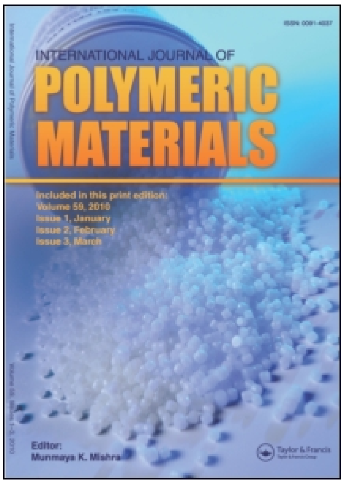

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Effect of Fiber Content and Chemical Treatment on the Thermal Properties of *Spartium junceum* Fiber-Reinforced Polypropylene Composites

S. Nekkaa[a]; M. Guessoum[a]; F. Chebira[a]; N. Haddaoui[a]
[a] Laboratoire Physico-Chimie des Hauts Polymères, Département de Génie des Procédés, Faculté des Sciences de l'Ingénieur, Université Ferhat Abbas Sétif, Algerie

To cite this Article Nekkaa, S. , Guessoum, M. , Chebira, F. and Haddaoui, N.(2008) 'Effect of Fiber Content and Chemical Treatment on the Thermal Properties of *Spartium junceum* Fiber-Reinforced Polypropylene Composites', International Journal of Polymeric Materials, 57: 8, 771 — 784

To link to this Article: DOI: 10.1080/00914030801963283

URL: http://dx.doi.org/10.1080/00914030801963283

International Journal of Polymeric Materials, 57:771–784, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030801963283

Effect of Fiber Content and Chemical Treatment on the Thermal Properties of *Spartium junceum* Fiber-Reinforced Polypropylene Composites

S. Nekkaa
M. Guessoum
F. Chebira
N. Haddaoui
Laboratoire Physico-Chimie des Hauts Polymères, Département de Génie des Procédés, Faculté des Sciences de l'Ingénieur, Université Ferhat Abbas Sétif, Algerie

The thermal and crystallization behavior of PP/Spartium junceum fiber composites were studied by thermogravimetry (TGA) and differential scanning calorimetry (DSC). The surface modification of Spartium junceum fibers was carried out using silane coupling agents in order to improve the interfacial adhesion between the fiber and the matrix. The effects of fiber content and chemical treatment on thermal properties were evaluated. It was found that Spartium junceum fiber degraded before the PP matrix but the thermal stability of the PP/Spartium junceum fiber composites was higher than those of the fiber and the matrix. DSC measurements showed that the incorporation of Spartium junceum fiber caused an increase in the crystallinity of the matrix. These effects have been attributed to the fact that the surfaces of Spartium junceum fibers act as nucleating agents for the crystallization of the polymer, promoting the growth and the formation of transcrystalline regions around the fibers.

Keywords: polymer composites, polypropylene, *Spartium junceum* fibers, surface treatment, thermal properties

INTRODUCTION

In recent years, significant efforts have been made to investigate the use of natural fibers as reinforcement in thermoplastic composites. The application of natural fibers is being driven by environmental

Received 11 January 2008; in final form 21 January 2008.

Address correspondence to S. Nekkaa, Laboratoire Physico-Chimie des Hauts Polymères, Département de Génie des Procédés, Faculté des Sciences de l'Ingénieur, Université Ferhat Abbas Sétif (19000), Algerie. E-mail: s_nekkaa@yahoo.fr

and economical concerns [1]. Natural fibers have some significant advantages as reinforcements in polymer composites, such as low cost, low density, biodegradability, availability of renewable natural resources and good mechanical properties [2–7]. However, the main disadvantage of these natural fiber/polymer composites seems to be the incompatibility between the hydrophilic natural fibers and the hydrophobic thermoplastic matrix [8–14].

Thus, in order to develop composites with good properties, it is necessary to improve the interfacial adhesion between the matrix and the cellulosic fibers. There are various methods to promoting interfacial adhesion in systems where cellulosic fibers are used as fillers, such as esterification, silane treatment, graft copolymerization, use of compatibilizers, plasma treatment and treatment with other chemicals [15–18]. These methods are usually based on the use of reagents, which contain functional groups that are capable of bonding to the hydroxyl groups of cellulosic fibers [19].

The properties of most polymers are generally subjected to mechanical, physical, and thermal degradations. Temperature and the formation of thermal residual stress during processing of composite materials accelerate these degradations. The thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses can give us fundamental information regarding the thermal stability of these materials [20].

