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Composites of low-density polyethylene and short sisal fibres: the effect of wax addition and peroxide treatment on thermal properties

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Abstract

The influence of sisal fibre content, peroxide cross-linking, and wax addition on the thermal properties of LDPE–sisal composites was investigated using differential scanning calorimetry and thermogravimetric analysis. It was found that the presence of wax and sisal fibre, as well as peroxide treatment, has an effect on the LDPE crystallinity. In the presence of sisal, the melting temperature of peroxide treated samples decreases substantially, and this decrease becomes more pronounced with increasing sisal content. The presence of wax reduces the extent to which the melting temperature decreases. It was further found that the presence of wax and sisal fibre, as well as peroxide treatment, has an effect on the thermal stability of the composites.

Keywords: Sisal; Polyethylene; Fibre composite; Wax; DSC; TGA

1. Introduction

Reinforcement of a polymer matrix using inorganic fillers is a widely used method for improving its properties. However, in recent years, organic fillers, such as cellulose-based fibres, had started to replace synthetic materials [1–14]. So far, enhanced moisture absorption and poor adhesion between hydrophilic fibres and the hydrophobic polymer matrix could be a disadvantage for their successful application. Wax is a well-known processing agent added to improve the processing of different polymers, but especially polyolefins. Paraffin wax has been found to have a considerable influence on the thermal and mechanical properties of LDPE [15,16], and cross-linking as a means to improve the mechanical properties of LDPE–short-sisal fibre composites has been investigated [3,17].

The addition of wax to blends and composites may not only improve their processability, but also their mechanical properties. Kim et al. [18,19] investigated the effect of liquid–liquid phase separation (LLPS) on the crystallization behaviour and mechanical properties of poly(ethylene-*ran*-vinyl acetate) and paraffin wax blends. They found that the LLPS between EVA and wax could profoundly affect the flexural modulus of a binder consisting of an EVA/wax blend, as well as a feedstock comprising the binder and metal powders. In our previous paper [15] the effect of cross-linking on the thermal properties of LDPE/wax blends was investigated. It was found that, at low peroxide and high wax concentrations, part of the wax is grafted onto the LDPE chains. It was also observed that there was complete miscibility of wax in LDPE at wax concentrations up to 10%, but only partial miscibility at higher wax concentrations. Djokovic et al. [16] found that, for blending of an oxidized paraffin wax with LDPE, small wax concentrations improved the physical properties of the blends. Co-crystallization of LDPE and wax chains leads to an increase in blend crystallinity, while there is an improvement in the elastic modulus and stress at yield. They did, however, find that crystal phase separation at higher wax concentrations, as well as the presence of short wax chains in the amorphous fraction, caused deterioration of the thermal and mechanical properties.

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As far as thermal stability is concerned, unoxidized paraffin wax seems to reduce the thermal stability of the blends [15], while low concentrations of oxidized paraffin wax considerably improved their thermal stability [16]. However, phase separation at higher concentrations could clearly be seen from the TGA curves. Investigation of the thermal stability of sisal fibre–polystyrene (PS) composites [20] showed that the sisal fibre degraded before the PS matrix, and that the composites are more stable than both components. It was further shown that the thermal stability of acetylation treated fibre composites is higher than the untreated ones. Joseph et al. [20] made similar observations in their TGA analyses of untreated and treated PP–sisal fibre composites. In the same paper they investigated the crystallisation behaviour of PP in the presence of sisal fibre. They concluded that the surfaces of sisal fibre act as nucleating sites for the crystallization of the polymer, promoting the growth and formation of transcrystalline regions around the fibre.

In the past, results have been published on polymer/polymer and polymer/wax blends, as well as on polymer-fibre composites. Both wax and fibre were found to have an influence on the thermal and mechanical properties of the blends and composites. In the present research our aim was to blend both wax and short sisal fibre with LDPE, and to investigate the influence of the presence of wax, cross-linking and fibre content on the thermal properties of LDPE—short sisal fibre composites.

