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THERMAL ANALYSIS OF AGED HDPE BASED COMPOSITES

J. J. Suñol[*] *and J. Saurina*

Department of Physics, EPS (P II), Universitat de Girona, 17071 Girona, Spain

Abstract

HDPE based composites were produced with 10–20–30 and 40% composite mass of wood fiber. The coupling agents were epolene and silane. The thermal behavior of composite samples was analyzed as a function of the coupling agent content, the exposure time and the wood fibers content by means of differential scanning calorimetry.

Calorimetric curves of all samples of first and second heating shows a similar behavior. Some significant relation has been observed between the exposure time and the degree of crystallinity for the same percentage of fiber samples. A linear relation between the melting enthalpy average *vs.* content in cellulosic fibers is detected. Nevertheless, the fibers non-pretreated with coupling agent show a lower loss of crystallinity of the HDPE matrix at low wood fiber content (10%). A slight diminution of the melting peak temperature is detected as increasing the exposure time.

Keywords: aging, DSC, HDPE based composites

Introduction

Thermoplastic matrices reinforced with cellulosic fibers have originated a new concept of composites, with a growing interest in the research and industrial fields [1–3]. The microstructure and thermal behavior change caused by different types of degradation in polymeric materials is one of the most studied topics on the last decades [4–7]. Moreover, degradation phenomena of aging in environmental exposed polymeric materials have aroused great interest because the aging influences the service life of the polymer. Consequently, several research tasks were carried out whose main objective was predicting the durability of these materials [8, 9]. A great number of HDPE based composites systems can be found in bibliography [10–12].

In this work, the thermal behavior of HDPE based composites was analyzed as a function of the coupling agent, the exposure time and the wood fibers content.

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[*] Author for correspondence: E-mail: joanjosep.sunyol@udg.es

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Experimental

Materials and methods

The high-density polyethylene polymer, HDPE 2909 from DuPont Canada, with the following technical characteristics has been used: fluidity index=1.35 g min^{-1} and density 0.96 g cm^{-3}. Cellulosic fibers were short fibers of aspen (*Populus tremula*), the length/diameter ratio of which is L/D=8.7 and were used to produce composites. The wood fiber content (mass%) was 10–20–30 and 40%. The coupling agents with different organ-functional groups were: maleated ethylene (Epolene C-18, Eastman Kodak) and –methacryloxypropytrimethoxy silane (Silane A-174, Union Carbide).

The wood fibers were pretreated with a coupling agent in a roll mill (Brabender number 065) before compounding them with the polymer [2, 3]. The procedure to carry out the pretreatment and the mixing process was described in previous works. Samples in the form of dog-bones were exposed to drastic environmental conditions, as described in [13], during different periods of time: 15, 30, 60 and 90 days before to perform the thermal analysis.

Differential scanning calorimetry (DSC) has been used to determine the thermal changes of HDPE induced by the environmental exposure of samples, the wood fiber content and the thermal treatment. A DSC 30 Mettler instrument with liquid nitrogen was used to obtain the DSC curves. The sample mass was between 2.0 and 3.0 mg, small enough to prevent problems caused by heat and material transfer. The heating/cooling rate was 10 K min^{-1} and the temperature range was between 50 and 200°C. Calibration of temperatures and energies was made with a standard of In, Pb and Zn under the very same conditions used in the sample analysis. Several experiments were performed to obtain average values of temperature and enthalpy.

Moreover, the microstructure of samples was characterized by scanning electron microscopy (SEM) in a Zeiss DSM 960 A apparatus. Resolution was 3.5 nm, acceleration voltage was 15 kV, and working distance was between 10 and 20 mm. Samples had been sputtered previously with a K 550 Emitech equipment.

Results and discussion

Calorimetric curves of all the samples show a similar behavior. As an example, Fig. 1 corresponds to a HDPE composite in heating/cooling scans. The second heating was performed to analyze the stability of the crystalline behavior. In all cases, the second melt enthalpy and temperatures has been found to be similar to the first one. Average melting enthalpies are given in Table 1.

The non-existence of any significant relation between the environmental aged exposure time and the loss of crystallinity for the same percentage of fibers has been observed. Similar results were found in HDPE composites under environmental exposure [14]. Values given in Table 1 show enthalpy averages taking account all exposure time data. In general, there was not a directly relationship between the crystallinity loss and the exposure time. This phenomenon has been attributed to the

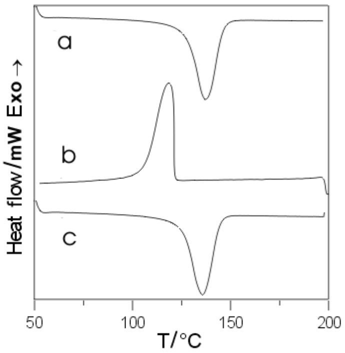

Fig. 1 DSC scans of a HDPE composite a – first heating, b – cooling, c – second heating

following: the cellulosic fibers can regulate (as a function of the exposure conditions) the transfer of water molecules from inside the fibers to the composite interface, this being independent of the exposure time.

