

PROPERTY IMPROVEMENT AND DEGRADABILITY CONTROL OF POLYOLEFIN BASED COMPOSITES CONTAINING NATURAL FIBRES AND MINERAL FILLERS

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ABSTRACT

Composites of isotactic polypropylene (PP) with hemp fibres and of polystyrene (PS) with cellulose, oat and CaCO₃ respectively, obtained by batch mixing, were examined. Either the modification of fibres with glycidyl methacrylate (Hemp-GMA) and the addition of various compatibilizers containing reactive groups (PP-*g*-GMA, SEBS-*g*-MA, PS-*co*-MA) were carried out to improve the fibre–matrix interfacial interactions. The modified components and their composites were characterised by FT-IR analysis, POM and SEM microscopy, WAXS, DSC, TGA and mechanical tests. The properties of binary and ternary composites were analysed as a function of the fibre amount and compatibilizer. The compatibilized systems showed enhanced fibre dispersion and interfacial adhesion as a consequence of chemical interactions between the functional groups on the polymer chains and the polar groups of the fibres. The thermal stability and phase behaviour of the composites resulted to be affected by the chemical modification of the fibres. Changes in the spherulitic morphology and overall crystallisation rate of PP were also observed in PP/Hemp composites due to the nucleating effect of the fibres. The mechanical properties of both PP and PS composites were found to depend at large extent on the fibre amount and on the structure and concentration of compatibilizer. Generally, higher tensile modulus and lower elongation at break were observed with increasing the fibre content; the addition of PP-*g*-GMA and PS-*co*-MA in PP/Hemp and PS/Cell composites, respectively, resulted in a higher stiffness as consequence of the improved fibre–matrix adhesion.

1. INTRODUCTION

Polymer composites based on natural fibres (vegetal fibres, cellulose and derivatives) are attracting great attention as alternative materials to glass or synthetic fibre reinforced plastics in several applications, mostly for automotive, appliance and packaging products. The main advantage of employing natural fibres is that these are biodegradable and renewable, and exhibit low cost, low density and high toughness [1, 2]. However the low compatibility between fibres and polymer matrix generally leads to weak mechanical performances, limiting the use of these materials. Other factors which can largely affect the composite properties are concerned with the size, geometry and dispersion of filler particles in the matrix. 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 is 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]. Maleated PP (PP-*g*-MA) has been extensively used as compatibilizer in various polyolefin composites with natural fibres [4, 5]. The other important opportunity is the physical and chemical modification of the fibres, such as the use of surface treatments or the insertion of functional molecules which can be exploited in secondary reactions (i.e., radical grafting) with the polymer matrix, providing a stable network of bonding between the components [6].

We analysed the effect of reactive compatibilization processes on the morphological, thermal and mechanical properties of thermoplastic composites, both crystalline and amorphous, based on isotactic polypropylene (PP) and polystyrene (PS) as matrix, containing hemp, cellulose or oat as natural fillers, respectively. In the case of PS based systems the properties of composites reinforced with CaCO_3 particles were also investigated. In particular, the study was aimed at evaluating the role of various compatibilization methods, processing conditions and compatibilizer structure, as well as the type and concentration of filler, on the interfacial interaction phenomena, the crystallization processes of the polymer matrix and, finally, the degradation behaviour of these materials.

2. EXPERIMENTAL PART

2.1 Materials

Isotactic polypropylene (PP) with MFR= 12 g/10min was purchased from Targor (Italy). Polystyrene (PS) was a (1:1) mixture of crystal type and high impact Polystyrene supplied by TERMOPAIF (Italy).

Hemp fibres (*cannabis sativa*) were supplied by Technical University of Poznan (Poland); the fibres were grounded in a laboratory miller (Frish-Pulverisette 14, GmbH) up to a length less than 250 μm and then treated with caustic soda to remove surface impurities (Hemp-OH). Oat particles (*avena sativa*) derived from ground oat husks (size smaller than 75 μm) were supplied by Chemical Net (Poland). According to the supplier, the particles contained 50 wt.% cellulose, 25 wt.% hemicellulose and 3-5 wt.% lignin. Cellulose fibres (Technocel 75), with average length of 75 μm and cellulose content of 99.6 %, were provided by Neuchem (Italy).