2. Experimental

2.1. Materials

Agave sisalana (Sisal) fibre was obtained from the National Sisal Marketing Committee in Pietermaritzburg, South Africa. It has a diameter range of 100–300 μm, average tensile strength of 490 MPa, average modulus of 11350 MPa, and elongation at break of 5%. The hard, brittle, crystalline, straight hydrocarbon-chain paraffin wax was supplied by Sasol Wax, and has an average molar mass of 785 g mol^{-1}, a melting point of 90 °C, and decomposes at 250 °C. It is white with exceptional opacity and has an *iso*-paraffin content of approximately 10%, is chemically inert, inhibited against oxidation and free of aromatics. LDPE, supplied by Sasol Polymers, has an MFI of 20 g/10 min, melting point of 103 °C, a MW of 96,000 g mol^{-1}, and a density of 0.93 g cm^{-3}. Dicumyl peroxide (DCP) obtained from Sigma, was used as the oxidizing agent.

2.2. Preparation of the composites

The fibre was chopped into small pieces that fit in a CYCLOTEC 1093 sample mill for grinding. Short sisal fibre (1–2 mm in length) was first soaked in petroleum ether at 40 °C for 4–5 h, with regular shaking, and then washed thoroughly with warm distilled water. Finally the fibre was oven dried at 80 °C. Composites were prepared by mechanically mixing LDPE, sisal and the corresponding amount of DCP (2%) and wax (0 and 5%) in a coffee mill at room temperature for about 2 min. The samples were then melt pressed at 180 °C into 100 mm × 80 mm × 0.7 mm sheets by using an AMS 10-ton hot melt press. Table 1 shows the different mass ratios of the components in each of the 20 g samples. Gel content was determined through xylene extraction of the DCP treated samples. For pure LDPE the gel content was 75%, and this value decreased to 60 and 50%, respectively, with increasing sisal content in the samples. The presence of wax did not substantially change these values.

2.3. Methods

Differential scanning calorimetry (DSC) analyses were performed in a Perkin-Elmer DSC7 thermal analyzer in flowing nitrogen atmosphere. The samples, approximately 10 mg each, were heated from 25 to 150 °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 150 °C at the same rate. Thermogravimetric analyses (TGA) were performed in a Perkin-Elmer TGA7 thermal analyser in flowing nitrogen atmosphere. The samples, approximately 10 mg each, were heated from 25 to 650 °C at a rate of 10 °C min^{-1}. For both DSC and TGA three analyses were performed on each sample composition, and the average temperature and enthalpy values were calculated. Since the correlation between the repeat results was very good, the standard deviations were very small.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC)

The DSC curves are shown in Figs. 1–7.The onset and peak temperatures of melting, as well as the experimental and theoretically expected melting enthalpies, are summarised in Table 2. The DSC heating curves of uncross-linked composites in Fig. 1 show endothermic peaks at about 100 °C. There is a slight increase in onset temperature of melting, and the melting enthalpy (relative to LDPE content) decreases, with increasing sisal content. The slight increase in onset temperature of melting may hint at some transcrystallisation [20], but in our case there is a definite decrease in total LDPE

Table 1
List of the samples used in the present study

LDPE/wax/sisal/DCP (w/w)	LDPE/wax/sisal/DCP (w/w)
100/0/0/0	100/0/0/2
80/0/20/0	80/0/20/2
60/0/40/0	60/0/40/2
95/5/0/0	95/5/0/2
75/5/20/0	75/5/20/2
55/5/40/0	55/5/40/2