Thermogravimetric data indicate a number of stages of thermal breakdown, weight loss of the material in each stage, and threshold temperature. Both TGA and derivative thermogravimetry (DTG) provide information about the nature and extent of degradation of the material. In differential scanning calorimetry, the heat flow rate associated with a thermal event can be measured as a function of time and temperature allowing quantitative information about melting and phase transitions of the composite system to be obtained [21].

Recently *Spartium junceum* fibers were used for the reinforcement of polypropylene in this laboratory by Nekkaa et al. [22,23]. The influence of fiber content and fiber treatment on the mechanical, dynamic mechanical and morphological properties has been studied. The aim of this work is the study of the crystallization and the thermal behavior of *Spartium junceum* fiber (both chemically treated and untreated) reinforced polypropylene. Experiments are performed by means of thermogravimetric analysis and differential scanning calorimetry.

EXPERIMENTAL

Materials

The polymer matrix used in this study was polypropylene (PP) "B-UP 123" (Exxon Mobil Chemical), having a density of 905 kg/m^3 and a melt flow index (MFI) experimentally determined to be 8.7 g/10 min at 230°C. Polypropylene was selected as the matrix because it is one of the major commodity plastics which may be processed below the decomposition temperature of cellulosic fibers (about 220°C).

Spartium junceum fiber was prepared in our laboratory. The *Spartium junceum* fiber was obtained from local sources. The shrub can be cultivated manually, and the fiber was cleaned and chopped to the desired length ranging from 2 to 4 mm.

As pretreatment, the fibers were dewaxed by stirring in toluene/ethanol solution (2:1) for 24 h to remove the seizing (potato starch and waxes) followed by washing the fibers in distilled water. After filtration, the fibers were dried at 105°C for 15 h.

Fiber Treatment

N [-3 Trimethoxysilyl propyl] ethylene diamine (Z-6020) was dissolved in distilled water. Then, the *Spartium junceum* fiber was immersed in the solution and kept there for 15 h with stirring at ambient temperature. The *Spartium junceum* fiber was filtered and then kept in the oven at 105°C for 15 h. The quantity of silane used was calculated at different concentrations: 0.5, 1, 1.5 and 2 wt% of the fiber content.

Processing

The composite materials were prepared by mixing the polymer matrix and the fibers in a two-roll mixer at 180°C. Different PP/*Spartium junceum* fiber composites were prepared; the *Spartium junceum* fiber amounts employed were 10, 20, 30, 40 and 50 wt%.

Pressed sheets of the composites were obtained by compression molding at 190°C under a pressure of 250 kg/cm^2, followed by air cooling.

Thermogravimetric Analysis

TGA and DTG were carried out using TA Instruments TGA 2050 CE, in an inert atmosphere and at a heating rate of 10°C per min.

Differential Scanning Calorimetry

A differential scanning calorimeter (DSC 2920 Modulated, TA instrument) was used. Samples (10–20 mg) were cut from a dumbell specimen and then placed in aluminum pans. The heating rate was 10°C per min. A nitrogen flow (50 ml/min) was maintained throughout the test. Thermograms were calibrated by using indium at the heating rate at which samples were analyzed. The melting point (Tm) was determined from the maximum of the melting peak.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Thermogravimetric Analysis of PP

The weight loss of virgin polymer PP as a function of temperature is commonly determined by the technique of TGA (Figure 1) and is an irreversible process due to thermal degradation. The thermal degradation of PP reveals that PP shows a single stage of weight loss and decomposes at a temperature of 307°C. The major peak of the DTG curve of PP (Figure 2) is observed at 407.8°C, which indicates the scission of all the inter-carbon bonds in polypropylene [24].

Thermogravimetric Analysis of Spartium junceum Fiber

Figure 3 depicts the weight loss as a function of temperature for the *Spartium junceum* fiber untreated and treated with silane at different concentrations of Z-6020. The thermal degradation of *Spartium junceum* fiber can be represented as the sum of thermal degradation