PP was functionalized with glycidyl methacrylate (PP-g-GMA, 5 wt.% grafted GMA) according to a melt radical grafting procedure reported elsewhere [7] and employed as compatibilizer for PP/Hemp. A styrene-(ethylene-butene)-styrene block copolymer grafted with maleic anhydride (SEBS-g-MA) by Shell (Kraton FG-1901X, MFR= 20-25 g/10min) containing 1 wt.% MA, and a poly(styrene-co-maleic anhydride) copolymer (PS-co-MA) by Sigma-Aldrich (M_w = 224.000, MFR= 1.7 g/10min) containing 7 wt.% MA, were used as compatibilizers for PS/Cell samples. Low molecular weight poly(ethylene glycol) (PEG) with M_w = 600 by Sigma-Aldrich was employed in PS/Oat composites. Before use all materials were carefully dried under vacuum at 90 °C in order to reduce the moisture content.

Composites of PP and PP-g-GMA with hemp (PP/Hemp, PP-g-GMA/Hemp) and modified hemp (PP/Hemp-GMA) at various composition ratios were prepared in a Brabender internal mixer at 170 °C (60 rpm, 7 min) using different compounding procedures. Composites of PS with cellulose (PS/Cell) or oat (PS/Oat) and with CaCO_3 (PS/ CaCO_3) were obtained by melt mixing the components in Brabender at 180/200 °C (50 rpm, 8 min). For these materials, the natural fillers were used as received, without any surface treatment. Compatibilized systems, with various fibre amount (10-40%) and compatibilizer content (2-16 phr), were prepared by feeding all components together into the mixer. Plain polymers (PP, PS) and their mixtures with copolymers were processed under the same conditions; the torque moment in the mixer was also monitored as a function of the mixing time.

2.2 Analytical techniques

The morphology of blends was examined on the surfaces of bulk samples and films freeze-fractured in liquid nitrogen; the samples were sputter-coated with a fine layer of

gold in an Edward sputter coater and analysed with a Jeol T300 scanning electron microscope.

FT-IR spectra of films of composites and plain components, obtained by compression moulding at 170/180 °C, were recorded by means of a Perkin-Elmer spectrophotometer (mod. 2000) in the 4000–400 cm⁻¹ frequency range, with a resolution of 2 cm⁻¹.

Wide-angle X-ray scattering (WAXS) analysis of PP composites was performed at room temperature with DRON-20 diffractometer connected with a Phillips generator operating at 50 kV and 30 mA, using the CuK α radiation (λ = 0.1546 nm).

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 for 2 min, then cooled to room temperature and again heated up to 190 °C (2nd heating run). Temperatures and heats of transition were measured at the max and from the areas of the crystallization/melting peaks. Glass transition temperatures were determined at the midpoint of the heat capacity change. For the isothermal crystallization kinetics, PP/Hemp samples were melted up to 190 °C at 10 °C/min, kept at this temperature for 5 min in order to erase any previous thermal history and then rapidly cooled (100 °C/min) to a prefixed T_c , recording the heat of crystallization as a function of time.

Thermal degradation of composites and pure components was analysed with a TGA MK2 (Rheometric Scientific) in the range from 50° to 800 °C at a heating rate of 10 °C/min, in N₂ atmosphere.

Mechanical analysis was carried out by means of an Instron testing machine. Sheets of 1 mm and 0.4 mm thickness were obtained for PP and PS composites, respectively, by compression moulding in a Carver laboratory press at 170/190 °C for 5 min, followed by slow cooling at room temperature. Test specimen were cut from the sheets in bar shape with length of 50 mm and width of 10 mm. Tensile tests were carried out at room temperature on at least 5 specimens of each sample, using cross-head speeds of 0.5 mm/min for PP composites and 5 mm/min for PS composites.

