Introduction of the high modulus sisal fibres into the PE matrix enhances the modulus of the resultant material. It can be also seen in Fig. 8 that up to 30% of fibre, the tensile modulus of samples treated with 1% of DCP is close to that of the untreated composite. At higher sisal loadings (>30%) the modulus of the untreated samples starts to decrease, probably as a result of poor wetting of the fibres by the matrix. The samples melt pressed with 3% DCP also show lower elastic moduli values than the pure samples and the samples with 1% DCP. If we assume that the melting enthalpies in Fig. 2 correspond to the matrix crystallinities, reducing the crystal fraction induced by high DCP concentration could be responsible for the lower moduli of these samples, especially at low fibre contents. The modulus of the composite is, to a certain extent, a linear combination of the moduli of the matrix and fibres. Because a decrease in crystallinity reduces the modulus of the matrix, the modulus of the composite will also be reduced. Our former results [15] support this discussion. It was observed that the modulus of pure LLDPE decreases after it is crosslinked with DCP. It also seems that DCP reduces the detrimental effects of the poor wetting on the tensile modulus at higher sisal contents (>30%). Fig. 8 shows that above 30% fibre, DCP treated samples have higher elastic moduli than the untreated ones. Finally, the values of the elastic moduli obtained in the present study are close to those reported in literature. Depending on the preparation conditions, moduli of the randomly oriented sisal fibre-LDPE composites were in the range of 300–400 MPa for melt mixed [4] to more than 1 GPa for solution mixed composites [4, 5].

3.3. Stress relaxation

Typical relaxation curves of the semicrystalline polymers [16, 17] and polymer composites [5, 18] are obtained in the stress relaxation measurements (Fig. 9). In the beginning (up to 100 s), stress decay is fast but gradually slows down with time. The initial stresses

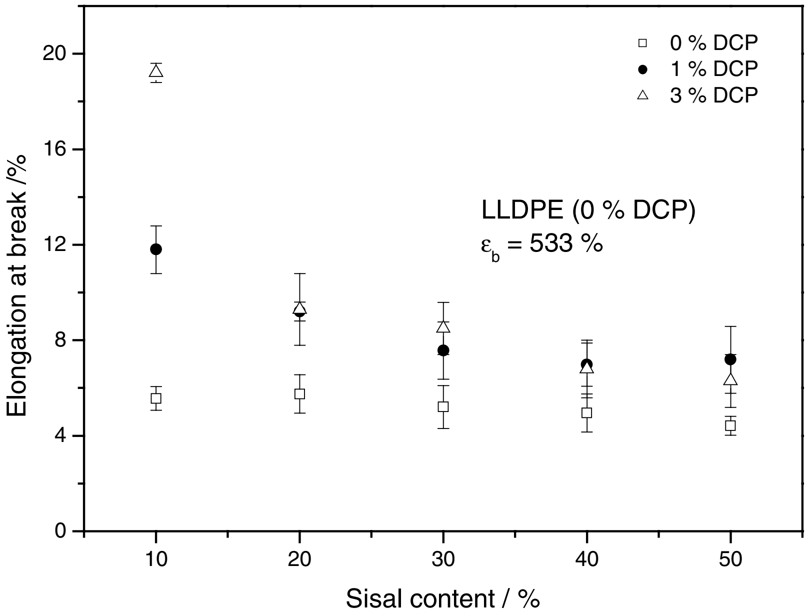

Figure 7 Elongation at break vs. sisal content for untreated (0% DCP) and peroxide treated composites (1 and 3% DCP).

