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Thermal and microstructural characterization of compatibilized polystyrene/natural fillers composites

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Abstract Composites of polystyrene (PS) with cellulose microfibres and oat particles, obtained by melt mixing, were examined. The compatibilization of the composites was carried out by addition of maleic anhydride-functionalized copolymers (SEBS-*g*-MA, PS-*co*-MA) and poly(ethylene glycol) to improve the fibre–matrix interfacial interactions. The plain components and their composites were characterised by FT-IR, DSC, TGA, SEM microscopy and mechanical tests. The properties of the various systems were analysed as a function of both fibre and compatibilizer amount. The compatibilized PS composites showed enhanced fibre dispersion and interfacial adhesion as a consequence of chemical interactions between the anhydride groups on the polymer chains and the hydroxyl groups on the fibres, as demonstrated by FT-IR spectroscopy. DSC analysis pointed out a neat increase of T_g of composites on addition of SEBS-g-MA, as compared to PS-co-MA. The thermal stability of composites was also influenced by the type and amount of fibres, as well as by the structure and concentration of compatibilizer. The effect of the reactive copolymers on the composites properties was accounted for on the basis of the polymer–polymer miscibility and chemical interactions at the matrix/filler interface.

Keywords Polymer composites · Natural fibres · Reactive compatibilization · Thermal properties · Phase interactions

Introduction

Polymer composites based on natural fibres (vegetal fibres, cellulosics and derivatives) are attracting great attention as alternative materials to glass or synthetic fibre reinforced plastics in several applications, mostly for automotive, appliances and packaging products. The main advantage of employing natural fibres is that these are biodegradable and renewable, and exhibit low cost, low density, high toughness and good thermal resistance [1, 2]. However, the weak compatibility between fibres and polymer matrix, the low degree of dispersion of the filler into the matrix as well as the poor resistance to moisture generally leads to weak physical–mechanical properties, limiting the performances of these materials.

In order to improve the interfacial interactions between polymer and fibres, surface modification of the fibres and/or polymer functionalization, as well as addition of compatibilizers are required [1]. Polymer modification with reactive molecules (such as anhydrides, epoxides, amines, etc.) is a largely explored way to enhance interfacial adhesion, especially for polyolefin-based composites [3–5]. The other important opportunity is the physical and chemical modification of the fibres, such as the insertion of functional molecules which can be exploited in secondary reactions (i.e., radical grafting) with the polymer matrix,

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providing a stable network of bonding between the components [6–8].

In previous articles we examined the compatibilization processes and the properties of thermoplastic composites based on isotactic polypropylene [8], poly(L-lactide) [9] and ethylene–vinyl acetate copolymers [10] with hemp, cellulose and other natural fillers. For composites of PP with hemp fibres, it was found that the morphological characteristics, the crystal growth as well as the thermal, rheological and mechanical properties of these systems were largely influenced by addition (or even in situ generation) of copolymers containing epoxy or anhydride functional groups (PP-*g*-GMA, SEBS-*g*-GMA and EVA-*g*-MA). The results demonstrated the interactions at the polymer/fibre interface and thus the physical/mechanical behaviour were strictly depending on the copolymer structure and content.

In this article we investigate the compatibilization and the properties of composites with PS matrix containing cellulose or oat as natural fillers. In particular, the study was aimed at evaluating the role of addition of PS copolymers containing reactive functional groups—namely PS-*co*-MA and SEBS-*g*-MA copolymers—on the interfacial interaction phenomena which control the phase structure, phase transitions and thermal degradation behaviour of the composites.

Experimental

Materials

Polystyrene (PS) is a commercial product (extrusion grade) composed of PS crystal type and HIPS (1:1 by weight) in form of pellets. Styrene–(ethylene–butene)–styrene block copolymer grafted with maleic anhydride (SEBS-*g*-MA, Kraton FG-1901X) with MFR = 20–25 g/10 min and containing 1 wt% MA were supplied by Shell (Milano, Italy). Poly(styrene-*co*-maleic anhydride) copolymer (PS-*co*-MA) with $M_w = 224.000$, MFR = 1.7 g/10 min and containing 7 wt% MA were supplied by Sigma-Aldrich (Schnelldorf, Germany). Low molecular weight poly(ethylene glycol) (PEG) with $M_w = 600$ was supplied by Sigma-Aldrich (Milano, Italy). Cellulose fibres (Technocel 75), with average length of 75 µm and cellulose content of 99.6%, were provided by Neuchem (Milano, Italy). Oat particles (*Avena sativa*) derived from ground oat husks (size smaller than 75 µm) were produced by Chemical Net (Warszawa, Poland). According to the supplier, the particles contained 50 wt% cellulose, 25 wt% hemicellulose and 3–5 wt% lignin. Before use all materials were carefully dried under vacuum at 90 °C for 4 h in order to reduce the moisture content.

