A differential scanning calorimetric characterization of the sorption and desorption of water in cellulose/linear low-density polyethylene composites

Y. H. Zang and S. Sapieha*

Pulp and Paper Research Institute of Canada, and Chemical Engineering Department, Ecole Polytechnique de Montréal, PO Box 6079, Station 'A', Montréal, Québec, H3C 3A7, Canada

Thermal properties of composites based on natural cellulose fibre and linear low-density polyethylene have been investigated using differential scanning calorimetry (d.s.c.). The observed endothermic peak consists of two main components corresponding to polymer fusion and the dehydration of cellulose. It has been shown that the composition, degree of crystallinity and water content of the composite can be easily determined from the d.s.c. thermograms. A simple method to distinguish between the energy of dehydration and the enthalpy of fusion of the composites is proposed.

INTRODUCTION

Cellulose added to thermoplastics affects many of their physical properties[1]. For example, the presence of microcrystalline cellulose fibres shifts the glass transition temperature[2] and may cause transcrystallization in crystalline polymers[3]. Also, due to the hydrophilic nature of cellulose fibres, the water sorption properties of the resulting composites are increased[4-6].

Differential scanning calorimetry (d.s.c.) is often used to determine polymer crystallinity, thermal degradation behaviour, and the glass transition temperature[7-9], blend miscibility[10] and composition[11], and free and bound water content in hydrophilic systems[4,12]. Studies of cellulose/polymer composites using d.s.c. have been reported recently by several groups[13-15]. Pure cellulose showed an endotherm due to dehydration (or desorption of water) in the temperature range from 80 to 160°C[5,16,17]. This temperature range overlaps with the melting temperature of many commodity thermoplastics. Therefore, in the polymer composites containing hydrophilic fibre, both the crystallinity of the polymer matrix and the water absorbed by the fibre may contribute to the apparent enthalpy of fusion.

The present paper reports on the application of d.s.c. to characterize the sorption and desorption properties of cellulose-containing composites. A simple method to distinguish between the energy of dehydration of cellulose and the enthalpy of fusion of the polymer matrix has been proposed.

EXPERIMENTAL

A linear low-density polyethylene (LLDPE; Escorene LL-3010, ESSO Canada) having a density of 0.918

g cm^{-3} and a melt index of 0.8 was used as polymer matrix. The cellulose fibre was a highly bleached hardwood pulp fibre from Sigma Co. Composites containing 0–50% of cellulose fibre by weight were prepared by blending the components in a Brabender Plasticorder at 160°C. Processing time was 12 min. The composites were then press-moulded at 160°C and quickly quenched in cold water to room temperature. Detailed processing conditions are described elsewhere[18,19].

The samples, typically 10 mg, were conditioned either at constant relative humidity (RH) or by immersion in distilled water for different times. The water content, β, in the composites was determined by weighing the sample before and after the first d.s.c. scan using a Mettler Analysis Balance, AE 240, with an accuracy of ± 0.01 mg. External surface water was removed from the sample by blotting with filter paper. The water content was calculated from the following equation:

$$\beta = [(M_{s1} - M_{s2})/M_{s1}] \times 100 \qquad (1)$$

where M_{s1} and M_{s2} are the mass before and after the first d.s.c. scan respectively.

D.s.c. measurements were performed using a DuPont 9900 instrument, calibrated with a high-purity indium sample. The temperature range was from 30 to 220°C, at a heating rate of 10°C min^{-1}. After reaching 220°C, the sample was cooled to room temperature in the d.s.c. instrument (a procedure lasting about 10 min), immediately after which a second scan was performed. The melting temperature of the LLDPE was determined from the peak of the melting endotherm T_{pm} and from the extrapolated onset temperature T_{om}. The apparent enthalpy of fusion ΔH_a was calculated from the area of the melting endotherm between 50°C and 210°C using DuPont software. The apparent enthalpy of fusion

obtained from the third and subsequent scans was within 5% and the melting temperature was within 1°C of that obtained from the second scan. Therefore only the first and second scans are discussed in the present work.

RESULTS AND DISCUSSION

Figure 1 shows typical d.s.c. thermograms obtained during the first (a) and second (b) scans for composites following immersion in water. The broad fusion range observed in the d.s.c. thermograms indicates a wide distribution of crystallite sizes of the LLDPE[11,20]. For the LLDPE containing high concentrations of cellulose or following immersion in water, a shoulder at temperatures above the melting peak ($T_{pm} = 124$°C) was observed during the first scan (*Figure 1a*). This shoulder is believed to be due to the desorption energy of water from cellulose[5,13,14].