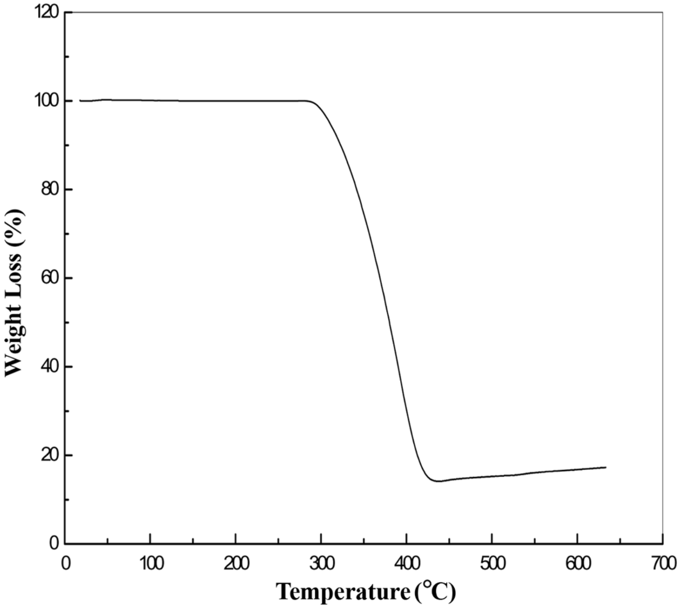

FIGURE 1 Thermogravimetric curve of PP.

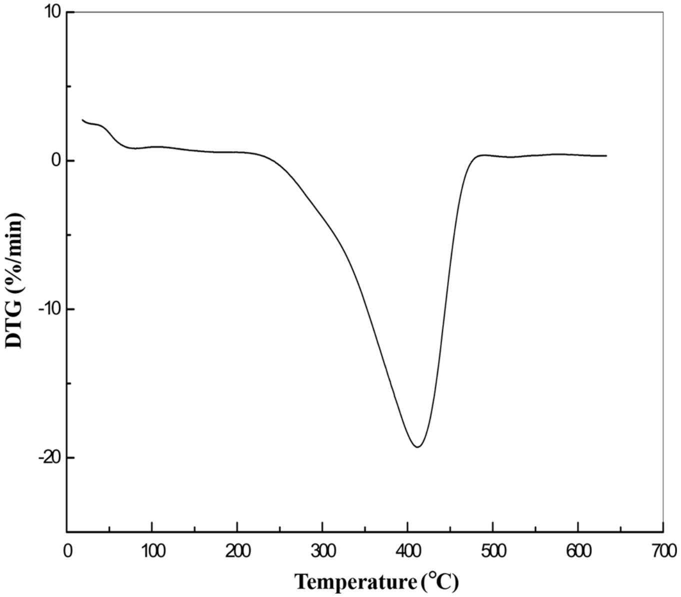

FIGURE 2 DTG curve of PP.

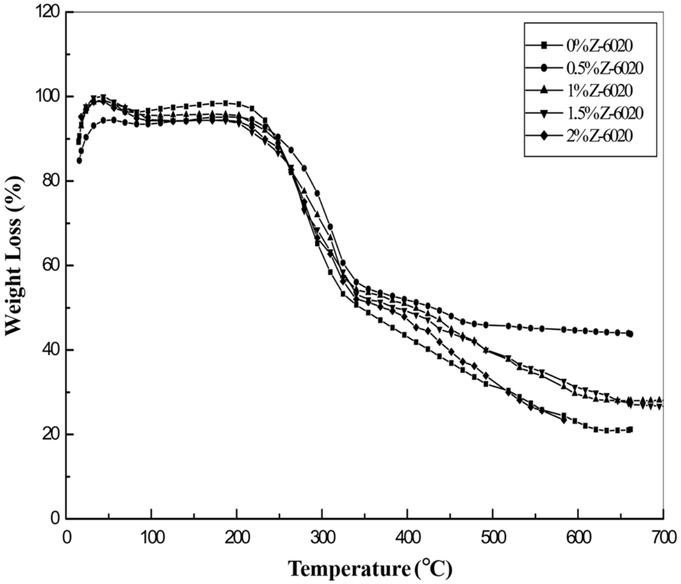

FIGURE 3 Thermogravimetric curves of *Spartium junceum* fiber untreated and treated at different silane concentrations.

reactions of the individual components, namely cellulose, hemicellulose and lignin. It can be deduced that cellulose and hemicellulose components of *Spartium junceum* are the major contributors to decomposition between 200°C and 350°C (stage 1), whereas lignin is mainly responsible for char formation of the *Spartium junceum* at 350°C and above (stage 2).

The thermal degradation of cellulose occurs in the temperature range from 310°C at around 350°C. Hemicelluloses are less thermally stable than celluloses. The hemicelluloses degrade at temperatures from 200°C to around 260°C. Aliphatic side chains start splitting off from aromatic rings at 300°C. Finally, the carbon-carbon linkage between lignin structural units is cleaved at 370°C and 400°C. The final degradation reaction of lignin occurs at high temperatures (550°C) [25].

