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Mechanical properties of short flax fibre bundle/poly(ε-caprolactone) composites: Influence of matrix modification and fibre content

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Abstract

Composites were prepared by mixing biodegradable poly(ε-caprolactone) thermoplastic (PCL) with short flax fibre bundles. In order to improve fibre/matrix adhesion, poly(ε-caprolactone)-*g*-maleic anhydride copolymer (PCL-*g*-MA) compatibilizer was prepared in an internal mixer. The grafting reaction of maleic anhydride (MA) onto PCL polymer was carried out in presence of dicumyl peroxide as initiator. Mechanical properties were analysed as a function of compatibilizer concentration and fibre amount. In addition, thermal properties of flax/PCL and flax/PCL-*g*-MA composites were also examined by thermogravimetric (TG) analysis. Composites fabricated with flax fibre bundles and PCL-*g*-MA matrix showed the highest tensile and flexural strength. Scanning electron microscopy (SEM) of fractured surfaces confirmed the adhesion improvement between flax fibre bundles and PCL-*g*-MA matrix. Results obtained by thermogravimetric analysis showed that fibre addition and matrix modification slightly reduced the thermal stability of composites. The correlation between the experimental mechanical properties of short flax fibre bundle reinforced PCL composites with values calculated by various empirical models has also been analysed. For composites based on PCL-*g*-MA matrix, a good agreement was found between empirical model and experimental values for all fibre contents. However, for composites based on PCL matrix a good agreement only existed until 20 wt% flax fibre content, and beyond this value, experimental strength felt well below predictions.

Keywords: Flax fibres; Polymer–matrix composites; Polycaprolactone; Compatibilization; Mechanical properties

1. Introduction

The growing environmental awareness and new rules and regulations are forcing the industries to seek more ecologically friendly materials for their products (Oksman, Skrifvars, & Selin, 2003). The use of disposable plastic materials increases the undegradable waste portion, making it necessary the development of more recyclable and/or biodegradable plastics to reduce the amount of plastic to landfill (Iannace, Nocilla, & Nicolais, 1999). Most composite materials currently available in the market are made from no degradable polymeric matrices and fibres (Luo & Netravali, 1999). These synthetic polymers are based on non-renewable petroleum resources that do not degrade easily in the environment (Lee & Ohkita, 2003), causing many environmental problems associated with their disposal (Shimao, 2001; Wu, 2003). Therefore, much effort has been made in recent years to develop biodegradable materials which could contribute to the solution for waste-disposal problems associated with traditional no biodegradable synthetic polymers (Curvelo, de Carvalho, & Agnelli, 2001; Matzinos, Tserki, Gianikouris, Pavlidou, & Panayiotou, 2002; Mohanty, Misra, & Hinrichsen, 2000). However, these polymers are still very expensive and therefore not economically competitive when compared with commodity plastics (Amass, Amass, & Tighe, 1998; Corradini, Mattoso, Guedes, & Rosa, 2004). Properties and cost of biodegradable polymers can be modified and improved through the use of lignocellulosic fibres that reduce the cost of the material without modifying their biodegradability (Iannace et al., 1999). In the literature there already exist some reports on biocomposites (Luo & Netravali, 2001; Nishino, Hirao, Kotera, Nakamae, & Inagaki, 2003; Plackett, Andersen, Pedersen, & Nielsen, 2003; Shibata, Yosomiya, Ohta, Sakamoto, & Takeishi, 2003). Natural fibres have proven to be suitable reinforcement materials for composites as they combine good mechanical properties with environmental advantages as they are abundant and biodegradable (Bledzki & Gassan, 1999).