Table 1 summarizes the melting temperatures T_{om2}, T_{pm2} and apparent enthalpy of fusion ΔH_{a2} obtained from the second scan as well as the difference with respect to the first scan $T_{om1} - T_{om2}$, $T_{pm1} - T_{pm2}$ and $\Delta H_{a1} - \Delta H_{a2}$. The experimental enthalpy of fusion of pure LLDPE, 111 J g^{-1} is in fair agreement with that of 122 J g^{-1} reported for a similar LLDPE[11]. No effect due to water on the apparent enthalpy of fusion was observed in the case of pure LLDPE.

It is seen in *Table 1* that T_{pm} and T_{om} are virtually unaffected by the presence of cellulose. However, an increase in T_{om} and a decrease in T_{pm} has been observed from the first to the second scans for all samples analysed. The narrowing of the fusion peak indicates that crystallites with a narrower size distribution are formed during the slower cooling in the d.s.c. apparatus than those formed during the initial press-moulding and rapid quenching.

An increase in apparent enthalpy of fusion ΔH_a between the first and second scans for pure LLDPE has been observed. This can be attributed to the increased degree of crystallinity in the second scan, which results from slower cooling in the d.s.c. instrument. A similar effect was observed for LLDPE/cellulose composites containing less than 15% cellulose. However, for higher cellulose contents a decrease in ΔH_a has been found. Samples conditioned in similar environments show a water content that is proportional to the cellulose content[6].

This suggests that the apparent enthalpy ΔH_{a1} of the

first scan represents a sum of the enthalpy of fusion $\Delta H_{m1}(\alpha)$, and the energy of dehydration $\Delta H_{d1}(\beta)$, required to desorb water from the cellulose and composite:

$$\Delta H_{a1} = \Delta H_{m1}(\alpha) + \Delta H_{d1}(\beta) \qquad (2)$$

where α is the degree of crystallinity and β is the water content in the composite.

Thus two competing phenomena contribute to the change in apparent enthalpy of fusion in going from the first to the second scan: (a) an increase in the degree of crystallization and (b) a decrease in the water content.
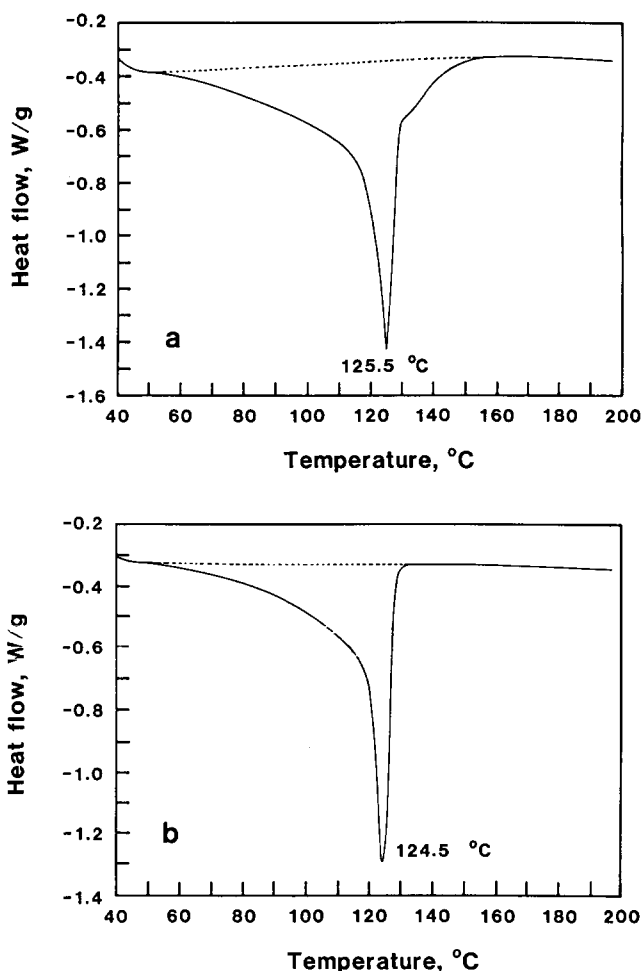

Figure 1 D.s.c. thermograms of composite containing 29% cellulose fibres following immersion in water for 5 h: (a) first scan, (b) second scan

Table 1 Melting temperatures T_{om}, T_{pm} and apparent enthalpy of fusion ΔH_a of cellulose/LLDPE composites conditioned at constant RH^a