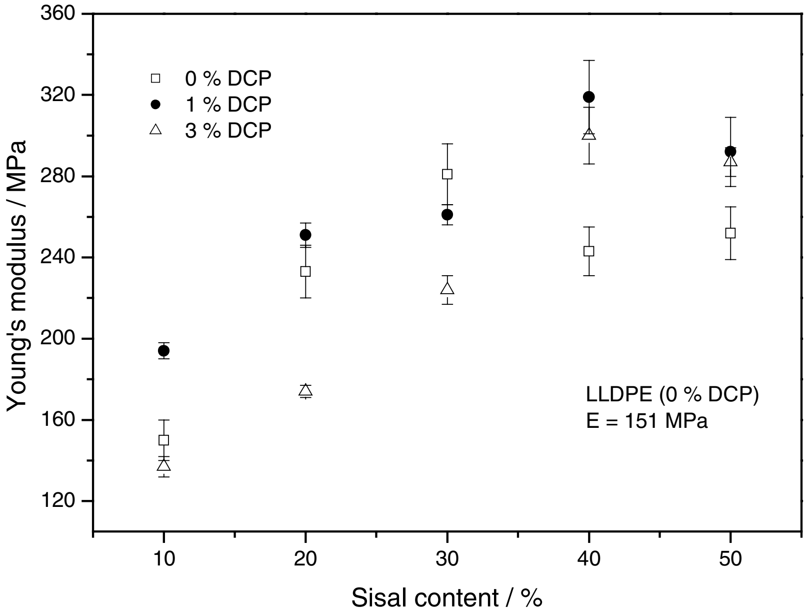

Figure 8 Young's modulus vs. sisal content for untreated (0% DCP) and peroxide treated composites (1 and 3% DCP).

also follow the changes in the elastic modulus with an increase in sisal content. In order to establish the effects of sisal loadings on the degree of stress decay, the relaxation curves are normalized in Fig. 10 with respect to the initial stress. It can be seen that the residual stresses in Fig. 10 show the same dependence on sisal content as the initial stresses. On the other hand, composites of sisal fibres and natural rubber show opposite behaviour [5]. The stress relaxation rate increases with an increase in the amount of sisal i.e., the normalized stress is the highest in pure rubber. Different effects of sisal fibres on PE and natural rubber can probably be attributed to the different relaxation mechanisms in these matrices.

Stress relaxation in a semicrystalline polymer, such as polyethylene, can be well explained in terms of the two-process model [16, 17]. This model treats the stress relaxation in semicrystalline polymers as a superposition of two thermally activated processes, each connected to one phase of the material, crystal or amorphous. It is assumed that in the beginning of stress relaxation, taut tie chains, which actually carry the applied load, are pulled out from the crystal lamellae because they impose large local stresses. Taut tie molecules are, in fact, defects in the crystal structure at the points where they enter lamellae, and the stress concentration in these points is very high. Stress concentration induces defect propagation through the lamella, so called *c*-axis slip. As a consequence of this crystal process, the average distance between the lamellae increases until stretching of formerly loose tie molecules takes place. Since the applied stress is now re-distributed over a larger number of tie chains, their propagation will be partially reduced and relaxation will start to slow down. This can explain the presence of fast and slow relaxation processes in the experimental

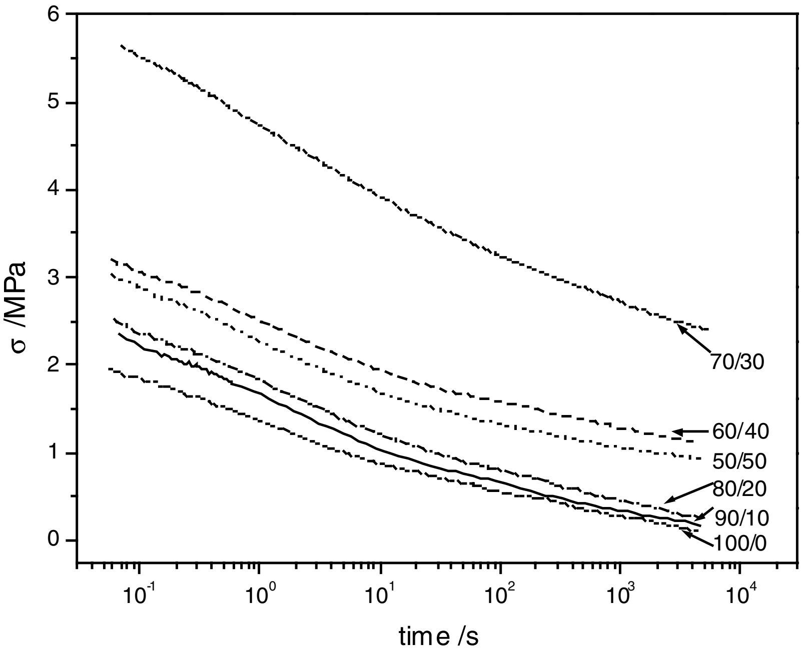

Figure 9 Stress relaxation curves of untreated composites (0% DCP) for pure LLDPE and various LLDPE/sisal compositions.