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One of the most important biodegradable polymer is poly(ε-caprolactone), PCL, which is a synthetic semicrystalline linear aliphatic polyester (Elzein, Nasser-Eddine, Delaite, Bistac, & Dumas, 2004) that can be degraded by microorganisms (Shimao, 2001). Different possibilities (Nitz, Semke, Landers, & Mülhaupt, 2001; Shibata et al., 2003; Tserki, Matzinos, & Panayiotou, 2003) to improve lignocellulosic fibre and biodegradable polymer matrix adhesion and compatibility can be found in the literature survey. Shibata et al. (2003) found that tensile strength of PCL/abaca composites was improved by abaca fibre surface treatment with acetic anhydride or butyric anhydride in the presence of pyridine. One of the most successful methods to improve composites strength is the addition of a compatibilizer. Tserki et al. (2003) found for cotton fibre/biodegradable polyester composites that the addition of biodegradable polyester-*g*-MA compatibilizer improved their mechanical properties. Nitz et al. (2001) found that mechanical properties of reinforced PCL compounds based on wood flour and lignin enhanced with the addition of PCL-*g*-MA compatibilizer. As flax fibre and wood flour contain similar functional groups, grafting of maleic anhydride onto PCL polymer can be expected to improve the compatibility between flax fibre and PCL matrix.

The objective of this work was to analyse the influence of addition of PCL-*g*-MA copolymer, prepared by grafting maleic anhydride onto PCL, on the mechanical properties of PCL composites with different amounts of flax fibre contents. Morphological and thermal properties of flax/PCL and flax/PCL-*g*-MA composites have been examined by scanning electron microscopy and thermogravimetric analysis, respectively. In addition, empirical models have been used to predict composites mechanical performance.

2. Experimental

2.1. Materials

A commercially available poly(ε-caprolactone) CAPA 6800 produced by Solvay with a melting temperature of 60–62 °C and a melt flow index of 7.29 g/10 min (at 230 °C and 2.16 kg) was used as polymeric matrix (Solvay Company, 2001). As reinforcement flax fibre bundles obtained by a retting process were used. These fibre bundles were kindly supplied by Finflax (Finland). The density of the flax was estimated to be 1.4 g/cm^3. Maleic anhydride (MA), kindly supplied by Cepsa, and dicumyl peroxide with a purity of 98% supplied by Aldrich Co., were used for grafting MA onto PCL.

2.2. Preparation of the PCL-g-MA

PCL-*g*-MA copolymer was prepared by grafting maleic anhydride onto PCL in an internal mixer (Haake Rheomix 600 with two Banbury rotors) using dicumyl peroxide as initiator. After PCL melting 4.5 wt% MA (respect to PCL content) and 0.4 wt% dicumyl peroxide (respect to PCL content) were added and mixed at 40 rpm for 10 min at 150 °C.

2.3. GPC measurements

Analytical gel permeation chromatography (GPC) was performed with a Perkin–Elmer LC-295 chromatograph equipped with refractive index detector LC-30 RI to determine the changes in molecular weight and molecular weight distribution with grafting maleic anhydride onto PCL. A kit of three Waters styragel columns, HR 1, HR 2 and HR 4, whose molecular weight range detection is 100–5000, 500–20,000 and 50,000–500,000, respectively, was used. The mobile phase was tetrahydrofuran at a flow rate of 1 mL/min at room temperature. Number and weight average molecular weights were calculated using a universal calibration method with polystyrene standards. Mark–Houwink corrections were performed to determine average molecular weights ($K_{\mathrm{PS}}=1.25\times10^{-4}$ dL/g, $a_{\mathrm{PS}}=0.707$; $K_{\mathrm{PCL}}=1.09\times10^{-3}$ dL/g, $a_{\mathrm{PCL}}=0.600$) (Singh, Pandey, Rutot, Degee, & Dubois, 2003).

2.4. Compounding and processing

Compounding was carried out using an internal mixer and mixing temperature was set at 150 °C. For composites based on PCL matrix, first PCL and previously prepared PCL-*g*-MA pellets were fed and after melting, dried flax fibre bundles were added. On the other hand, for composites based on PCL-*g*-MA matrix, after PCL melting maleic anhydride and dicumyl peroxide were added, then mixing the blend at 40 rpm for 1 min. Then dried flax fibres were added and whole mixing process last about 10 min. The loading of flax fibres varied from 0 to 60 wt%. Finally, the blend was pelletized and pellets were moulded using an injection-moulding machine (Battenfeld Plus 250).