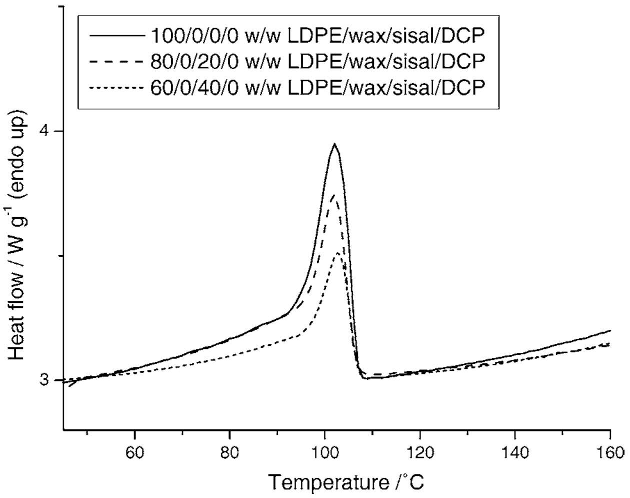

Fig. 1. DSC heating curves of uncross-linked LDPE–sisal composites and pure PE.

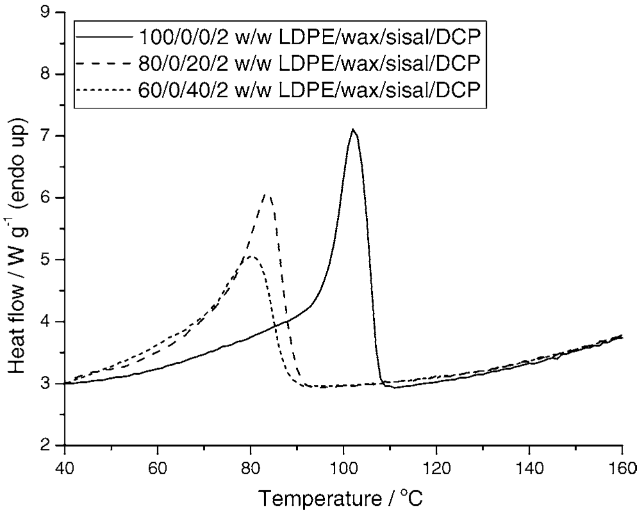

Fig. 2. DSC heating curves of LDPE–sisal composites cross-linked in the presence of 2% DCP.

crystallinity, which indicates that sisal fibre definitely does not act as a nucleating agent in the system that we investigated.

Cross-linking causes a drastic decrease (approximately 20 °C) in the melting temperature of LDPE in the presence of sisal (Fig. 2, Table 2), but virtually no change in the absence of sisal. Previous work by Joseph et al. [3] and ourselves [17] strongly indicated that, in the presence of organic peroxides, there is grafting between sisal and LDPE chains. This grafting restricts chain folding, which results in only epitaxial crystallization of LDPE chains on the surfaces of the sisal fibres. This causes the formation of relatively thin lamellae, with the resultant decrease in melting temperature. This would also explain the strong decrease in melting enthalpy values (relative to LDPE content), because the total LDPE crystallinity decreases as a result of the grafting to sisal fibre.

The presence of wax in the absence of DCP (Fig. 3, Table 2) causes a slight increase in peak temperatures of melting. This is probably due to the result of co-crystallization of LDPE and wax, favoured by shorter wax chains, which can easily be incorporated in the LDPE lamellae. The melting enthalpy values (relative to LDPE content) are also slightly higher than those of the non wax-containing samples, indicating a slight increase in sample crystallinity. Kim et al. [19] found similar behaviour during their investigation of EVA–wax blends.