Figure 4 shows the DTG curves of *Spartium junceum* fiber untreated and treated with silane. The peak observed at 65°C corresponds to the heat of water vaporization from the fiber. The second peak at about 300°C is due to the thermal depolymerization of hemicellulose and cleavage of glycosidic linkages of cellulose. The results of

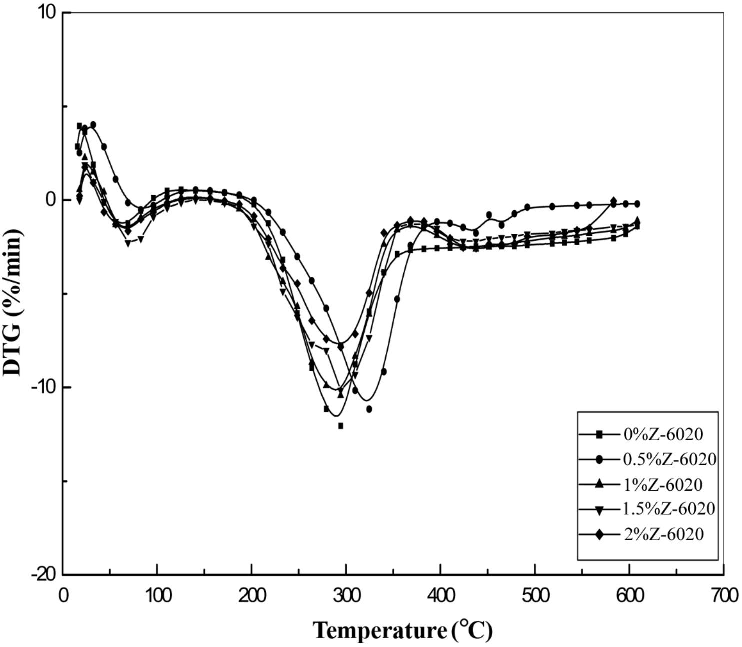

FIGURE 4 DTG curves of *Spartium junceum* fiber untreated and treated at different silane concentrations.

TABLE 1 *Spartium junceum* Fiber Thermal Degradation Kinetic Parameters

Samples	Decomposition temperature T_d (°C)	Temperature at the maximum degradation T_{dmax} (°C)
Untreated fiber	233	293
Fiber/0.5% Z-6020	216	307
Fiber/1% Z-6020	212	293
Fiber/1.5% Z-6020	203	296
Fiber/2% Z-6020	213	289

thermogravimetric analysis of *Spartium junceum* fiber untreated and treated are represented in Table 1. As is shown, the decomposition temperature (T_d) was determined at the starting point of severe weight loss and increased with increased heating rate. The results of Table 1 show a decrease of decomposition temperature of treated fibers. In theory, this temperature is generally related to the fiber Tg temperature. The observed decrease in T_d with the treatment can be explained by the fact that the chemical modification of the fiber surface reduces the hydroxyl groups present at the surface which decreases the intensity of the fiber-fiber interaction. The decomposition temperature decreases as the Z-6020 content increases. Although treatment can remove impurities from the surface of the fibers, it could not improve the thermal stability of cellulose. These results are in agreement with those presented by Ouajai et al. [26].

Thermogravimetric Analysis of Composite PP/Untreated Spartium junceum Fiber

Figure 5 represents TGA thermograms for PP at different levels of loading of *Spartium junceum* fiber (0–50%). The addition of *Spartium junceum* fiber to PP produces a decrease of the decomposition onset temperature as the fiber content increased. It is about 337°C for pure PP and its values are 265, 282, 248 and 247°C for the composites filled with 20, 30, 40 and 50 wt% fibers respectively. Also, we can notice from Figure 6 that the temperature at the maximum degradation rate was not significantly affected by the fiber content.

Thermogravimetric Analysis of PP/Treated Spartium junceum Fiber Composites

TGA and DTG thermograms of PP/treated *Spartium junceum* fiber composites (90/10) are presented in Figures 7 and 8. We observe that