Blending

Composites of PS with cellulose (PS/Cell) or oat (PS/Oat) and composites of PS with cellulose and compatibilizer (PS/Cell/PS-*co*-MA and PS/Cell/SEBS-*g*-MA) were obtained by melt mixing the components in a Brabender Plasticorder internal mixer at 180 °C using a rotor speed of 50 rpm for 8–10 min. For the processing, the natural fillers were used as received without any surface treatment. Two mixing procedures, single- and double-step, were employed for the preparation of the compatibilized systems: (a) binary and ternary systems with fibre amount of 10, 20, 30 and 40 wt% and different compatibilizer content (using fibre/compatibilizer weight ratios of 1:5 and 1:2.5, respectively) were prepared by feeding all components into the Brabender mixer at same time; (b) in a first step a batch mixture of cell and compatibilizer (50/50 wt%) was prepared into the mixer; then, in a second step, plain PS was added to the batch (50/50) to get the desired composition and processed in the same conditions. The compositions of all examined PS/Cell and PS/Oat systems are listed in Tables 1 and 2. Plain PS and its blends with the functionalized-copolymers (PS/PS-*co*-MA, PS/SEBS-*g*-MA) were also prepared under the same conditions and analysed. The variation of torque moment during the mixing process was monitored for all samples as a function of the mixing time.

FT-IR analysis

The FT-IR spectra of films of composites and plain components, obtained by compression moulding at 170/180 °C, were recorded at room temperature by means of a Perkin–Elmer Spectrophotometer (Mod. 2000) in the range 4000–400 cm^{-1} at a scanning speed of 2 mm/s, with a resolution of 4 cm^{-1}. The number of scans was set to 64.

Scanning differential calorimetry

The thermal behaviour of all materials was examined with a Pyris Diamond DSC (Perkin–Elmer) at a heating/cooling rate of 10 °C/min under nitrogen flow. The samples (5–10 mg) were first heated to 190 °C and kept at this temperature for 2 min, then cooled to room temperature and again heated up to 190 °C (2nd heating run). The DSC temperature scale and heat flow were calibrated by using a standard indium sample. Glass transition temperatures were determined at the half of delta-Cp step from the heating curves of the samples at 10 °C/min.

Thermogravimetry

Thermal degradation of composites and pure components was analysed with a TGA MK2 (Rheometric Scientific) in

Table 1 Compositions of PS/Cell and compatibilized PS/Cell composites

Sample code[a]	PS/wt%	Cellulose/wt%	SEBS-*g*-MA/phr	PS-*co*-MA/phr
PS	100	0	–	–
PS/Cell 90/10	90	10	–	–
PS/Cell 80/20	80	20	–	–
PS/Cell 70/30	70	30	–	–
PS/Cell 60/40	60	40	–	–
PS/Cell/SEBS-*g*-MA 90/10-2	90	10	2	–
PS/Cell/SEBS-*g*-MA 80/20-4	80	20	4	–
PS/Cell/SEBS-*g*-MA 70/30-6	70	30	6	–
PS/Cell/SEBS-*g*-MA 60/40-8	60	40	8	–
PS/Cell/SEBS-*g*-MA 80/20-8	80	20	8	–
PS/Cell/SEBS-*g*-MA 70/30-12	70	30	12	–
PS/Cell/SEBS-*g*-MA 60/40-16	60	40	16	–
PS/Cell/PS-*co*-MA 90/10-2	90	10	–	2
PS/Cell/PS-*co*-MA 80/20-4	80	20	–	4
PS/Cell/PS-*co*-MA 70/30-6	70	30	–	6
PS/Cell/PS-*co*-MA 60/40-8	60	40	–	8
PS/Cell/PS-*co*-MA 80/20-8	80	20	–	8
PS/Cell/PS-*co*-MA 70/30-12	70	30	–	12
PS/Cell/PS-*co*-MA 60/40-16	60	40	–	16
SEBS-*g*-MA/Cell 50/50	–	50	50	–
PS-*co*-MA/Cell 50/50	–	50	–	50
PS-*co*-MA/Cell 60/40	–	40	–	60
PS-*co*-MA/Cell 70/30	–	30	–	70

[a] The concentration of the compatibilizer is given in part per hundred (phr)

the range 50–700 °C at a heating rate of 10 °C/min, both in N_2 atmosphere and air.