Crosslinking of the LDPE–sisal fibre composites in the presence of wax gives rise to very interesting behaviour (Fig. 4, Table 2). In the absence of sisal fibre the sample melts at a slightly higher temperature, and the melting enthalpy is slightly higher, compared to the non wax-containing sample. The wax that we used is highly crystalline, and it does not crosslink at such low wax and DCP contents [21]. The short wax chains therefore probably co-crystallise with the uncrosslinked LDPE chains, giving rise to thicker lamellae and higher crystallinity. In the presence of sisal fibre there is a small decrease in melting temperature compared to the non-sisal fibre containing sample, but this decrease is much smaller than the decrease observed for crosslinked LDPE–sisal fibres in the absence of wax. This

Table 2
Summary of DSC data for cross-linked and uncross-linked LDPE/wax–sisal fibre composites

PE/wax/ sisal/DCP (w/w)	$T_{o,m}$ (°C)	$T_{p,m} = T_m$ (°C)	ΔH_m (J g^{-1}) (Experimental)	ΔH_m (J g^{-1}) (Relative to LDPE content)
100/0/0/0	95.5	102.2	48.7	48.7
80/0/20/0	95.9	102.1	34.4	43.0
60/0/40/0	96.6	102.1	20.5	34.2
100/0/0/2	96.7	102.8	25.8	25.8
80/0/20/2	74.9	83.7	23.5	29.4
60/0/40/2	71.8	81.4	10.3	17.2
95/5/0/0	96.3	102.7	51.3	54.0
75/5/20/0	94.8	102.7	32.4	43.2
55/5/40/0	97.5	103.2	19.5	35.5
95/5/0/2	95.5	104.7	30.7	32.3
75/5/20/2	89.6	98.4	29.4	39.2
55/5/40/2	88.5	98.7	19.5	35.5

$T_{o,m}$: onset temperature of melting; T_m: melting temperature; ΔH_m: specific enthalpy of melting.

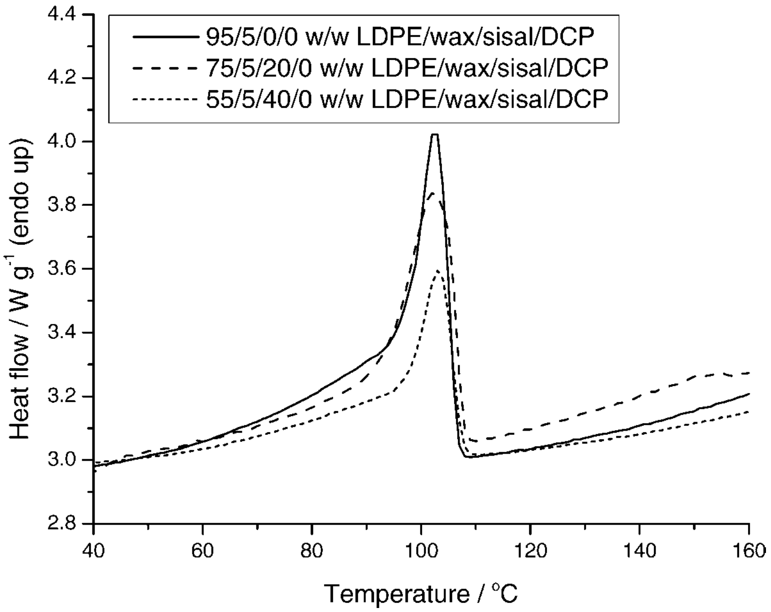

Fig. 3. DSC heating curves of uncross-linked LDPE–wax–sisal composites.