Degradability tests were carried out on PS dish samples manufactured and supplied by TERMOPAIF (Italy), incorporating pro-degradant additives. The oxidation level of the samples was monitored within the time by the determination of the carbonyl index (CO_i) by means of FT-IR spectroscopy, weight variation, and molecular weight analysis by SEC chromatography. The CO_i index was calculated as the ratio of the optical density of the absorption bands at 1690 and 1840 cm⁻¹ (carbonyl peak), and the optical density of the overtone band at 1940 cm⁻¹ of the aromatic ring. At the end of each thermal degradation test, the samples showing the higher oxidation levels were selected for assessing the ultimate biodegradation propensity under different environmental conditions. Respirometric tests based on the determination of the CO₂ evolution according to ISO standard procedures are ongoing on pre-aged samples both in river water (ISO 14852) and soil (ISO 17556).

3. RESULTS

3.1 PP/Hemp composites

Modification of hemp fibres was performed by exploiting the reaction of the hydroxyl groups of hemp (after treatment with NaOH) with glycidyl methacrylate monomer in triethylamine solution, which gives rise to the formation of ether bonds at the fibre surface (Hemp-GMA), according to the procedure described in ref. [8]. After reaction, the modified fibres were separated by filtration and rinsed with acetone to remove the unreacted reagent and possible GMA homopolymer formed during the reaction. The Hemp-GMA fibres could react with PP during the melt mixing, in the presence of a

radical initiator (BTP), through the attack of PP macroradicals to the double bond of methacrylate moiety of GMA.

The grafting reaction was monitored by means of FT-IR spectroscopy: spectra of modified fibres, recorded at different reaction times, showed a marked absorption in the carbonyl region (1710 cm^{-1}) and peaks (1668 and 1630 cm^{-1}) associated with the methacrylic ester bond and the double bond of GMA respectively. The SEM analysis of PP/Hemp-GMA and PP/Hemp/PP-g-GMA composites clearly indicated an improved adhesion of the fibres to the matrix as a consequence of the effective interactions at the interface (Figure 1).

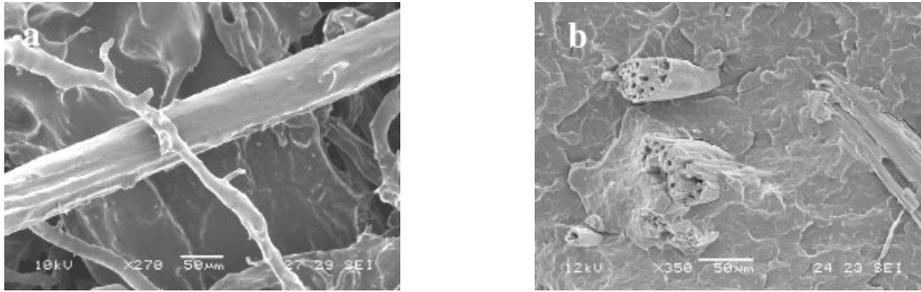


Fig. 1: SEM micrographs of (a) GMA modified hemp fibres and (b) PP/Hemp 90/10 compatibilized with PP-g-GMA (10 phr) [8].

The effect of fibres modification and concentration on the phase behaviour of polymer matrix was examined by DSC under dynamic and isothermal conditions. The addition of hemp to PP resulted in an increase of crystallization temperature and crystallinity of PP matrix, and a further increase was observed in the presence of modified fibres (PP/Hemp-GMA). The crystallisation behaviour of the matrix was examined by studying the isothermal crystallization kinetics of the various samples in the range 120–138 °C using the Avrami model [9]:

$$X_t = 1 - \exp[-K_n t^n] \quad (1)$$

where K_n is the kinetic constant and n the Avrami exponent, depending on growth geometry and nucleation type of the crystals.

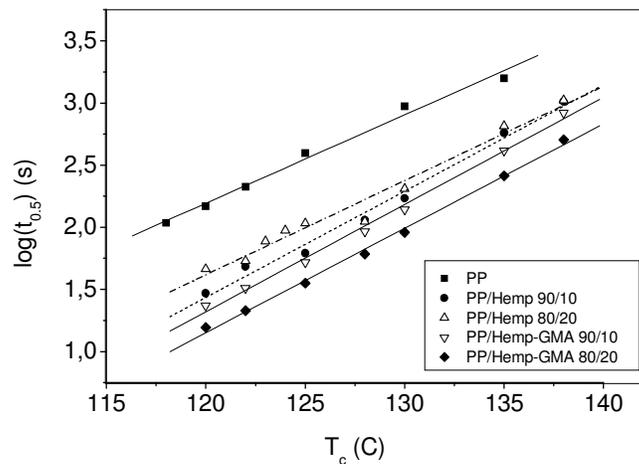


Figure 2: Temperature dependence of the crystallization half-time for PP, PP/Hemp and PP/Hemp-GMA composites isothermally crystallized from the melt.