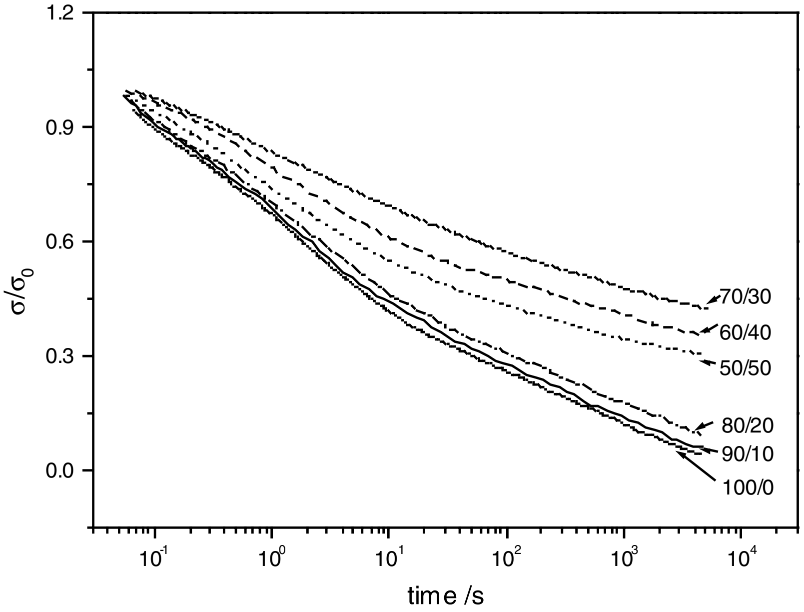

Figure 10 Stress relaxation curves of untreated composites (0% DCP) normalized with respect to initial stress.

curves in Fig. 9. In principle, the above approach can also be applied to polymer composites if one treats the fibres as "crystals" embedded in an amorphous matrix. However, instead of a crystal process or *c*-axis slip, a matrix fibre de-bonding process should be considered. The results on natural rubber-sisal fibre and natural rubber-carbon black composites could support the former conclusion [5, 18]. Pure rubber shows only one distinguishable relaxation mechanism, whereas rubber composites show two. The crystallinity of natural rubber is relatively low, and the relaxation process takes place almost solely in the amorphous phase, which explains the presence of just one relaxation mechanism. A second, slow relaxation process arises after introduction of the fibres, through a progressive rubber-fibre de-bonding similar to the slow realising of the stress at the lamellar defect points in a semicrystalline polymer. Raman spectroscopy measurements by Van Eijk *et al.* [19] on polyethylene are also in line with the former discussion. They showed that, in the later stage of relaxation, the number of high stress bearing C—C bonds decreases with time in the same way as the macroscopic stress. In the polyethylene sisal fibre composites the relaxation behaviour is more complicated, because the crystal lamellae also contribute to the overall process. This could be the reason for the different effects of sisal fibre on the stress relaxation as was mentioned above. It is possible that sisal fibres in the polyethylene matrix act like a shield, which prevents to some extent defects propagating through the lamellae. As long as the interaction between the fibres and polyethylene chains is good, it will stabilise the stress decay and the stress will

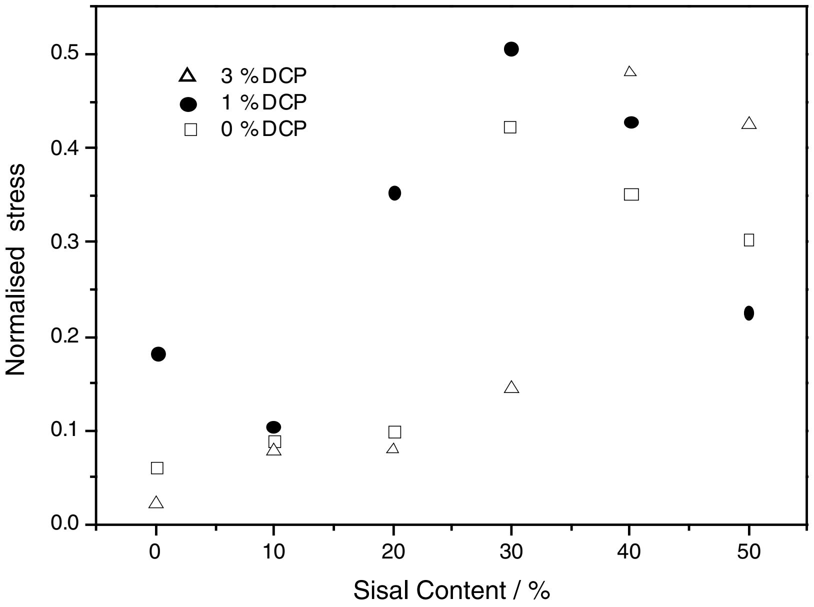

Figure 11 Normalized stress vs. sisal content for the untreated (0% DCP) and peroxide treated composites (1 and 3% DCP).