PE (wt%)	T_{om2} (°C)	T_{pm2} (°C)	ΔH_{a2} (J g^{-1})	$T_{om1} - T_{om2}$ (°C)	$T_{pm1} - T_{pm2}$ (°C)	$\Delta H_{a1} - \Delta H_{a2}$ (J g^{-1})	ΔH_{d1} (J g^{-1})
100	120.0	124.9	111.0	−2.6	0.2	−10.7	0.0
95.2	119.6	124.3	109.0	−2.6	0.3	−7.4	2.8
87.0	119.5	124.3	96.6	−2.8	0.2	−0.2	9.1
83.3	119.5	124.1	89.8	−2.4	0.6	3.2	12.1
76.9	119.5	124.2	84.6	−1.9	1.0	10.8	19.0
71.4	118.5	124.1	78.8	−1.6	1.0	11.0	18.6
66.7	119.3	123.9	76.7	−2.7	0.4	9.9	17.0
62.5	119.5	124.3	73.6	−3.2	0.6	16.4	23.1
55.6	119.3	124.3	63.2	−2.8	0.4		
50.0	118.6	124.3	60.2	−3.4	0.6		

^{a}Subscripts 1 and 2 refer to the first and second scans, respectively

Table 2 Melting temperatures and apparent enthalpy of fusion of cellulose/LLDPE composites following immersion in water for 2 days

PE (wt%)	T_{om2} (°C)	T_{pm2} (°C)	ΔH_{a2} (J g^{-1})	$T_{om1} - T_{om2}$ (°C)	$T_{pm1} - T_{pm2}$ (°C)	$\Delta H_{a1} - \Delta H_{a2}$ (J g^{-1})	ΔH_{d1} (J g^{-1})
100	120.0	124.5	111.5	−2.6	0.2	−11.0	(0.3)
87.0	119.3	124.3	100.7	−3.8	0.4	24.0	33.3
83.3	119.2	123.5	96.6	−2.7	0.4	23.4	32.3
76.9	119.5	123.8	83.8	−3.6	0.2	48.1	56.3
71.4	119.2	123.7	79.5	−4.0	0.5	62.9	70.5

At low cellulose content, the effect of the crystallinity change is predominant, and consequently the apparent enthalpy of fusion increases in the second scan. With increasing cellulose content the effect of the water desorption process becomes dominant. As a result the apparent enthalpy of fusion decreases in the second scan, since the water was already removed during the first scan.

Table 2 shows the fusion temperature and apparent enthalpy for composites following a two-day immersion in water. It is seen that the apparent enthalpy of fusion ΔH_{a2} of the second scan is virtually identical for composites conditioned either at constant humidity or those following immersion in water. Moreover, comparison of *Tables 1* and *2* shows that the apparent enthalpy ΔH_{a1} of the first scan is significantly higher for the composites immersed in water than that for materials conditioned at constant *RH*. Since the crystallinity of the LLDPE is not affected by the sorbed water, the increase in ΔH_{a1} may be totally attributed to the increased energy of dehydration ΔH_{d1} due to a higher water content in composites following immersion in water.

Since the apparent enthalpy of fusion determined from the second and subsequent scans is almost identical, one can assume that the moisture was completely removed from the composite during the first scan[5,16]. Therefore, the energy of dehydration ΔH_{d2} during the second scan is near to or equal zero, and ΔH_{a2} corresponds to the heat of fusion ΔH_{m2} of the LLDPE matrix.

Figure 2 shows that the apparent enthalpy of fusion ΔH_{a2} is directly proportional to the LLDPE content, thus demonstrating that ΔH_{a2} corresponds to the heat of fusion of the polymer matrix ΔH_{m2}. In this work we cannot distinguish between transcrystallization and bulk crystallization. However, the linear relationship between ΔH_{a2} and LLDPE content indicates that cellulose fibres have little effect on the overall crystallinity of the LLDPE.

Assuming that the increase in the enthalpy of fusion of the polymer matrix between the first and second scans (due to the increased degree of crystallinity) is proportional to the polyethylene content, the energy of dehydration ΔH_{d1} can be represented by the following relation:

$$\Delta H_{d1} = C(\alpha_i, \alpha_j) \times \text{PE}(\%) + [\Delta H_{a1}(\alpha_i, \beta) - \Delta H_{a2}(\alpha_j, 0)] \tag{3}$$

where $C(\alpha_i, \alpha_j)$ is the change in enthalpy of fusion of the polymer matrix. It is equal to 10.7 J g^{-1} under the experimental conditions used in the present work. α_i and α_j are the degrees of crystallinity. PE(%) is the weight fraction of polyethylene.