The variation of the crystallization half-time ($t_{0.5}$), i.e. the reciprocal of the overall crystallization rate, is pointed out in Figure 2 for all examined samples, as a function of the crystallization temperature (T_c). In all the investigated temperature range, it was noticed an increase of about one order of magnitude in the crystallization rate of composites with respect to neat PP, at the same T_c . Moreover, the composites with modified Hemp (PP/Hemp-GMA 90/10 and 80/20) displayed higher crystallization rates (lower $t_{0.5}$) than PP/Hemp. Since the overall crystallization rate of the polyolefin is related to the spherulite growth rate and the number of primary nuclei per unit volume [9], and as the growth rate is not affected by the fibre content, the increase of the overall crystallization rate in the composites can be ascribed to the increased crystal nucleation density on the fibres surface [10, 11]. This effect was more marked for composites with Hemp-GMA mainly as a consequence of the enhanced fibre–matrix interactions. The results of TGA analysis evidenced a higher thermal stability of the GMA modified fibres with a maximum degradation rate at 321 °C, as compared to the unmodified hemp (max at about 300 °C) and to NaOH treated hemp (max at about 315 °C).

Table 1. Tensile properties of PP, PP/Hemp and PP/Hemp/PP-g-GMA composites

Sample	Composition	PP-g-GMA	Tensile modulus	Stress at max	Stress at break	Elongation at break
	crystallization	(phr)	(MPa)	(MPa)	(MPa)	(%)
PP	100	–	1800	31.8	19.8	18.0
PP/Hemp	90/10	–	2600	27.0	25.4	4.0
PP/Hemp	90/10	5	1900	27.9	27.2	3.5
PP/Hemp	90/10	10	3100	27.8	26.9	2.6
PP/Hemp	80/20	–	2800	25.7	24.8	2.8
PP/Hemp	80/20	5	2500	23.1	22.2	2.2
PP/Hemp	80/20	10	3000	25.7	25.3	2.3

For all composites the tensile tests showed a rather brittle behaviour otherwise that observed for plain PP. As reported in Table I, a marked increase of the Young modulus was found for PP/Hemp samples when compared to plain PP, while the strength at max and elongation at break decreased, as found for other natural fibre reinforced polypropylene composites [12]. An increase of stiffness was observed in the presence of PP-g-GMA, which can be related to the effect of the compatibilizer on the interfacial adhesion: values of modulus above 3000 MPa were found for PP/Hemp samples added with 10 phr PP-g-GMA.

3.2 Composites with PS matrix

The SEM analysis of fracture surfaces of PS composites with cellulose or oat displayed in all cases a good filler dispersion with a poor adhesion between matrix and particles (Figure 3).

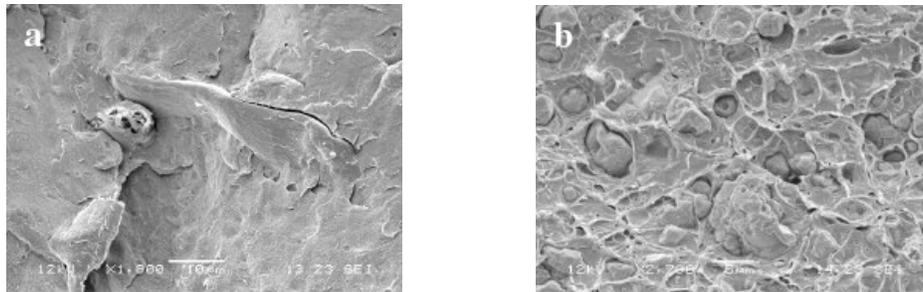


Figure 3: SEM micrographs of (a) PS/Cell and (b) PS/Oat composites.

For PS/Cell the addition of compatibilizers containing reactive groups - able to give rise to chemical reactions with the hydroxyl groups on the fibre surface - determined an improvement of the interfacial adhesion with reduced pull-out phenomena.