Table 1 Melting enthalpy averages

	Wood fiber/%	HDPE + wood fibers/J g^{-1}	HDPE + wood fibers + epolene/J g^{-1}	HDPE + wood fibers + silane/J g^{-1}
First melt	10	182.5±3.7	169.8±2.3	172.9±2.8
	20	153.8±1.9	148.4±1.9	158.6±1.5
	30	132.0±5.2	136.0±2.5	132.8±2.2
	40	112.7±1.7	113.4±3.9	115.8±2.6
Second melt	10	180.9±1.5	168.5±4.8	174.7±1.8
	20	146.8±2.6	151.6±1.5	153.8±1.1
	30	128.1±4.5	134.6±1.2	132.3±1.5
	40	109.2±2.7	107.7±1.6	110.6±3.4

Figure 2 shows the DSC scans (first melt) of HDPE before exposure without and with coupling agents. Apparently no significant changes were detected in the as pre-

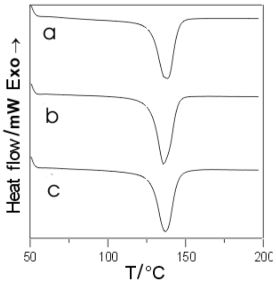

Fig. 2 DSC scans (first melt), a – HDPE, b – HDPE + epolene, c – HDPE + silane

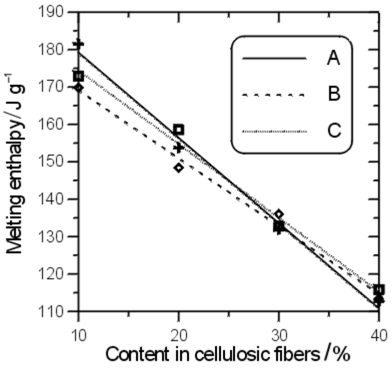

Fig. 3 Linear regression. Melting enthalpy average *vs.* wood fibers content. A – without coupling aggent, B – with epolene, C – with silane

pared samples, a detailed analysis is necessary to detect small differences. From values Table 1 we can state in that the loss of crystallinity of the HDPE matrix is directly related to the percentage of cellulosic fibers (as shown in Fig. 3). This figure shows the apparent linear relation between the average melting enthalpy and the content in cellulosic fibers. The linear fit values are given in Table 2. The R^2 coefficient values are close to 1. Moreover, the loss of crystallinity of the HDPE matrix at low wood fiber content (10%), was directly less significant when cellulosic fibers were non-pretreated with coupling agents. The values become similar to 20–30–40 wood fiber content. This means that the coupling agent was not an effective protector against environmental aging at low fiber content. Perhaps an inhomogeneous distribution of the fibers contributes to this behavior. Similar results were found in other wood-HDPE composite environmental degradation [15].

Table 2 Linear regression (first melt)

Sample	Linear regression: $y=Ax+B$		
	A	B	R^2
HDPE + wood fibers	–2.282	202.05	0.993052
HDPE + wood fibers + epolene	–1.816	187.3	0.988732
HDPE + wood fibers + silane	–1.971	194.3	0.988586

Table 3 shows the peak temperature average values at all exposure time. As increasing the exposure time, a slight diminution of the peak temperature is detected. The decrease on peak temperature can be related with a low thermal stability of the samples when subjected to environmental exposure. Nevertheless, no melting enthalpy changes were detected. Crystalline content is not affected by exposure, but several crystalline parts become smaller, because the higher the polymer molecular mass, the higher the melting temperature.

Table 3 Peak temperature averages

	Exposure time/days	HDPE + wood fibers/°C	HDPE + wood fibers + epolene/°C	HDPE + wood fibers + silane/°C
First melt	15	139.8±0.5	140.5±0.6	139.6±0.8
	30	139.1±0.8	138.9±0.8	139.5±0.6
	60	138.4±0.5	137.0±0.7	138.6±0.9
	90	135.6±0.7	135.4±0.8	136.5±0.5
Second melt	15	139.4±0.5	138.5±0.5	138.5±0.8
	30	138.4±0.4	137.5±0.9	137.0±0.7
	60	137.1±0.6	136.2±0.6	135.6±0.2
	90	135.0±0.7	134.4±0.6	134.6±0.4

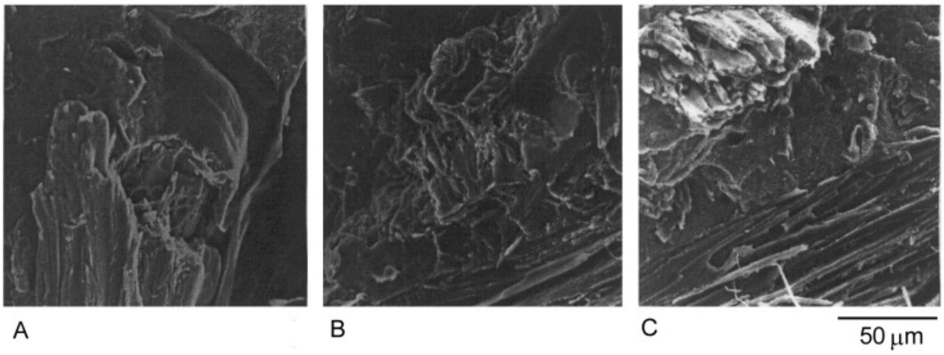

Fig. 4 SEM micrographs, A – HDPE, B – HDPE + epolene, C – HDPE + silane

Morphology information about samples after mechanically induced break is given by SEM micrographs. Figure 4 shows the fracture zone of several samples. All micrographs are similar. Further studies on mechanical properties and structure analysis can help us to understand better the thermal differences between the composite samples. As an example, the presence of the coupling agent largely contributes to the adhesion between the matrix and the reinforcement, with the modification of properties, i.e. a greater increase in the interfacial adhesion promotes higher tensile properties [15].

Conclusions

It has been demonstrated from the calorimetric results that the loss of crystallinity of the HDPE matrix is directly related to the percentage of cellulosic fibers and, also, that there was no relationship between the exposure time and the crystallinity loss for the same percentage of fibers. The variation of the average enthalpy is more perceptible at 10% content when cellulosic fibers have not been pretreated, probably due to an inhomogeneous distribution in the composite.

A slight diminution on the melting peak temperature and a low thermal stability of the samples when subjected to environmental exposure is detected. Nevertheless, no melting enthalpy changes were detected.

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