2.5. Matrix modification

In order to compare the effect of compatibilizer amount on mechanical properties, 30 wt% flax fibre bundle composites were prepared. PCL matrix was modified adding previously prepared PCL-*g*-MA compatibilizer agent. 1, 2, 3, 4, 5, 10, 20 and 40 wt% amounts respect to fibre bundle content were used. These amounts correspond to 0.30, 0.60, 0.89, 1.19, 1.48, 2.91, 5.66 and 10.7 wt% respect to the total composite weight, respectively. PCL-*g*-MA was fed directly into the melt mixer. On the other hand, in order to compare, 30 wt% flax fibre bundle content composites were fabricated also using PCL-*g*-MA polymer as matrix.

2.6. Mechanical testing of composites

Tensile and three-point bending tests were carried out using a universal mechanical testing machine Instron, model 4206. The crosshead rates used were 5 and 1.7 mm/min for tensile and flexural tests, respectively. The gauge length used was 115 mm for tensile test and the span for flexural test was 64 mm. At least five specimens were tested for each set of samples being the mean values reported.

2.7. Thermogravimetric analysis measurements

In order to study the thermal stability of flax fibre, neat PCL and composites, thermogravimetric (TG) analyses have been carried out using a Setaram thermoanalyser (Model 92) in helium atmosphere. Thermograms were recorded from room temperature to 800 °C at a heating rate of 10 °C/min.

2.8. Scanning electron microscopy (SEM)

Scanning electron microscopy, JEOL JSM-5510, was used to analyse as fractured surfaces of composites. Prior to the analysis, the specimens were coated with a thin gold/palladium alloy layer using a sputter coater Bal-tec SCD005 to avoid charging.

2.9. Polarized optical microscopy: crystallinity

Morphology studies were carried out using a Nikon Eclipse E600W polarized optical microscope equipped with a Mettler hot stage (model FP82HT). Single fibre-embedded PCL and PCL-*g*-MA film samples were prepared by placing a fibre on the molten polymer and covering with a cover slip. The system was heated above the melting point of polymer and maintained at 85 °C for 5 min to erase the previous thermal history. Then sample was cooled at a rate of 10 °C/min to 45 °C crystallization temperature.

2.10. Analysis of tensile properties

Several models have been used to predict mechanical properties for composites based on lignocellulosic fibres and polymeric matrices (Garkhail, Heijenrath, & Peijs, 2000; Kalaprasad, Joseph, Thomas, & Pavithran, 1997; Van den Oever, Bos, & Van Kemenade, 2000). In this work as a first approach, experimental values were fitted to the following equations (Ali, Iannace, & Nicolais, 2003):

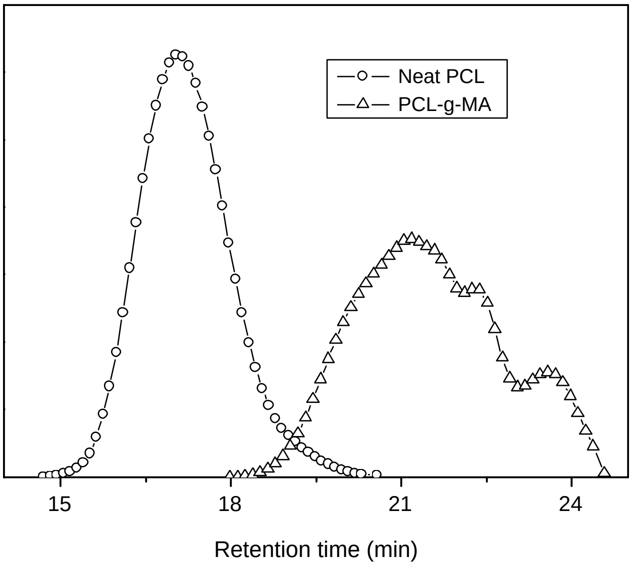


Fig. 1. GPC chromatograms for the neat PCL and PCL-*g*-MA samples.

$$\sigma_c = k_S V_f \sigma_f + (1 - V_f)\sigma_m \tag{1}$$

$$k_S = k_0 k_1 \tag{2}$$

where σ_f and σ_m are fibre tensile strength and matrix strength, respectively, and V_f is the fibre volume fraction. k_S is a strength efficiency factor which depends on k_0 and k_1. k_0 is the efficiency factor related to the orientation of the fibres in the composite and k_1 is related to the effectiveness of load transfer between fibres and matrix, and

$$E_c = k_E V_f E_f + (1 - V_f)E_m \tag{3}$$

where E_f and E_m are fibre tensile modulus and matrix modulus, respectively, and k_E is the modulus efficiency factor related to the orientation of the fibres in the matrix.