PS/Cell samples containing SEBS-*g*-MA and PS-*co*-MA copolymers were analysed by FT-IR spectroscopy to investigate the effect of the compatibilizer at the polymer-fibre interface. The occurrence of interactions between maleic anhydride and hydroxyl groups of cellulose was carefully examined in the frequency ranges 2000-1650 cm^{-1} and 1200-850 cm^{-1} respectively. FT-IR spectra of composites are shown in Figure 4. Significant shifts of the MA carbonyl stretching band (ν_{CO}) at about 1780 cm^{-1} and relevant ester band (ν_{COO}) near to 1740 cm^{-1} were recorded, as well as the changes of alcohol (ν_{COH}) and ether (ν_{COC}) stretching in the spectra of cellulose at 1164, 1114, 1060 and 1033 cm^{-1} respectively, were supporting the formation of stable ester bonding at the fibre/matrix interface.

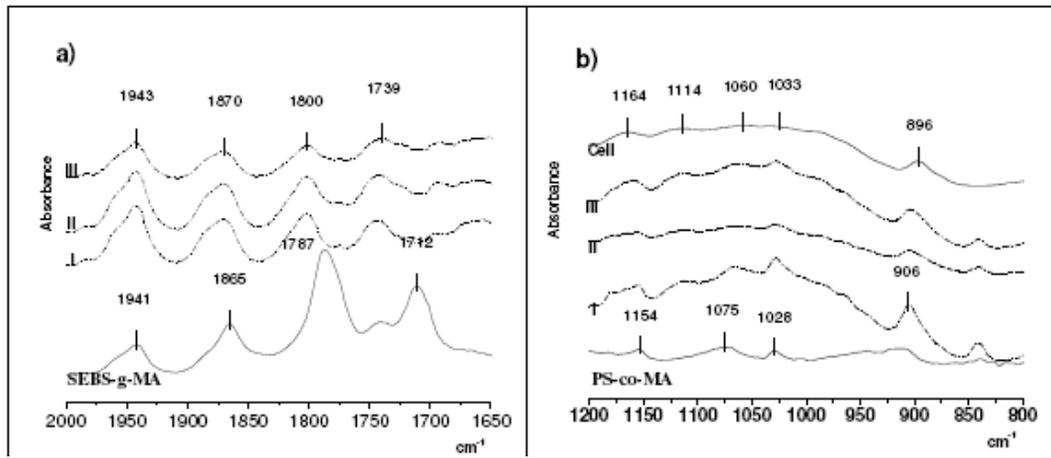


Figure 4: FT-IR spectra of PS/Cell compatibilized with (a) SEBS-*g*-MA and (b) PS-*co*-MA; samples containing (I) 20%, (II) 30% and (III) 40% by weight of cellulose.

The glass transition behaviour of the PS matrix in the composites was examined by DSC as a function of the filler content and type of compatibilizer. For uncompatibilized PS/Cell samples a variation of T_g was observed only at higher contents of cellulose, while a significant effect was recorded on the addition of compatibilizer. For samples containing SEBS-*g*-MA, T_g increased with increasing the fibre content from 94 °C (plain PS) to about 100 °C (40% Cell), but a minor increment was found for samples compatibilized with PS-*co*-MA.

The values of tensile modulus, for binary composites of PS with Cell, Oat and CaCO_3 , are compared in Figure 5 for filler contents ranging from 10 to 40 wt.-%. PS/Cell and PS/Oat samples showed a rather brittle behaviour similar to that observed for PP/Hemp. The variation of tensile modulus for PS/Cell composites, compatibilized both with PS-*co*-MA and SEBS-*g*-MA, is reported as a function of fibre content in Figure 6. A marked increase of the modulus up to about 1750 MPa was found for PS/Cell (60/40) upon addition of PS-*co*-MA (16 phr), while the strength at max and elongation at break decreased, as compared to plain PS and uncompatibilized samples. Otherwise, the addition of SEBS-*g*-MA copolymer caused a ductile behaviour with lower modulus and increased elongation at break, owing to the ethylene-butene elastomeric block in the copolymer chain [13]. However, as it was pointed out by SEM analysis of fracture

surfaces of binary SEBS-g-MA/Cell samples, a stronger surface adhesion accompanied by extended fibre fraying was noticed with respect to PS-co-MA/Cell samples. For PS/Oat composites the addition of PEG (5-10 phr), as plasticizer, resulted in a decrease of modulus and tensile strength, but with a neat improvement of the elongation at break.