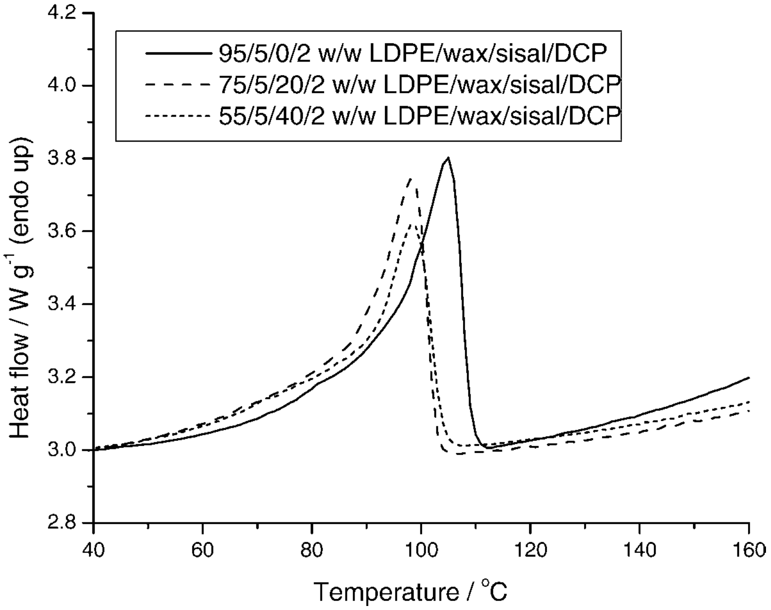

Fig. 4. DSC heating curves of LDPE–wax–sisal composites cross-linked in the presence of 2% DCP.

can be explained if the preparation procedure of the samples is taken into account. In this investigation the different components of the composite were thoroughly mechanically mixed, after which the powdery mixture was compression molded in a hot-melt press. Since the wax melts at a lower temperature than the LDPE, it will melt first and cover (at least part of) the surface of the sisal fibre. This will restrict LDPE–sisal grafting and minimize epitaxial crystallization, resulting in LDPE forming thicker lamellae than in the case of the non wax-containing samples. The enthalpies (and therefore crystallinities) are higher than those of the crosslinked non wax-containing samples, but lower than those of the uncrosslinked wax-containing samples.

The influence of wax addition and peroxide treatment on the thermal properties of LDPE–sisal fibre composites is neatly illustrated in Figs. 5–7. Fig. 5 clearly shows that the presence of wax gives rise to thicker lamellae and higher crystallinities, while crosslinking reduces the sample crystallinity. Figs. 6 and 7 clearly show increased crystallinity of

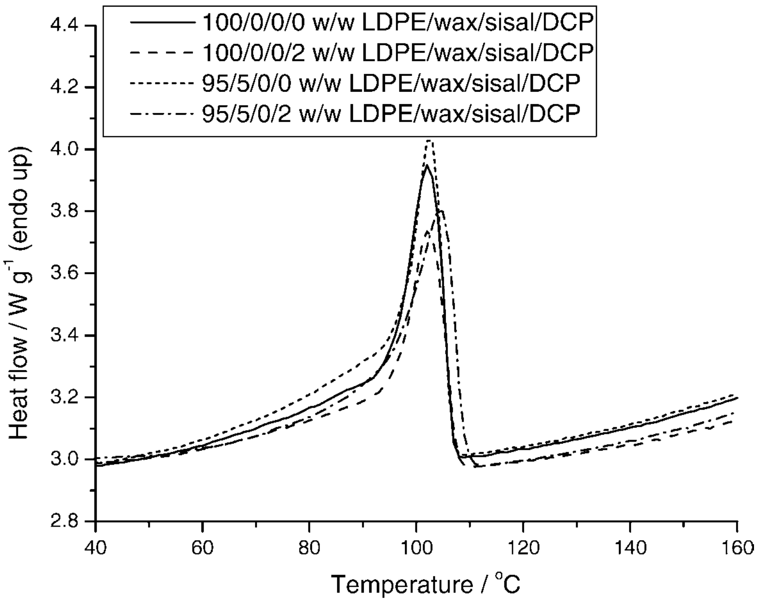

Fig. 5. DSC heating curves of cross-linked and uncross-linked LDPE composites in the absence of sisal.