SEM analysis

The morphology of composites was examined on the surfaces of bulk samples and films freeze-fractured in liquid nitrogen. All samples were sputter-coated with a fine layer of gold in an Edward sputter coater and analysed with a Jeol JSM5600 LW scanning electron microscope, operating at 20 kV.

Results and discussion

Phase interactions

The presence of anhydride functional group on the copolymers' chains can give rise to the chemical reactions with the hydroxyl group of cellulose, leading to a stable bonding of copolymer chains on the fibre surfaces and therefore improving the fibre dispersion into the polymer matrix. The scheme of possible reaction between cellulose and PS-*co*-MA copolymer is reported in Fig. 1; the same reaction holds in the case of SEBS-g-MA.

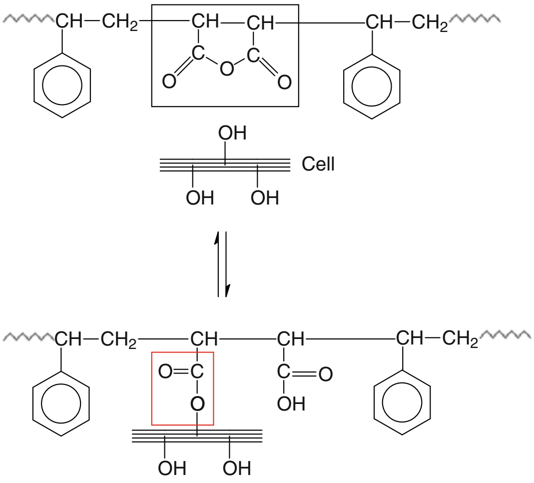

Fig. 1 Reaction scheme of PS-co-MA with cellulose

To investigate the polymer–fibre interactions, binary and ternary systems containing SEBS-*g*-MA and PS-*co*-MA copolymers at various cellulose content, were analysed

Table 2 Compositions of PS/Oat and PS/Oat/PEG composites

Sample code[a]	PS/wt%	Oat/wt%	PEG/phr
PS	100	0	–
PS/Oat 90/10	90	10	–
PS/Oat 80/20	80	20	–
PS/Oat 70/30	70	30	–
PS/Oat 60/40	60	40	–
PS/Oat/PEG 90/10-5	90	10	5
PS/Oat/PEG 80/20-5	80	20	5
PS/Oat/PEG 70/30-5	70	30	5
PS/Oat/PEG 60/40-5	60	40	5
PS/Oat/PEG 90/10-10	90	10	10
PS/Oat/PEG 80/20-10	80	20	10
PS/Oat/PEG 70/30-10	70	30	10
PS/Oat/PEG 60/40-10	60	40	10
PS/PEG 100-5	100	–	5
PS/PEG 100-10	100	–	10

[a] The concentration of the compatibilizer is given in part per hundred (phr)

by FT-IR spectroscopy. The composite's spectra are shown in Fig. 2. The occurrence of interactions between maleic anhydride and hydroxyl groups of cellulose was carefully investigated in the frequency ranges 2000–1650 and 1200–850 cm^{-1}, respectively. Significant shifts of the MA carbonyl stretching band (νCO) at about 1780 cm^{-1} and relevant ester band (νCOO) near to 1740 cm^{-1} were recorded for composites with SEBS-g-MA (Fig. 2a) [11, 12]. Moreover, changes of alcohol (νCOH) and ether (νCOC) stretching bands in the spectra of cellulose at 1164, 1114, 1060 and 1033 cm^{-1}, respectively (not shown here) were observed, supporting the existence of interactions at the fibre/matrix interface likely due to the formation of ester bonds, in agreement with that reported for other polyolefin/natural fibre composites compatibilized with SEBS-g-MA [13]. Minor changes were observed in the carbonyl stretching region for the composites with PS-co-MA (Fig. 2b). However, a net improvement of polymer–fibre adhesion in all compatibilized systems was confirmed by the microscope observations, as it will be later on discussed.