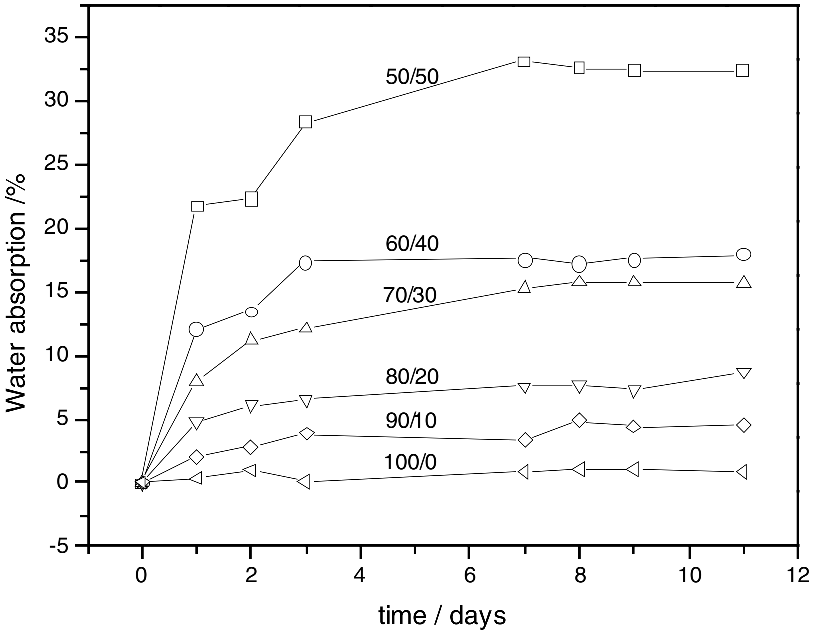

Figure 12 Variation of mass% of water absorbed with time for untreated composites (0% DCP) at different sisal contents. Numbers above the curves represent LLDPE/sisal compositions.

also increase. At higher sisal loadings (40 and 50%), poor wetting of fibres by the matrix enables easier conformational rearrangements of PE-chains during stress relaxation. As a result, the stress decay will be more pronounced (Fig. 10). It should be noted that the composites with DCP show similar relaxation behaviour as the untreated ones. Normalised stresses follow the changes of initial stress with sisal content for one specific DCP concentration. This is why we did not include these figures, but decided to plot the normalised stress versus sisal content in Fig. 11. An increase in normalised stress implies improved stability of the material upon prolonged loading, and Fig. 11 actually shows the changes in the viscoelastic properties with both sisal content and DCP concentration. Assuming that the application of stress leads to the debonding process between matrix and fibres, the results in Fig. 11 again suggests the importance of the strength of their interaction. It can be seen that the composites, melt-pressed in the presence of 1% DCP, show higher values of normalised stress than the untreated composites, because of the strong interaction between the phases. Stress relaxation also depends on the viscosity coefficient of the material, which depends on chain mobility. After fibre-matrix debonding, the mobility of the chains increases, which reduces the viscosity and leads to a more intense cold flow. Debonding effects will obviously be reduced after grafting between sisal fibres and PE chains during melt pressing with 1% DCP, which will improve the stability of the material on loading. At low sisal contents (less then 30%), the composite samples with 3% DCP show lower values of stress than the untreated composite with the