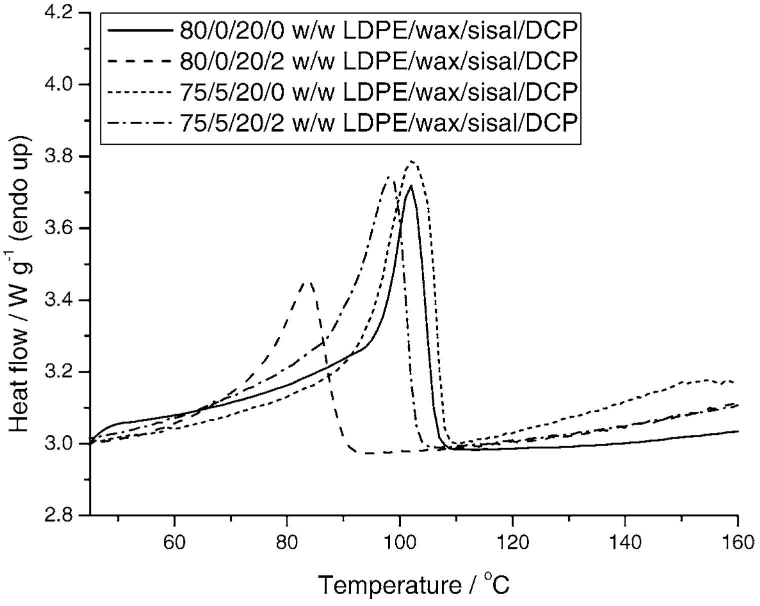

Fig. 6. DSC heating curves of cross-linked and uncross-linked LDPE–wax–sisal composites (20% sisal).

the uncrosslinked samples in the presence of wax, and substantially decreased crystallinity and lamellar thickness of the crosslinked samples in the absence of wax. In the presence of wax, the same crosslinked samples have much higher crystallinity and thicker lamellae.

3.2. Thermogravimetric analysis (TGA)

Fig. 8 shows that LDPE starts decomposing at about 450 °C, while the composites clearly show a two-step decomposition process. The decomposition of sisal fibre starts at about 360 °C, which is in line with the observations by Manikandan Nair et al. [22] and Joseph et al. [20]. In our samples, however, the percentage of adsorbed water in the composites was very low. The presence of sisal fibre and/or wax seems to destabilise the LDPE matrix. This is in line with previous work done in our group [15], but it differs from the observation by Joseph et al. [20] that PP–sisal fibre composites are more thermally stable than PP or sisal fibre alone. From the figure it is also clear that

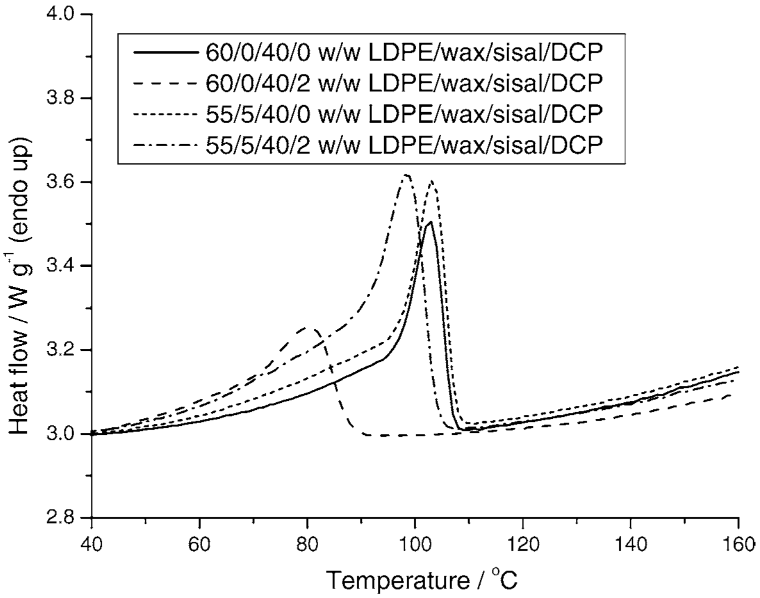

Fig. 7. DSC heating curves of cross-linked and uncross-linked LDPE–wax–sisal composites (40% sisal).