Thermal properties

The glass transition behaviour of PS in the composites was examined by DSC as a function of filler content and type of compatibilizer. DSC heating curves of plain polymers, binary and ternary composites are reported in Fig. 3-I and II for samples obtained by means of single- and double-step mixing procedure, respectively. Curves of binary reactive systems (PS-*co*-MA/Cell, SEBS-*g*-MA/Cell) are also shown (Fig. 3-II). Generally, for uncompatibilized PS/Cell samples minor changes of glass transition were observed on the heating run (not shown here) at higher contents of cellulose, whereas marked changes were recorded in the presence of compatibilizer.

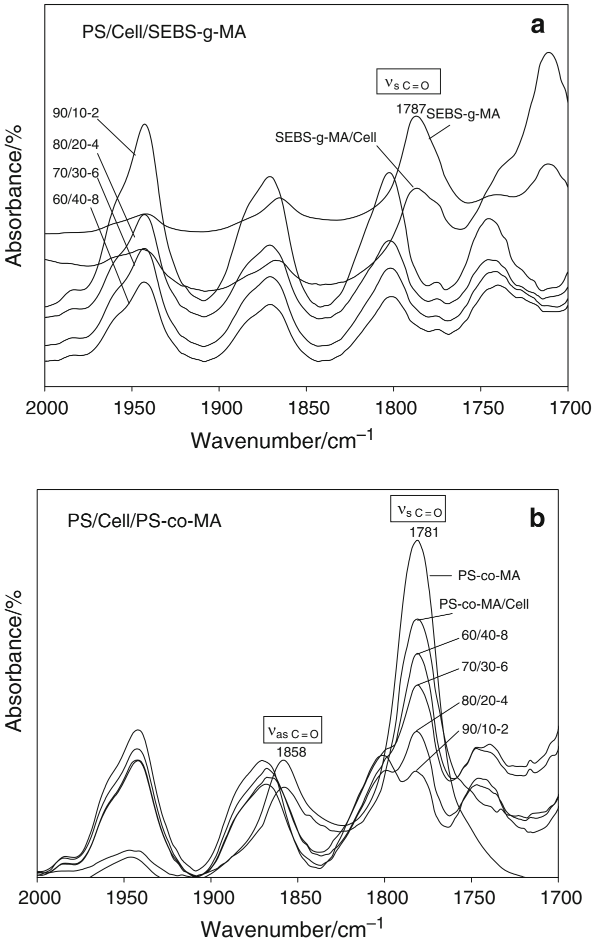

Fig. 2 The FT-IR spectra of compatibilized **a** PS/Cell/SEBS-g-MA and **b** PS/Cell/PS-co-MA

The T_g values of PS/Cell and composites with PS-*co*-MA and SEBS-*g*-MA compatibilizer content of 2–8 phr are plotted in Fig. 4 as a function of cellulose to PS weight ratio. For plain PS the observed T_g is 94 °C, for plain SEBS-*g*-MA and PS-*co*-MA copolymers the T_g are at about 90 and 115 °C, respectively. The uncompatibilized samples displayed a little increase of T_g with the cellulose content; otherwise, upon addition of SEBS-*g*-MA, T_g raised with increasing the fibre content from 94 to about 100 °C, for the sample with 40 wt% of cellulose. Samples compatibilized with PS-*co*-MA displayed only minor changes of T_g with the composition and their values resulted almost coincident with those recorded for PS/Cell samples. This behaviour is in agreement with the occurrence of strong interactions between the MA functional groups and hydroxyls of cellulose in the systems with

SEBS-g-MA, causing a reduction of the polymer chain mobility at the fibre–matrix interface.

The effect of interfacial interactions is confirmed by the analysis of the binary PS-co-MA/Cell and SEBS-g-MA/Cell samples. In Fig. 3-II, it may be noticed that PS-co-MA/Cell samples display higher T_g—in the range 117–118 °C—than the neat copolymer. However, a larger increase of T_g is found for samples containing SEBS-g-MA, as compared to the neat polymer. For ternary systems obtained by batch mixing (two-step procedure), a different trend is observed (Fig. 3-II). Two glass transitions are found in DSC curves of PS/Cell/PS-co-MA composites, the lower one corresponding to the PS transition (about 95 °C), the higher near to the PS-co-MA transition (about 115 °C), suggesting a partial phase separation of the polymers, in spite of the expected miscibility of PS-co-MA copolymer with PS [14].