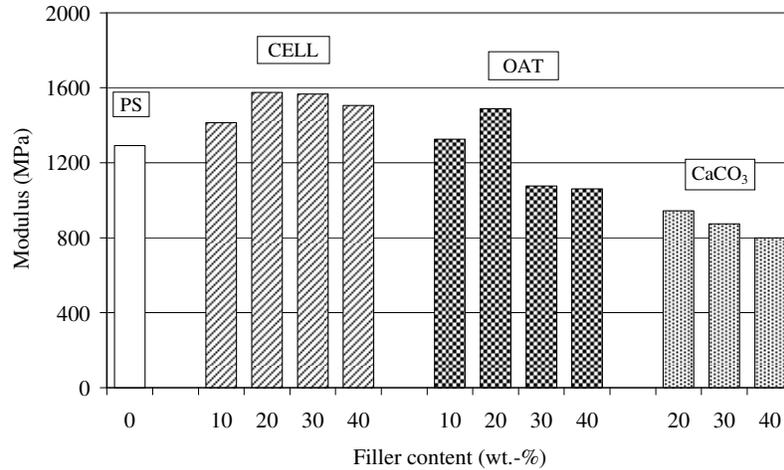


Figure 5: Values of elastic modulus for PS/Cell, PS/Oat and PS/CaCO₃ composites vs. filler content.

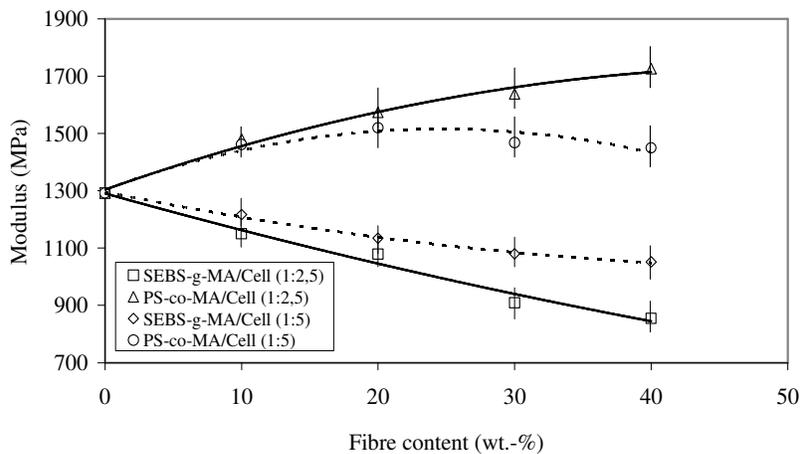


Figure 6: Elastic modulus of PS/Cell composites compatibilized with PS-co-MA and SEBS-g-MA (at different copolymer/fibre ratio) as a function of cellulose content.

3.3 Degradability tests

PS based composites containing pro-degradant additives were submitted to a preliminary investigation aimed at evaluating their oxo-biodegradation behaviour by means of thermal degradation eventually followed by biodegradation assays. Weight variation profiles of the analyzed materials recorded within 4 months thermal treatment in air-ventilated oven at 65°C are reported in Figure 7.

In the case of PS-II sample, a weight increase approaching 1.8 % has been recorded after 40 days of thermal aging. After 50 days the weight appeared to remain practically constant. Lower, but significant weight increase was recorded also in the case PS-I

sample containing a different pro-oxidant. On the contrary, the weight of the control pro-oxidant free PS sample starts to show an appreciable variation only after 80 days of thermal aging.

The observed weight increase of pro-oxidant containing samples can be attributed to the formation of oxidized functional groups, in accordance with the behaviour recorded in the case of thermal aging of low density polyethylene samples containing similar pro-degradant additives [14]. Furthermore, the increase of the weight was accompanied by a discoloration of the sample from the original white-grey to a light yellow colour. In order to verify if the supposed oxidation process, as induced by the presence of the pro-oxidant, is involving the polystyrene chains, thermally treated samples were also characterized by both FT-IR and SEC analysis. In accordance, no significant variations of either molecular weight or molecular weight distribution were detected within the 4 month treatment in air-ventilated oven at 65° C. The recorded data, are therefore suggesting that the oxidation process of thermally treated PS samples does not involve an appreciable random polymer chains scission, at least within the applied aging time, which has been instead repeatedly ascertained in the case of others pro-oxidant containing polyolefins such as poly(propylene) (PP) and LDPE [14, 15].