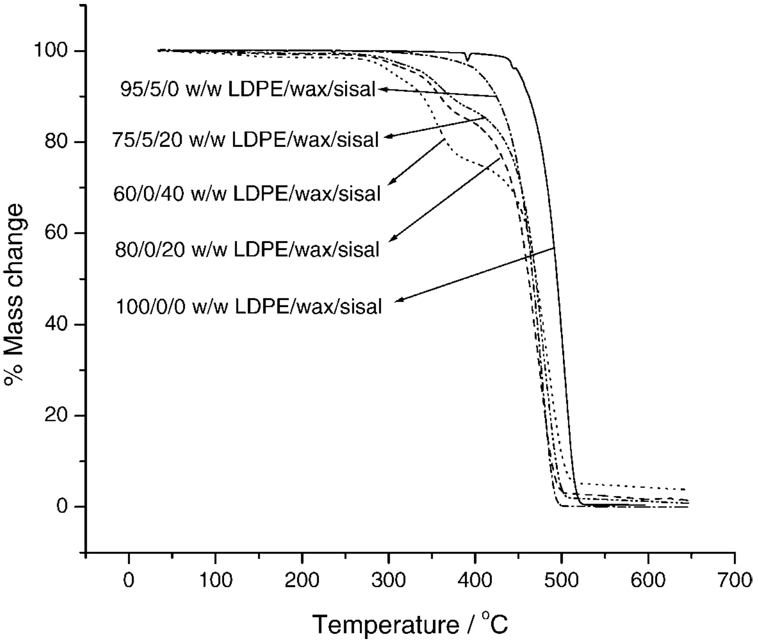

Fig. 8. TGA curves of uncross-linked LDPE/wax–sisal fibre composites.

not all the sisal fibre decomposes before the LDPE. About 40% of the initially added sisal fibre decomposes with the LDPE between 430 and 500 °C. The presence of wax also seems to retard the decomposition of both sisal fibre and LDPE.

In the absence of sisal fibre, crosslinked LDPE and LDPE/wax show similar decomposition behaviour (Fig. 9). However, the presence of wax substantially changes the decomposition pattern of LDPE–sisal composites. For both the 20% and 40% sisal-containing composites, the presence of wax results in the decomposition of almost all the sisal before the LDPE matrix starts decomposing, while in the absence of wax, some of the sisal decomposes in the same temperature range as the LDPE matrix. This is in line with our previous explanation that the wax covers the sisal fibre and changes the crosslinking mechanism from LDPE–sisal grafting to LDPE crosslinking, which results in reduced interaction between LDPE and sisal.

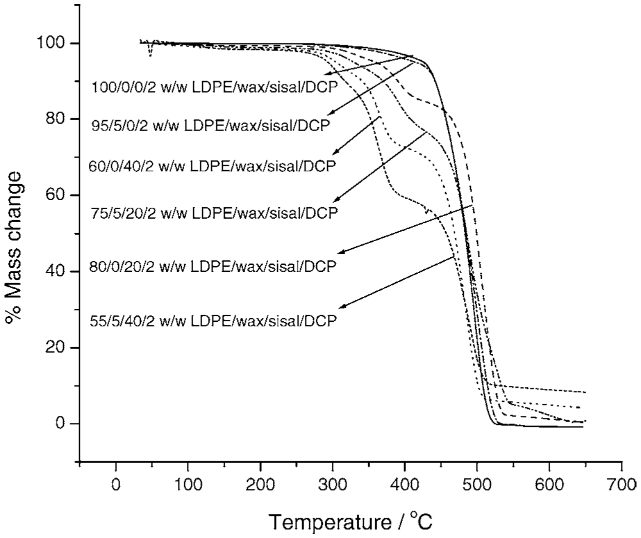

Fig. 9. TGA curves of cross-linked LDPE/wax–sisal fibre composites.