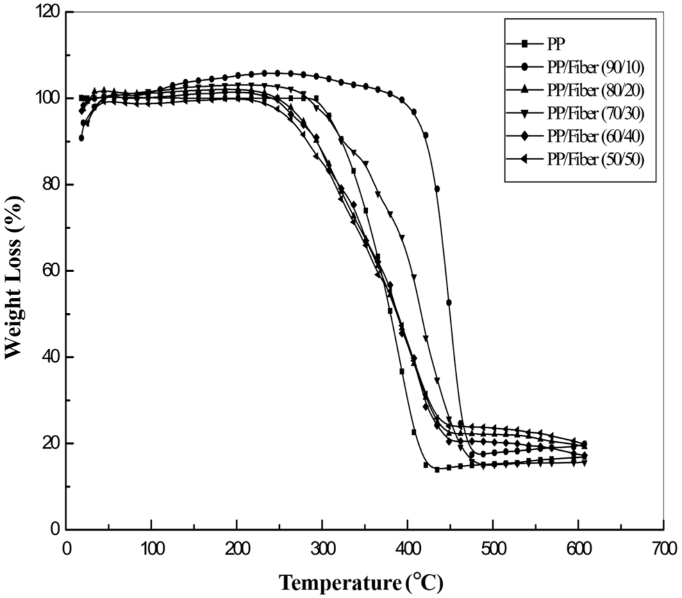

FIGURE 5 Thermogravimetric curves of PP/untreated *Spartium junceum* fiber composites.

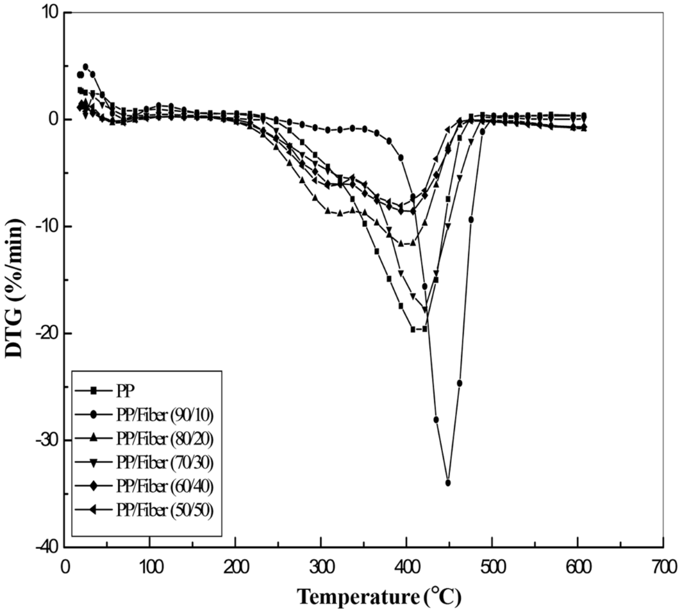

FIGURE 6 DTG curves of PP/untreated *Spartium junceum* fiber composites.

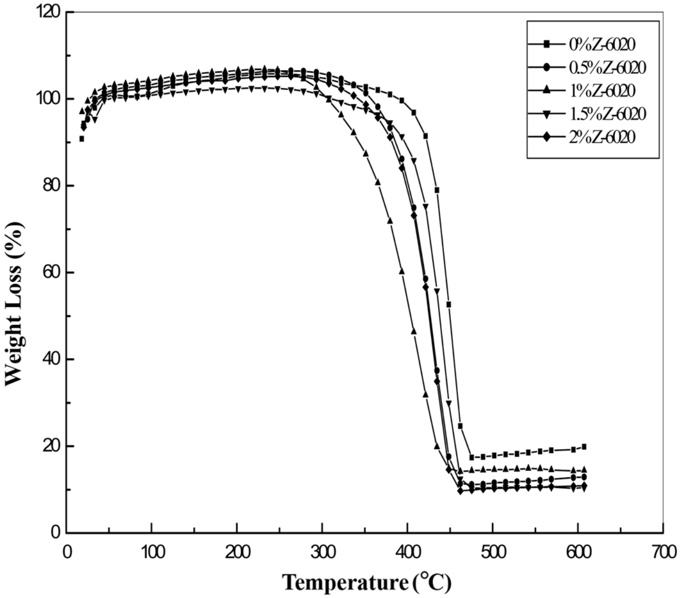

FIGURE 7 Thermogravimetric curves of (90/10) PP/treated *Spartium junceum* fiber composites.