The effect of filler content on the glass transition behaviour of PS/Oat composites is shown in Fig. 5. An increase of T_g with increasing the oat to PS weight ratio is observed in the range 0–40 wt% of filler. On addition of PEG the T_g values markedly decrease—about 10 °C—over all the examined composition range, due to plasticizing effect of the low molecular weight compound. Similar effects were also evidenced for PLA composites with hemp [9] and oat [15] in the presence of poly(ethylene glycol) and poly(propylene glycol), respectively, as plasticizers.

Thermal degradation behaviour

The weight loss derivative curves of PS composites containing both cellulose and oat are reported in Fig. 6. Large differences were observed in the TG analysis of the composites, depending on the filler nature, composition and compatibilization methods. Figure 6a and b show the DTG curves of both uncompatibilized and compatibilized PS/Cell composites recorded during heating in nitrogen and air, respectively. Cellulose exhibited a single decomposition step in nitrogen and two in air [16–18]. The main weight loss peak of cellulose in air (not reported here) appeared at 337 °C, due to the cleavage of the glucosidic

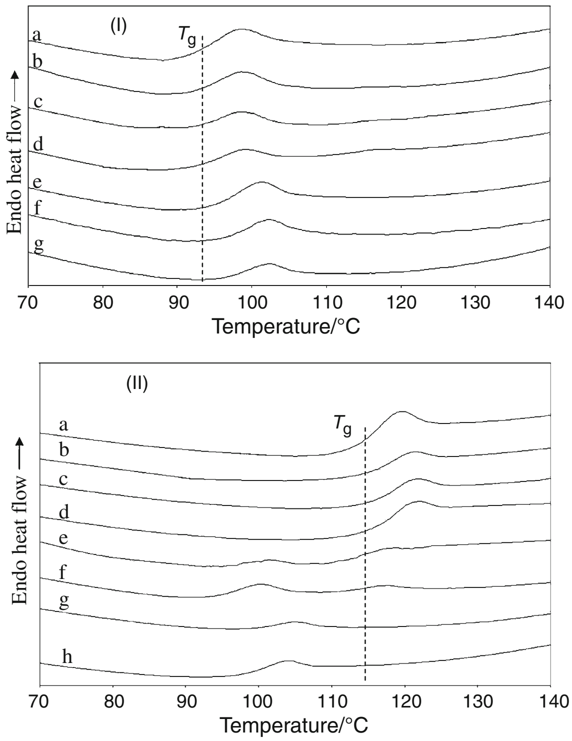

Fig. 3 DSC curves of PS composites in the glass transition region (2nd heating run, 10 °C/min); **I** one-step mixing: *a* PS; PS/Cell/PS-*co*-MA: *b* 80/20-8, *c* 70/30-12, *d* 60/40-16; PS/Cell/SEBS-g-MA: *e* 80/20-8, *f* 70/30-12, *g* 60/40-16. **II** two-step mixing: *a* PS-*co*-MA; PS-*co*-MA/Cell: *b* 50/50, *c* 60/40, *d* 70/30; PS/Cell/PS-co-MA: *e* 50/25/25, *f* 33.3/33.3/33.3; PS/Cell/SEBS-*g*-MA: *g* 50/25/25, *h* 33.3/33.3/33.3

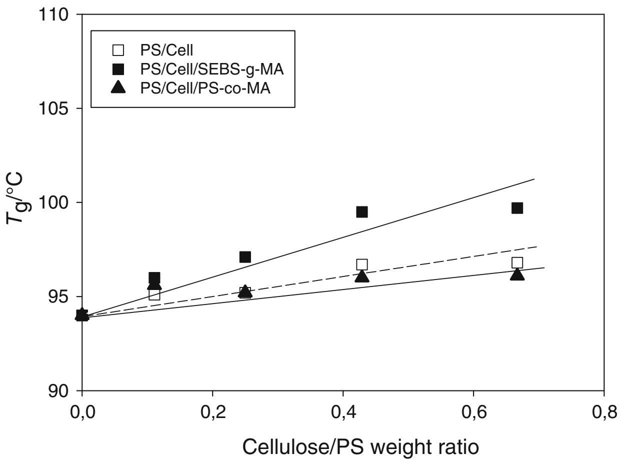

Fig. 4 Glass transition temperature of PS/Cell and compatibilized PS/Cell composites with 2–8 phr compatibilizer content (see Table 1) versus Cell/PS weight ratio