4. Conclusions

The influence of sisal content, peroxide cross-linking, and wax addition on the thermal properties of LDPE–sisal fibre composites was investigated. It was found that the presence of wax increases the crystallinity of the LDPE matrix, while the presence of sisal fibre decreases the crystallinity, as measured through the melting enthalpy with respect to LDPE content. Peroxide treatment reduces the crystallinity of pure LDPE, but has no influence on its melting temperature. In the presence of sisal, however, the melting temperature of peroxide treated samples decreases substantially, and this decrease becomes more pronounced with increasing sisal content. The presence of wax, however, reduces the extent to which the melting temperature decreases. These observations are probably the result of LDPE–sisal grafting and epitaxial crystallization, which are inhibited in the presence of wax as a result of wax covering the sisal fibre surface.

The presence of both wax and sisal fibre seem to reduce the thermal stability of LDPE in the absence of crosslinking. The TGA results of the crosslinked samples seem to support the explanation given for the DSC results of the same systems.

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References

[1] A.K. Bledzki, J. Gassan, Prog. Polym. Sci. 24 (1999) 221.
[2] Y. Li, Y.-W. Mai, L. Ye, Comp. Sci. Tech. 60 (2000) 2037.
[3] K. Joseph, S. Thomas, C. Pavitthran, Polymer 37 (1996) 5139.
[4] K. Joseph, S. Thomas, C. Pavitthran, M. Brahmakumar, J. Appl. Polym. Sci. 47 (1993) 1731.
[5] S. Varghese, B. Kuriakose, S. Thomas, J. Appl. Polym. Sci. 53 (1994) 1051.
[6] K. Joseph, S. Thomas, C. Pavitthran, Comp. Sci. Tech. 53 (1995) 99.
[7] C. Albano, J. Gonzalez, M. Ichazo, D. Kaiser, Polym. Deg. Stab. 66 (1999) 179.
[8] J.M. Felix, P. Gatenholm, J. Appl. Polym. Sci. 50 (1993) 699.
[9] A. Amash, P. Zugenmaier, Polym. Bull. 40 (1998) 251.
[10] K. Van de Veldeand, P. Kiekens, Polym. Test. 20 (2001) 885.
[11] G.C. Stael, M.I.B. Tavares, J.R.M. d'Almeida, Polym. Test. 20 (2001) 869.
[12] G. Kalaprasad, P. Pradeep, G. Mathew, C. Pavithran, S. Thomas, Comp. Sci. Tech. 60 (2000) 2967.
[13] R. Prasantha Kumar, K.C. Manikandan Nair, S. Thomas, S.C. Schit, K. Ramamurthy, Comp. Sci. Tech. 60 (2000) 1737.
[14] H.P.S.A. Khalil, H. Ismail, H.D. Rozman, M.N. Ahmad, Eur. Polym. J. 37 (2001) 1037.
[15] T.N. Mtshali, I. Krupa, A.S. Luyt, Thermochim. Acta 380 (2001) 47.
[16] V. Djokovic, T.N. Mtshali, A.S. Luyt, Polym. Int. 52 (2003) 999.
[17] M.A. Mokoena, V. Djokovic, A.S. Luyt, J. Mater. Sci. 39 (10) (2004) 3403.
[18] J.K. Kim, B.-K. Kim, J. Polym. Sci., Part B: Polym. Phys. 37 (1999) 1991.
[19] J.K. Kim, B.-K. Kim, M. Park, J. Polym. Sci., Part B: Polym. Phys. 38 (2000) 707.
[20] P.V. Joseph, K. Joseph, S. Thomas, C.K.S. Pillai, V.S. Prasad, G. Groenenckx, M. Sarkissova, Composites Part A 34 (2003) 253.
[21] I. Krupa, A.S. Luyt, Polym. Degr. Stab. 70 (2000) 111.
[22] K.C. Manikandan Nair, S. Thomas, G. Groeninckx, Comp. Sci. Tech. 61 (2001) 2519.