3. Results and discussion

3.1. Characterization of maleated-PCL

Fig. 1 shows GPC chromatograms for the original PCL and PCL-*g*-MA samples. The original PCL presents one peak at a retention time of 17 min. The peaks of PCL-*g*-MA appear at higher retention times suggesting that after anhydride maleic grafting onto PCL polymer chains scission occurred. Table 1 shows the number-average and weight-average molecular weights as well as polydispersity index of original PCL and PCL-*g*-MA samples. Results show that after anhydride maleic grafting onto PCL, the molecular weight clearly decreased becoming the distribution broader. During grafting process, three main reactions are feasible: acid-catalysed degradation of the polyester through the maleic anhydride, grafting of maleic anhydride onto PCL backbone and crosslinking of PCL (Nitz et al., 2001). As PCL-*g*-MA product obtained was soluble in THF, there was no crosslinking reaction occurring during grafting procedure, which is in agreement with results reported by other authors (John, Tang, Yang, & Bhattacharya, 1997; Nitz et al., 2001). Grafting conditions used in this study possibly led to acid-catalysed degradation of the original PCL producing short chains length PCL-*g*-MA.

3.2. Matrix modification with PCL-g-MA

Fig. 2a and b shows the effect of amount of PCL-*g*-MA coupling agent on tensile and flexural strength of composites. Flax fibre bundle content was set at 30 wt% and for comparison purpose tensile and flexural properties values of PCL-*g*-MA polymer reinforced with flax fibre bundle are also plotted. Both tensile and flexural strengths show similar trends. The addition

Table 1
Retention time and number-average and weight-average molecular weights as well as polydispersity index of original PCL and PCL-*g*-MA samples

Sample	Time (min)	M_w (g/mol)	M_n (g/mol)	I_{PD}
Neat PCL	17.0	207,625	102,265	2.03
PCL-*g*-MA	21.1	7141	4767	1.49
	23.5	1420	1376	1.03