These results seems to confirm the effectiveness of the used pro-oxidant additives in promoting and accelerating the thermal oxidation process of polyolefins, even though with market differences depending on the structural feature of the polyolefin. In particular, it was rather surprising to observe the absence of any evident chain scission of PS macromolecules if compared with the dramatic chain fragmentation recordable in analogous PP samples, which are characterized by substantial identical succession of easily oxidizable methyne carbon atoms in the main chains.

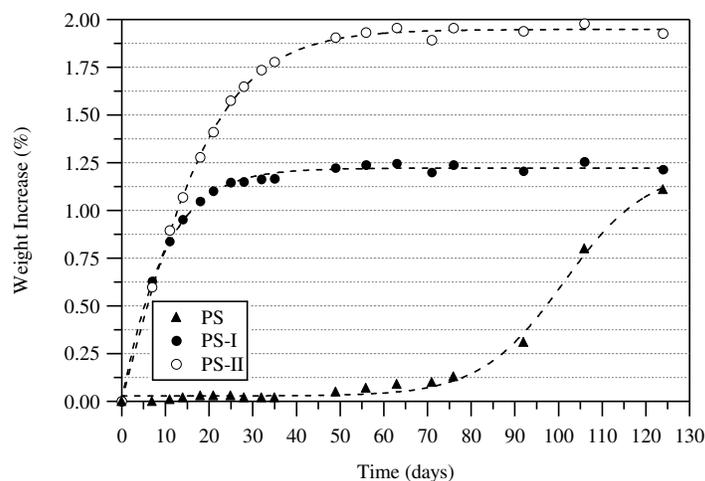


Figure 7: Time variation profiles of weight percent increase of PS additivated and PS control samples submitted to thermal treatment at 65°C in air-ventilated oven.

It is however to be mentioned that the mechanism of oxidation is rather complex and far from to be exhaustively understood at least from the results attained in time frame of performed test. In fact, different types of reactions starting from the formation of macroradicals by hydrogen abstraction mainly from tertiary carbon atoms of the PS backbone are involved with a formation of a free radical. Once formed, the macroradicals in the presence of oxygen are converted to peroxy-radicals and furthermore to hydroperoxy group by hydrogen abstraction from the polymer chain. The

decomposition of hydroperoxy groups, either by photolysis or thermolysis, leads to the formation of alkoxy macroradicals that may react in several ways leading to the formation of several low molecular weight degradation products including acetophenone, benzaldehyde, benzoic acid, formic acid, acetic acid, benzene, dibenzoylmethane, benzoic anhydride [16, 17]. These compounds are apparently deriving from a chain end oxidation-depolymerization mechanism. In accordance, only slight weight variations are appreciable, as consequence of the hindered chain fragmentation.

4. 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 paper the effect of chemical modification of fibres, as well as the addition of compatibilizers containing reactive groups (PP-*g*-GMA, SEBS-*g*-MA, PS-*co*-MA), on the morphological, thermal and mechanical characteristics has been examined for PP and PS composites containing hemp, 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. An increased thermal stability was found in PP composites with GMA modified hemp; moreover, marked changes in the morphology and overall crystallization rate of PP were observed in these composites due to the enhanced nucleating effect at the fibre surfaces as a consequence of polymer grafting reactions. For all examined materials, the mechanical analysis showed that modulus, tensile strength and elongation at break are largely affected by the type and amount of fibre, as by the structure (and concentration) of compatibilizer; in particular, the addition of functionalized polyolefins (PP-*g*-GMA, PS-*co*-MA) resulted in an increased stiffness owing to the improved fibre-matrix adhesion. 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. This can be ascribed to the fact that the block copolymer is mostly located at the interface between filler particle and matrix, giving rise to more effective interactions with the polar groups of the fibre.

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