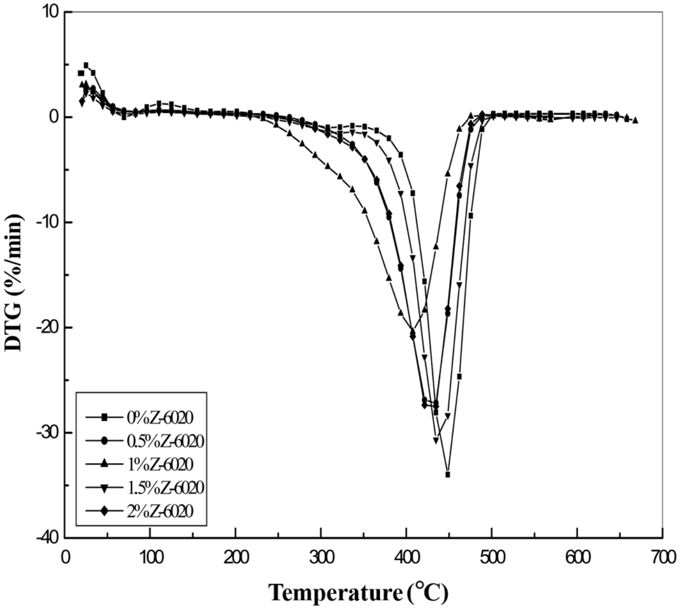

FIGURE 8 DTG curves of (90/10) PP/treated *Spartium junceum* fiber composites.

TABLE 2 Thermal Properties of PP and PP/Untreated *Spartium junceum* Fiber Composites

Samples	T_m (°C) first scan	T_m (°C) second scan	ΔH_m (J/g)	X_c (%)
PP	171	168	76	55
PP/Fiber (90/10)	166	166	83	60
PP/Fiber (80/20)	167	166	84	60
PP/Fiber (70/30)	167	165	100	72
PP/Fiber (60/40)	167	164	110	79
PP/Fiber (50/50)	168	165	120	86

the decomposition temperature increases with increasing silane content. This is due to the improved fiber/matrix adhesion as a result of the formation of bonds between the fiber and the matrix provided by the coupling agent. It is known that the methoxy groups ($-OCH_3$) in the silane can be hydrolyzed to produce silanol ($-Si\ (OH)_3$), during the fiber pretreatment process [27]. These silanol groups can either develop covalent siloxane bonds, or form hydrogen bonds with the $-OH$ groups of the cellulosic fiber. The amino groups have relatively high miscibility with polyethylene (PE) and PP. Thus, during the compounding of modified cellulosic fiber and PP, there will be a possible reaction of these functional groups with some polar groups present in PP [27]. We observe that the treatment of fiber has no significant effect on the temperature at the maximum degradation rate.

Differential Scanning Calorimetry Studies

The melting temperature, the melting enthalpy (ΔH_m) and the crystallinity (X_c), which were determined and calculated from the DSC thermograms, are summarized in Table 2. The fiber content is given as weight percentage. The crystallinity of the PP component was determined by using the equation:

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100$$

where a value of $\Delta H_m^0 = 138\,\mathrm{J/g}$ was taken for a 100% crystalline PP.

Effect of Fiber Content

Figure 9 shows an example of thermograms for the melting of neat PP and PP/*Spartium junceum* fiber composite. The results clearly show that the addition of amounts of fiber to PP results in an increase

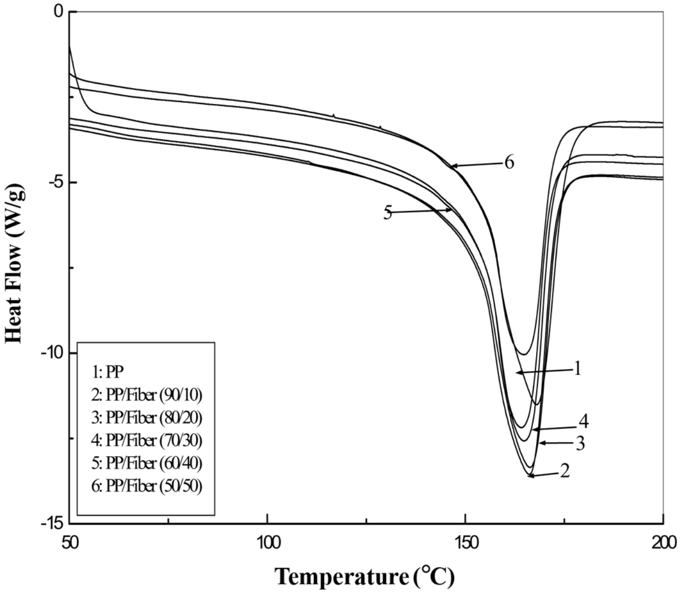

FIGURE 9 DSC thermograms of PP and different PP samples filled with untreated *Spartium junceum* fiber.

of crystallinity. This observation can be explained by the fact that the surface of cellulosic fiber acts as nucleation sites for the crystallization of the polymer, promoting the growth and the formation of transcrystalline regions around the fibers. These results are in agreement with those presented by Amash and Zugenmaier [8] and by Joseph et al. [21].