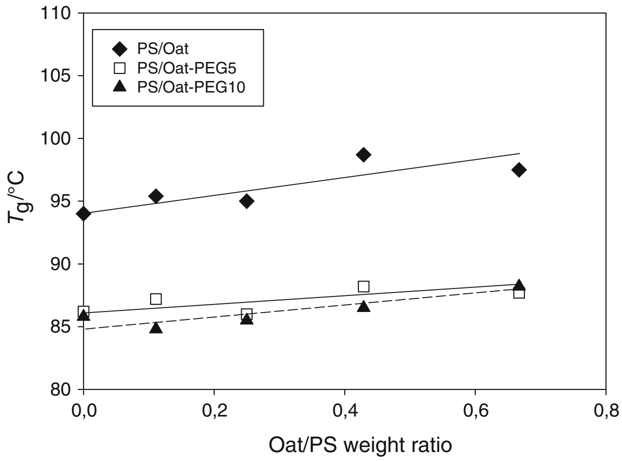

Fig. 5 Glass transition temperature of PS/Oat and PS/Oat/PEG composites versus Oat/PS weight ratio

linkages, while a minor one was at about 460 °C. In the case of PS, the DTG curve showed a broad peak with maximum at 425 °C [19]. For PS/Cell in air, the peak maxima are located at 341 and 481 °C for cellulose, and at 402 °C for PS, indicating an increase of stability of the dispersed fibres (on the 2nd decomposition step) and a decrease of stability for PS matrix. In the case of compatibilized composites, the DTG curves in nitrogen (Fig. 6a) does not show significant differences with respect to the uncompatibilized samples; in air (Fig. 6b), a shift of the PS peak—as compared to PS/Cell—is observed depending on the type and amount of compatibilizer. For PS/SEBS-g-MA/Cell composites the maximum of PS peak is at higher temperature than that of PS/PS-co-MA/Cell samples, suggesting a larger effect of SEBS-g-MA on the thermal stability of compatibilized systems.