Values of the energy of dehydration ΔH_{d1} calculated using equation (2) are given in *Tables 1* and *2* for composites conditioned at constant *RH* and following immersion in water, respectively. It can be seen that ΔH_{d1} increases linearly with the weight fraction of cellulose
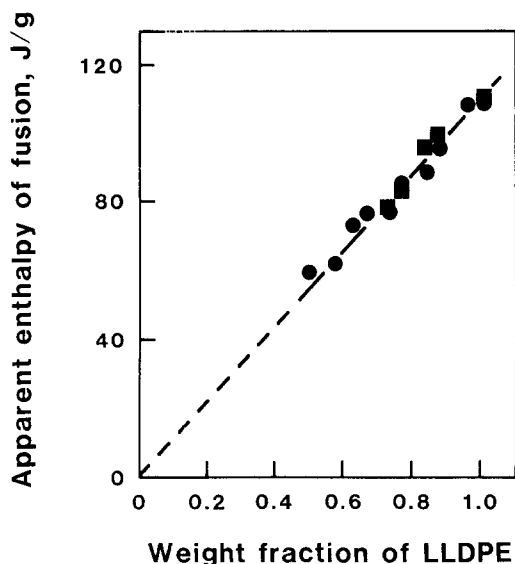
Figure 2 Apparent enthalpy of fusion ΔH_{a2} versus weight fraction of LLDPE; (●) samples conditioned at constant humidity; (■) samples following immersion in water
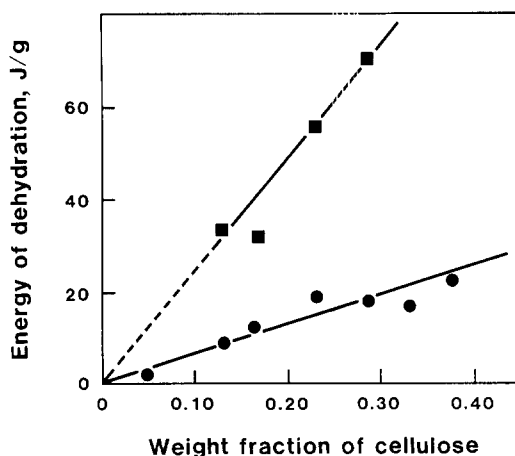
Figure 3 Energy of dehydration ΔH_{d1} as a function of weight fraction of cellulose: (●) samples conditioned at constant humidity for several months; (■) samples following immersion in water for two days

(*Figure 3*). In addition, for any given cellulose content, ΔH_{d1} is higher for samples following immersion in water.

Figure 4 shows the energy of dehydration ΔH_{d1} as a function of water content for composites with different cellulose concentrations. The linear relationship indicates that, in the range of water content between 3.5 and 12% per unit mass of cellulose, the energy of dehydration ΔH_{d1} depends only on β (water content) and is not dependent on cellulose concentration. The slope, equal to 2004 J g^{-1}, represents the energy required to remove
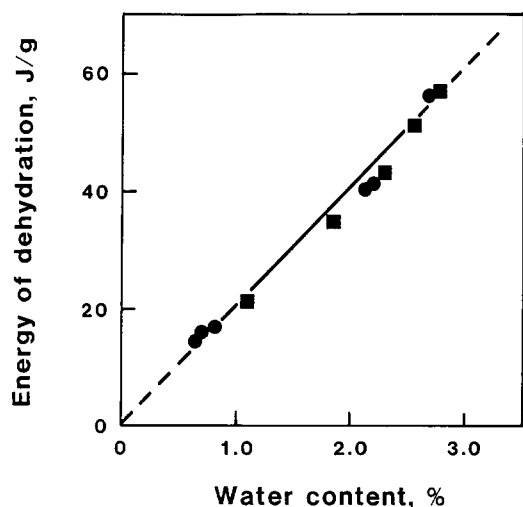
Figure 4 Energy of dehydration ΔH_{d1} as a function of water content β for composites: (●) 23% cellulose; (■) 29% cellulose

from the composite a unit mass of water. Considering the large number of possible phenomena involved, this value is acceptably close to the evaporation heat of water, 2263 J g^{-1}, under normal conditions. A similar value of the energy of dehydration, 2329 J g^{-1}, is obtained from analyses of Silva's results[16] on water desorption from pure cellulose. This may indicate that only the free water is removed from the cellulose during the d.s.c. scan. This may be a somewhat surprising result as one would expect the energy of dehydration to be higher than the energy of evaporation of pure water, since the bonds between cellulose and water must be broken. Moreover, some additional energy is needed for the transport of desorbed water through molten polymers. However, as our results indicate, the diffusion energy of water vapour through molten polyethylene is negligibly small in comparison to the heat of evaporation. Further investigation on the energetics of water desorption and its transport in thermoplastics using a cellulose fibre as a source of water is currently under way in our laboratory.

CONCLUSIONS

The thermal and water sorption and desorption properties of cellulose-containing thermoplastics have been examined using the d.s.c. method. The observed endo-

thermic peak consists of two main components corresponding to the polymer fusion and dehydration of cellulose. It has been shown that the composition, degree of crystallinity and water content of the composite can be easily determined from the d.s.c. thermograms. The apparent energy of dehydration is close to the heat of evaporation of water, suggesting that only free water is being removed from the composite and that the diffusion energy of the water vapour through molten polyethylene is negligibly small.

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