Effect of Treatment

Figures 10 and 11 permit the comparison between the different thermograms obtained from PP/*Spartium junceum* fiber composite (fiber treated with 1.5 wt% of silane) and from PP filled with 30 wt% of *Spartium junceum* fiber treated with different concentrations of silane. Thus, it appears that the fiber treatment has no significant effect on the melting temperature and on the crystallinity. The results of the thermal properties of PP and PP/treated *Spartium junceum* fiber composites are represented in Table 3. It is clear from Table 3 that the crystallinity of PP is increased when the content of *Spartium junceum* fiber increases. This result can be assigned to the fiber surface which acts as a nucleation agent for the crystallization of PP.

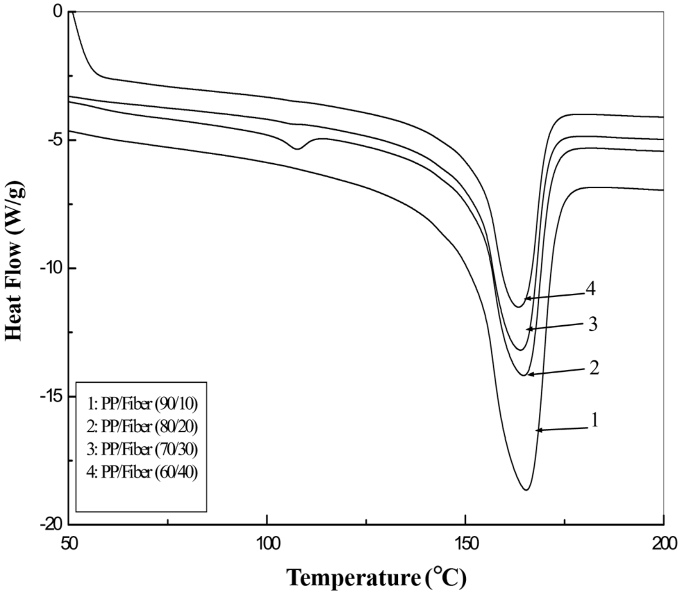

FIGURE 10 DSC thermograms of PP/*Spartium junceum* fiber composites with fiber treated at 1.5 wt% of silane.

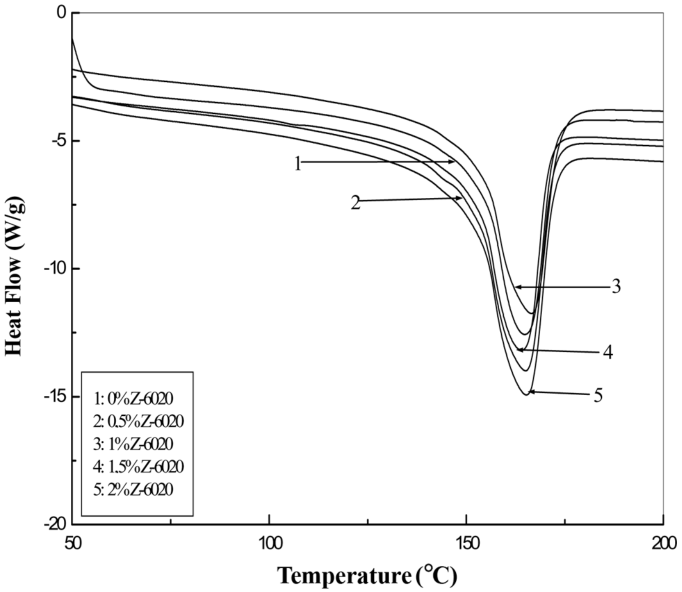

FIGURE 11 DSC thermograms of PP filled with 30 wt% of *Spartium junceum* fiber treated at different silane concentrations.

TABLE 3 Thermal Properties of PP/Treated *Spartium junceum* Fiber Composites

Samples PP/fiber/silane	T_m (°C) first scan	T_m (°C) second scan	ΔH_m (J/g)	X_c (%)
(90/10/1.5)	167	165	98	71
(80/20/1.5)	167	165	89	64
(70/30/1.5)	166	164	110	79
(60/40/1.5)	167	163	110	79
(70/30/0.5)	167	165	110	79
(70/30/1)	167	166	110	79
(70/30/2)	167	165	110	79

CONCLUSION

Thermogravimetric and differential scanning calorimetric analysis were carried out to study the thermal behavior of PP/*Spartium junceum* fiber composites.