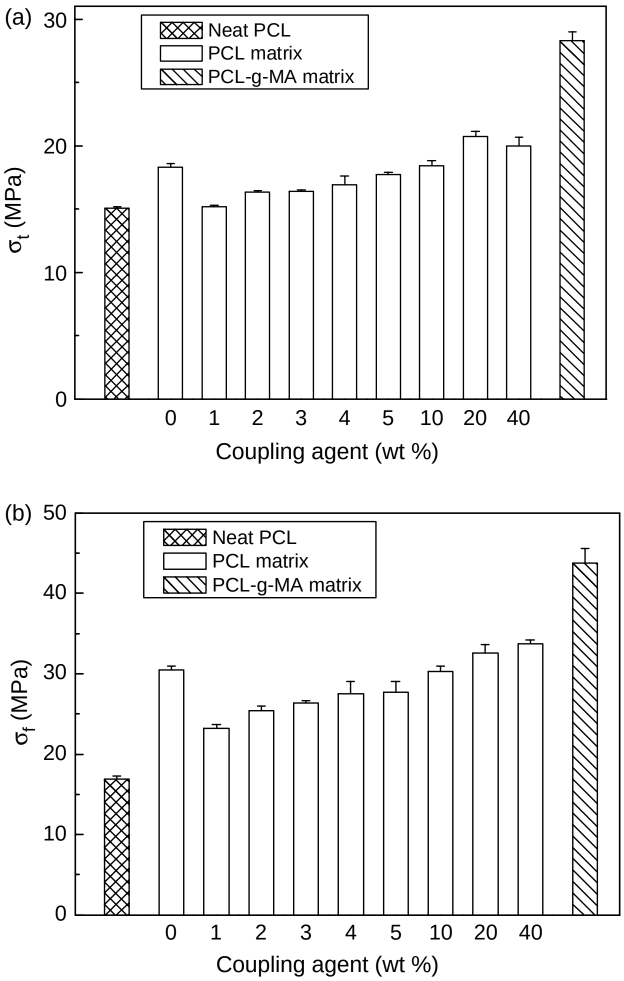


Fig. 2. (a) Tensile strength of 30 wt% flax fibre/PCL composites as a function of PCL-*g*-MA coupling agent amount. (b) Flexural strength of 30 wt% flax fibre/PCL composites as a function of PCL-*g*-MA coupling agent amount.

up to 5 wt% PCL-*g*-MA resulted in composites with lower tensile and flexural strength. This behaviour can be explained taking in account both molecular weight of PCL-*g*-MA coupling agent and samples morphology. Further addition of PCL-*g*-MA coupling agent gradually improved strength. The improvement of strength may be due to the formation of chemical bonds between anhydride groups of PCL-*g*-MA and hydroxyl groups of flax fibres (Nitz et al., 2001), thus enhancing stress transfer from the matrix to the fibres. When the matrix used is PCL-*g*-MA polymer, the improvement obtained for tensile and flexural strength are 54 and 44%, respectively. Fig. 3 shows the stress–strain behaviour for neat PCL, flax fibre/PCL and flax fibre/PCL-*g*-MA composites. After grafting MA onto PCL matrix, the obtained PCL-MA polymer was rather brittle and tensile samples for testing could not be produced. All curves extended into the non-linear region. Modulus, which was determined from the initial slope of the stress–strain curve, was increased after fibre addition. Besides, modulus was similar for both types of flax fibre/polymeric matrix composites. However, composites based on PCL-MA matrix showed highest tensile strength as a consequence of better fibre/matrix adhesion.

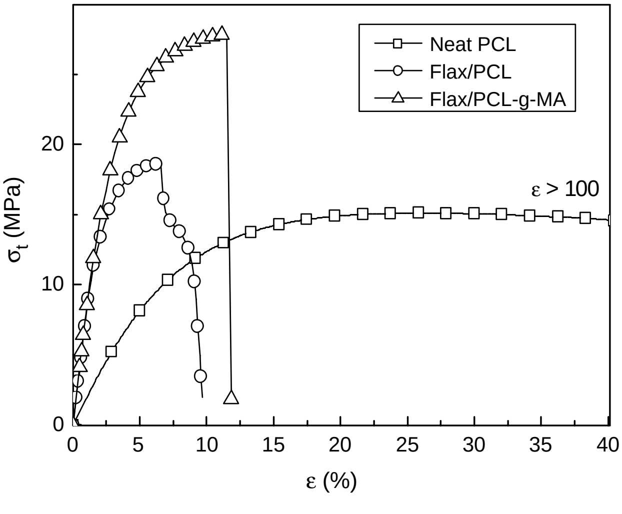


Fig. 3. Tensile stress vs. deformation curves for neat PCL, 30 wt% flax fibre/PCL and 30 wt% flax fibre/PCL-*g*-MA samples.

Fig. 4a and b shows the influence of PCL-*g*-MA coupling agent amount on tensile and flexural modulus. Both modulus also showed similar trends. When the compatibilizer was added, modulus values felt down. Beyond 1 wt%