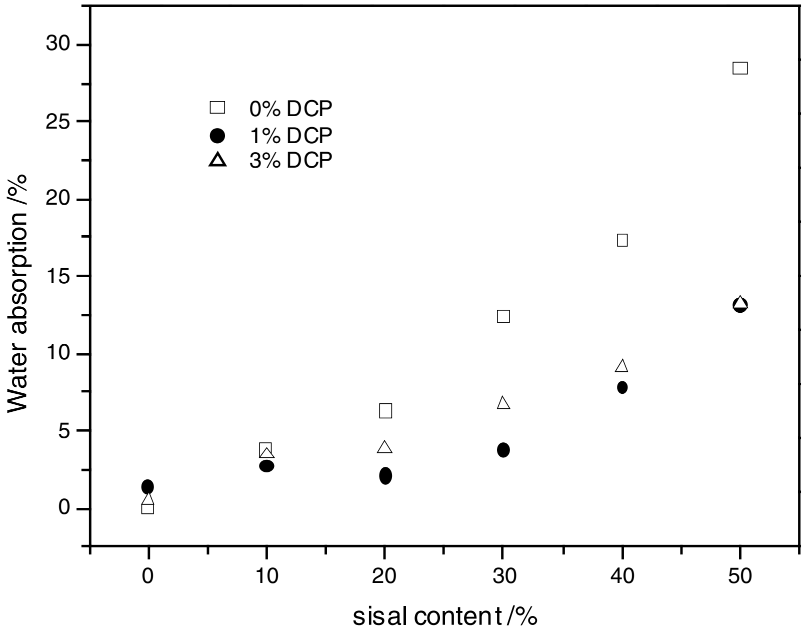

Figure 13 Variation of mass% of absorption, after three days of exposure to water, with an increase in sisal content for LLDPE/sisal composites at different DCP concentrations.

same amount of fibre (Fig. 11). The reason is degradation of the matrix at high peroxide concentrations. It is well known that the viscosity of the polymer decreases as its average molecular weight decreases. At high concentrations (3%) DCP will, besides crosslinking, induce a large number of oxidative chain scissions, which will reduce the viscosity and consequently the stress. However, when the sisal content exceeds 30%, grafting effects start to override the effects of scissions. This can be well seen in Fig. 11 as an increase in the normalised stress above the corresponding values of the samples with 0 and 1% DCP.

3.4. Water absorption

Fig. 12 shows the mass% of the water absorption versus time for the composites with various sisal-LLDPE compositions. It can be seen that the mass% of water absorption increases with sisal content due to the hydrophilic character of the cellulose based fibres. Also, for all composites, the mass% increases with time up to three days of exposure to water. After three days, it reaches a maximum and goes into saturation. In the case of pure polyethylene, because of its hydrophobic nature, the change in weight is independent from the exposure time.

Sisal-PE composites, prepared with DCP, show reduced water absorption, although the mass% of the absorption has the same dependence on time as the untreated composites. The influence of the peroxide treatment can be well seen in Fig. 13, where the mass% at maximum absorption (i.e., after three days of exposure) is plotted vs. sisal content. Significantly lower values of the mass% changes are obtained in the case of DCP treated composites, compared to untreated ones. Improved interfacial bonding is the probable reason for this behaviour. Grafting reactions reduce the number of voids between sisal and the PE matrix, and partially prevent fibres getting into contact with water. SEM micrographs (Figs 5 and 6) support the suggested explanation. On the other hand, another study [6] shows that chemical treatment of the fibres with the cardanol derivative toluene diisocyanate (CTDIC) before mixing with PE can reduce the absorption of boiling water. This is explained *via* changes of the hydrophilic nature of sisal fibres due to the high reactivity of the —N=S=O functional group towards cellulose —OH groups.

4. Conclusions

Addition of low concentrations (1%) of curing agent (DCP) to the composites prepared by mechanical mixing and subsequent melt pressing of LLDPE and milled sisal fibres, significantly improves their tensile and viscoelastic properties. Composite samples with 1% DCP have 70% higher strength than the untreated ones with the same amount of fibre. This is a consequence of peroxide induced grafting between the hydrophobic PE matrix and hydrophilic fibres, which improves their otherwise poor adhesion. Stress relaxation measurements showed that grafting reduces the degree of permanent deformation of the composites, while they are stretched for longer times at a constant strain. However, high DCP concentration (3%) also induces degradation of the matrix at low sisal contents (<30%). This is why these samples show higher stress relaxation rates during prolonged loadings than their untreated counterparts.

Increase in DCP concentration changes the functional dependence of the melting temperatures of the composites on the sisal content. The melting temperature of the untreated composites increases with increasing sisal content, while the samples with 3% DCP show opposite behaviour. Water absorption is reduced in the samples prepared by melt pressing with DCP. This is explained *via* the reduced number of voids between the matrix and the fibres due to improved interfacial bonding.

A general conclusion is that DCP has positive effects on the properties of mechanically mixed LLDPE-sisal composites. However, the concentration of the peroxide should be adjusted depending on the sisal content.

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