It was found that *Spartium junceum* fiber degraded before the PP matrix. In the case of *Spartium junceum* fiber, most of the cellulose is decomposed at a temperature of 350°C, whereas PP decomposed at a temperature 307°C. It was further observed that the thermal stability of the PP/*Spartium junceum* fiber composites was higher than the thermal stabilities of the fiber and the matrix.

Calorimetric investigations showed that the incorporation of *Spartium junceum* fiber in PP caused an apparent increase in the crystallinity. These effects can be attributed to the fact that the surface of *Spartium junceum* fiber acts as nucleating agents for the crystallization of the polymer, promoting the growth and the formation of transcrystalline regions around the fibers. But, fiber treatment has no significant effect on the crystallinity.

REFERENCES

[1] Bos, H. L., Mussig, J., and Van den Oever, M. J. A., *Composites Part A: Appl. Sci. Manuf.* **37**, 1591 (2006).

[2] Martinez Urreaga, J., Matias, M. C., de la Orden, M. U., Lechuga Munguia, M. A., and Conzalez Sanchoz, C., *Polym. Eng. Sci.* **40**, 407 (2000).

[3] Gassan, J. and Gutowski, V. S., *Comp. Sci. Tech.* **60**, 2857 (2001).

[4] Bengtsson, M. and Oksman, K., *Composites Part A: Appl. Sci. Manuf.* **37**, 752 (2006).

[5] Dalvag, H., Klason, C., and Stromvall, H. E., *Int. J. Polym. Mater.* **11**, 9 (1985).

[6] Park, B. D. and Balatinecz, J. J., *J. Thermoplast. Compos. Mater.* **9**, 342 (1996).

[7] Nogellova, Z., Kokta, B. V., and Chodak, I., *JMS Pure and Appl. Chem.* **A 35**, 1069 (1998).

[8] Amash, A. and Zugenmaier, P., *Polym. Bull.* **40**, 251 (1998).

[9] Tajvidi, M. and Ebrahimi, G., *J. Appl. Polym. Sci.* **88**, 941 (2003).

[10] Bledzki, A. K., Reihmane, S., and Gassan, J., *Polym. Plast. Techol.* **37**, 451 (1998).

[11] Khan, A. M. and Ikm, A., *Polym. Plast. Techol.* **36**, 179 (1997).

[12] Lai, S. M., Yeh, P. C., Wang, Y., Chan, H. C., and Shen, H. F., *J. Appl. Polym. Sci.* **87**, 487 (2003).

[13] Maldas, D. and Kokta, B. V., *Int. J. Polym. Mater.* **27**, 77 (1994).

[14] Espert, A., Vilaplana, F., and Karlsson, S., *Composites Part A: Appl. Sci. Manuf.* **35**, 1267 (2004).

[15] Gassan, J. and Bledzki, A. K., *Polym. Comp.* **18**, 179 (1997).

[16] Paunikallio, T., Suvanto, M., and Pakkanen, T. T., *J. Appl. Polym. Sci.* **91**, 2676 (2004).

[17] Liao, B., Huang, Y., and Cong, G., *J. Appl. Polym. Sci.* **66**, 1561 (1997).

[18] Ichazo, M. N., Albano, C., Conzàlez, J., Perera, R., and Candal, M. V., *Composites Structures* **54**, 207 (2001).

[19] Tserki, V., Matzinos, P., Kokkou, S., and Panayiotou, C., *Composites Part A: Appl. Sci. Manuf.* **36**, 965 (2005).

[20] Wielage, B., Lampke, T., Mark, G., Nestler, K., and Starke, D., *Thermochim. Acta.* **337**, 169 (1999).

[21] Joseph, P. V., Joseph, K., Thomas, S., Pillai, C. K. S., Prasad, V. S., Groeninckx, G., and Sarkissova, M., *Composites Part A: Appl. Sci. Manuf.* **34**, 253 (2003).

[22] Nekkaa, S., Chebira, F., and Haddaoui, N., *J. Eng. Appl. Sci.* **1**, 278 (2006).

[23] Nekkaa, S., Haddaoui, N., Grillet, A. C., and Merle, G., *Int. J. Polym. Mater.* **55**, 837 (2006).

[24] Doh, G. H., Kang, I. A., and Kong, Y. T., *Composites Structures* **68**, 103 (2005).

[25] Alvarez, V. A. and Vàzquez, A., *Polym. Degrad. Stab.* **84**, 13 (2004).

[26] Ouajai, S. and Shanks, R. A., *Polym. Degrad. Stab.* **89**, 327 (2005).

[27] Blascuriya, P. W., Ye, L., Mai, Y. W., and Wu, J., *J. Appl. Polym. Sci.* **83**, 2505 (2002).