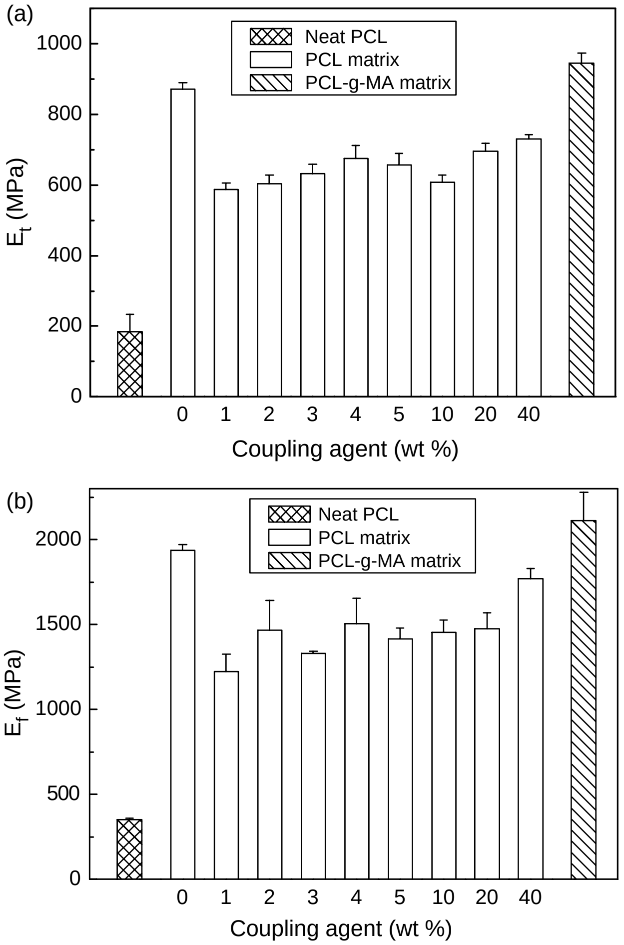


Fig. 4. (a) Tensile modulus of 30 wt% flax fibre/PCL composites as a function of PCL-*g*-MA coupling agent amount. (b) Flexural modulus of 30 wt% flax fibre/PCL composites as a function of PCL-*g*-MA coupling agent amount.

compatibilizer, modulus values increased up to a maximum was achieved. The variation of modulus could be probably due to crystallinity effects. Fracture surfaces of tensile specimens of flax fibre/PCL and flax fibre/PCL-*g*-MA composites are shown in Figs. 5a-b. SEM micrograph of composite based on PCL matrix shows clean fibres with almost no remaining matrix on the fibre surfaces, thus indicating poor wettability and lack of adhesion. On the contrary, for composites based on PCL-*g*-MA matrix a large amount of matrix adhering to the flax fibre bundle can be observed, thus indicating better fibre–matrix adhesion, which is in agreement with mechanical properties reported above.

Fig. 6a and b shows polarized light microscope micrographs of isothermally crystallized single flax fibre/PCL and single flax fibre/PCL-*g*-MA systems, respectively. In flax/PCL system (Fig. 6a), no transcrystalline (TC) layer was developed around flax fibre whereas for flax/PCL-*g*-MA system a thin TC layer was observed (Fig. 6b). Besides, the spherulite density on bulk is higher for PCL matrix, subsequently the average final spherulite diameter was lower than for PCL-*g*-MA matrix. Therefore, differences in microstructure could also affect mechanical behaviour of the samples.