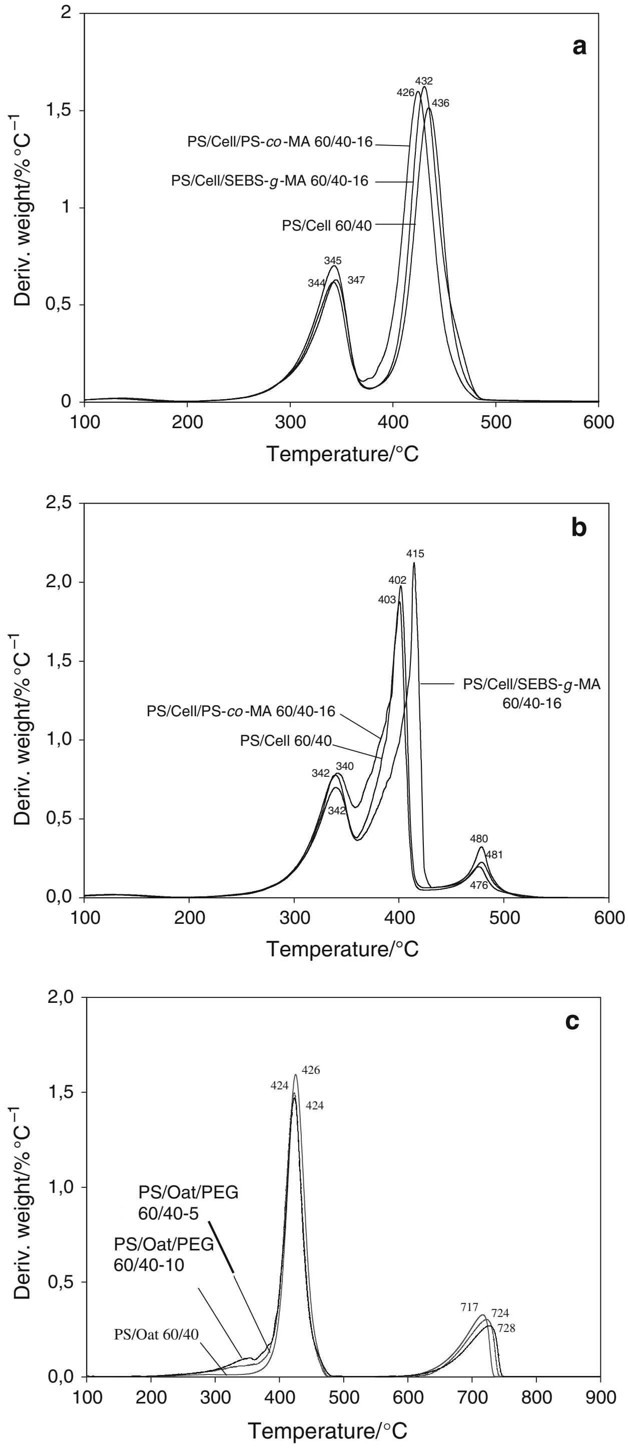

Fig. 6 DTG curves for uncompatibilized and compatibilized composites: **a** PS/Cell, PS/Cell/PS-co-MA, PS/Cell/SEBS-g-MA in nitrogen gas; **b** PS/Cell, PS/Cell/PS-co-MA, PS/Cell/SEBS-g-MA in air; **c** PS/Oat, PS/Oat/PEG in nitrogen gas (heating rate: 10 °C/min)

In the case of PS/Oat composites (Fig. 6c) the decomposition of the natural filler occurs at considerably higher temperature (above 600 °C) than cellulose. Addition of PEG do not significantly affects the degradation behaviour of these composites, although shifts of the maximum of oat peak are observed in the DTG curves, most likely due to interactions of the plasticizer with the filler particles [9].

Morphology

The SEM micrographs of the fracture surfaces of PS/Cell and compatibilized composites with PS-*co*-MA and SEBS-*g*-MA are shown in Fig. 7. Binary composites with cellulose (or oat) displayed in all cases enough fibre dispersion, but a weak adhesion between matrix and filler, accompanied by fibre pull-out, was observed throughout (Fig. 7a). The addition of reactive compatibilizers (Fig. 7b and c) determined in all cases an improvement of the interfacial adhesion and a reduction of pull-out phenomena.

The effectiveness of the reactive compatibilizers was clearly evidenced from SEM micrographs of binary SEBS-*g*-MA/Cell (50/50) sample (Fig. 7d), which point out the

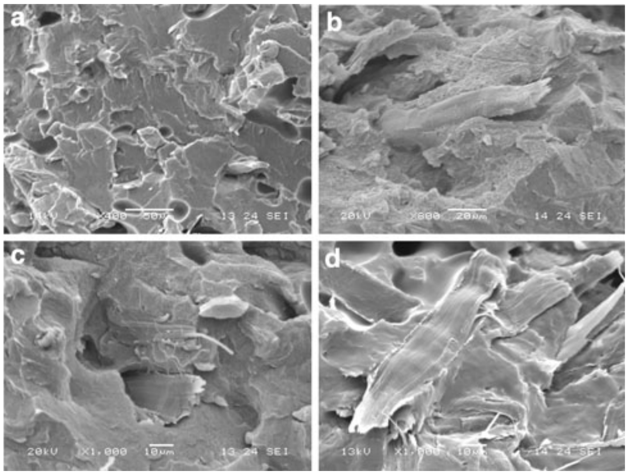

Fig. 7 SEM micrographs of fracture surface of: **a** PS/Cell (70/30), **b** PS/Cell/PS-co-MA (50/50-6), **c** PS/Cell/SEBS-g-MA (70/30-6), **d** SEBS-g-MA/Cell (50/50)

occurrence of extended chemical interactions at the fibre/polymer interface giving rise to strong bonding (and fibre fraying), which had consequent effects on the mechanical behaviour of the composites. Accordingly, tensile tests showed that modulus, tensile strength and elongation at break of the composites were strictly influenced by the fibre amount, and by the structure and concentration of compatibilizer [20].

Conclusions

The control of properties of natural fibres reinforced polymer composites is strictly depending on the possibility of modifying the interfacial adhesion, through the improvement of the fibre–matrix interactions. In this article the effect of the addition of compatibilizers containing reactive and/or groups (SEBS-*g*-MA, PS-*co*-MA, PEG), on the thermal, microstructural and morphological, characteristics has been examined for PS composites containing cellulose and oat. For all compatibilized systems an enhanced fibre dispersion and interfacial adhesion has been observed, supporting the occurrence of effective interactions between the functional groups on the copolymer chains and the polar groups of the fibres, as demonstrated by FT-IR analysis. The glass transition behaviour and the thermal degradability of the composites were correlated to the compatibilizing effect of the copolymers. Moreover, for all examined materials, mechanical tests showed that the tensile properties are markedly affected by the type and amount of fibre, as well as by the structure and concentration of compatibilizer [20]. In the case of PS/Cell composites a higher interfacial adhesion was noticed in samples compatibilized with the graft copolymer, SEBS-*g*-MA, as compared to those containing the random copolymer, PS-*co*-MA, in spite of the larger MA content of the latter. This can be ascribed to the fact that the block copolymer—which is only partially miscible with the PS matrix—is mostly located at the interface between filler particle and matrix, giving rise to more effective interactions of the anhydride groups with the hydroxyl groups on the fibre surface. Otherwise, the random copolymer—almost miscible with the PS matrix—results less effective to generate interactions at the interface.