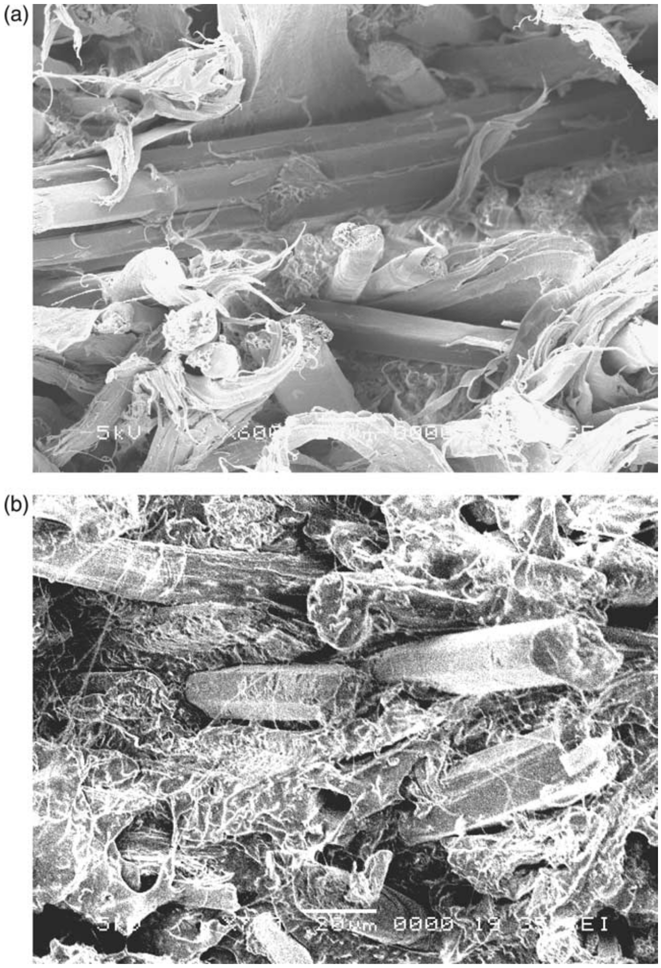


Fig. 5. (a) Fracture surface of tensile specimens of flax/PCL composites. (b) Fracture surface of tensile specimens of flax/PCL-*g*-MA composite.

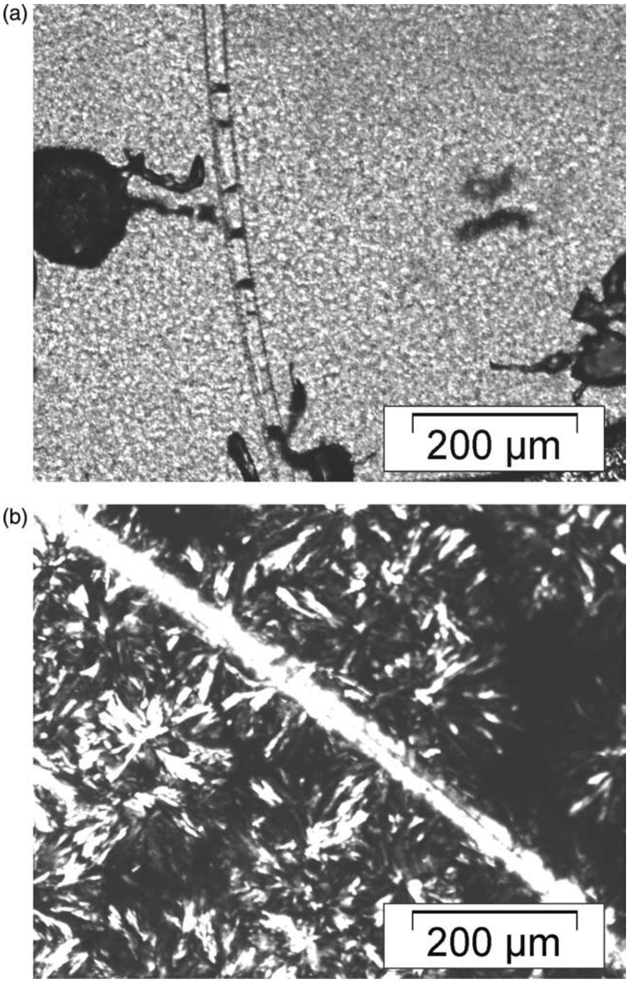


Fig. 6. (a) Polarized light microscope micrographs of single flax fiber/PCL system isothermally crystallized at 45 °C. (b) Polarized light microscope micrographs of single flax fiber/PCL-*g*-MA system isothermally crystallized at 45 °C.

Fig. 7 shows DSC thermograms for different samples as a function of PCL-*g*-MA content. These curves show single fusion endotherm which corresponds to matrix fusion. Results showed that the peak of neat PCL was shorter and broader than