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References

1. Nabi SD, Jog JP. Natural fiber polymer composites: a review. Adv Polym Technol. 1999;18:351–63.
2. Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. Prog Polym Sci. 2006;31:576–602.
3. George J, Sreekala MS, Thomas S. A review on interfacial modification and characterization of natural fiber reinforced plastic composites. Polym Engi Sci. 2001;41:1471–85.
4. Mwaicambo LY, Martuscelli E, Avella M. Kapok/cotton fabric–polipropilene composites. Polym Test. 2000;19:905–18.
5. Lopez Machado MA, Arroyo M, Biagiotti J, Kenny JM. Enhancement of mechanical properties and interfacial adhesion of PP/EPDM/flax fiber composite using maleic anhydride as a compatibilizer. J Appl Polym Sci. 2003;90:2170–8.
6. Joseph PV, Joseph K, Thomas S, Pillai CKS, Prasad VS, Groeninckx G, Sarkissova M. The thermal and crystallization studies of short sisal fibre reinforced polypropylene composites. Composites: part A. 2003;34:253–66.
7. Rozman HD, Saad MJ, Mohd Ishak ZA. Flexural and impact properties of oil palm empty fruit bunch (EFB)-polypropylene composites. Polym Test. 2003;22:335.
8. Pracella M, Chionna D, Anguillesi I, Kulinski Z, Piorkowska E. Functionalization, compatibilization and properties of polypropylene composites with hemp fibres. Compos Sci Technol. 2006;66:2218–30.
9. Masirek R, Kulinski Z, Chionna D, Piorkowska E, Pracella M. Composites of poly(L-lactide) with hemp fibres: morphology, thermal and mechanical properties. J Appl Polym Sci. 2007;105:255–68.
10. Haque MM, Pracella M. Reactive compatibilization of composites of ethylene-vinyl acetate copolymers with cellulose fibres. Composites: part A. 2010;41:1545–50.
11. Bellamy LJ. The infrared spectra of complex molecules. 3rd ed. London: Chapman and Hall; 1975.
12. Pouchert CJ. The Aldrich library of infrared spectra. Milwaukee: Aldrich Chemical Company; 1975.
13. Oksman K, Lindberg H, Holmgren A. The nature and location of SEBS-MA compatibilizer in polyethylene-wood flour composites. J Appl Polym Sci. 1998;69:201–9.
14. Ju MY, Chang FC. Compatibilization of PET/PS blends through SMA and PMPI dual compatibilizers. Polymer. 2000;41:1719–30.
15. Lezak E, Kulinski Z, Masirek R, Piorkowska E, Pracella M. Mechanical and thermal properties of green polylactide composites with natural fillers. Macromol Biosci. 2008;8:1190–200.
16. Albano C, Gonzalez J, Ichazo M, Kaiseer D. Thermal stability of blends of polyolefins and sisal. Polym Degrad Stabil. 1999;66:179–90.
17. Marcovich N, Reboredo MM, Aranguren MI. Modified woodflour as thermoset fillers: II. Thermal degradation of woodflours and composites. Thermochimica Acta. 2001;372:45–57.
18. Alvarez VA, Vázquez A. Thermal degradation of cellulose derivatives/starch blends and sisal fibre biocomposites. Polym Degrad Stabil. 2004;84:13–21.
19. Manikandan Nair KC, Thomas S, Groeninckx G. Thermal and dynamic mechanical analysis of polystyrene composites reinforced with short sisal fibres. Compos Sci Technol. 2001;61:2519–29.
20. Pracella M, Pancrazi C, D'Alessio A, Corti A, Chiellini E. Property improvement and degradability control of polyolefin based composites containing natural fibres and mineral fillers. 13th Eur conf on composite materials, ECCM13, June 2008, Stochkolm, Sweden, Proc. ID-2640.