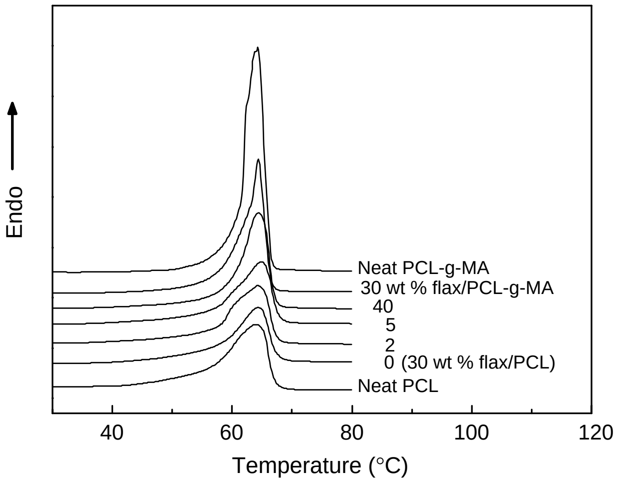


Fig. 7. DSC thermograms for samples containing 30 wt% flax bundles as a function of PCL-*g*-MA content.

neat PCL-*g*-MA peak. Besides as increasing PCL-*g*-MA content in flax/PCL composites resulted in higher and narrower peak. The thermal parameters as melting temperature (T_m), heat of fusion (ΔH_f) and percentage of crystallinity (X), are summarized in Table 2. The degree of crystallinity, X, of samples was calculated as follows (Barone, 2005; Joseph et al., 2003),

$$X = \frac{\Delta H_m}{\Delta H_m^o (1 - m_f)}$$

ΔH_m^o is the heat of fusion of a hypothetical 100% crystalline sample, ΔH_m^o was taken as 136 J/g (Avella et al., 2000) and m_f is the mass fraction of fibre.

The melting point T_m of the composites is almost unaffected by the addition of fibres, amount of PCL-*g*-MA and matrix type used. Under the assumption of similar melt enthalpy of 100% crystallines PCL and PCL-*g*-MA, the degree of crystallinity of PCL-*g*-MA is about 30% higher than for neat PCL. It is clear that addition of small amounts of PCL-*g*-MA decreases flax/PCL composites crystallinity. This crystallinity reduction could be the reason for lower mechanical properties. Besides, increasing PCL-*g*-MA content composites crystallinity was higher, thus improving mechanical properties, as also shown by other authors (Dasari, Rohrmann, & Misra, 2003; Iroh & Berry, 1996). At 40 wt% PCL-*g*-MA, the crystallinity was higher than for flax/PCL system thus improving mechanical performance. For flax/PCL-*g*-MA composites, the crystallinity and mechanical improvement obtained were the highest.

3.3. The effect of fibre bundle loading

Figs. 8a, b and 9a, b show both tensile and flexural properties of composites as a function of fibre bundle loading and matrix type. For composites based on PCL matrix, both tensile and flexural strength of composites show similar trends, strength slightly increased for higher fibre contents until a maximum was reached (around 30–40 wt% flax fibre). However, at higher fibre contents strength values showed a linear decrease suggesting that there was small stress transfer from the matrix to the fibres irrespective of the amount of fibre present. Similar behaviour has been reported by other authors for composites based on lignocellulosic fibres and polypropylene matrix (Arbelaiz, Fernández, Ramos, et al., 2005; Rana et al., 1998; Sanadi, Caulfield, Jacobson, & Rowell, 1995). Composites based on PCL-*g*-MA matrix showed higher strength values than those for composites based on PCL matrix and neat PCL. Tserki et al. (2003) found that for cotton cellulosic fibre/biodegradable polyester composites the addition of maleated biodegradable polyester as compatibilizer improved the mechanical properties of produced composites. In our work, use of PCL-*g*-MA matrix increased fibre–matrix adhesion being the strength improvement higher as increasing fibre content. For fibre bundle loading of 20 wt%, tensile and flexural strength increased by 22 and 19%, respectively. Meanwhile, for fibre bundle loading of 60 wt%, tensile and flexural strength increased by 131 and 126%, respectively. Strength increase can be attributed to improved fibre–matrix adhesion, which is in agreement with other works based on lignocellulosic material/PCL composites (Lee & Ohkita, 2003; Shibata et al., 2003). However, at 60 wt% fibre content a small drop of strength was observed which could be attributed to the incomplete wetting of fibres, the presence of some voids in the composite (Zarate, Aranguren, & Reboredo, 2000) and the presence of many fibre ends in the composites,

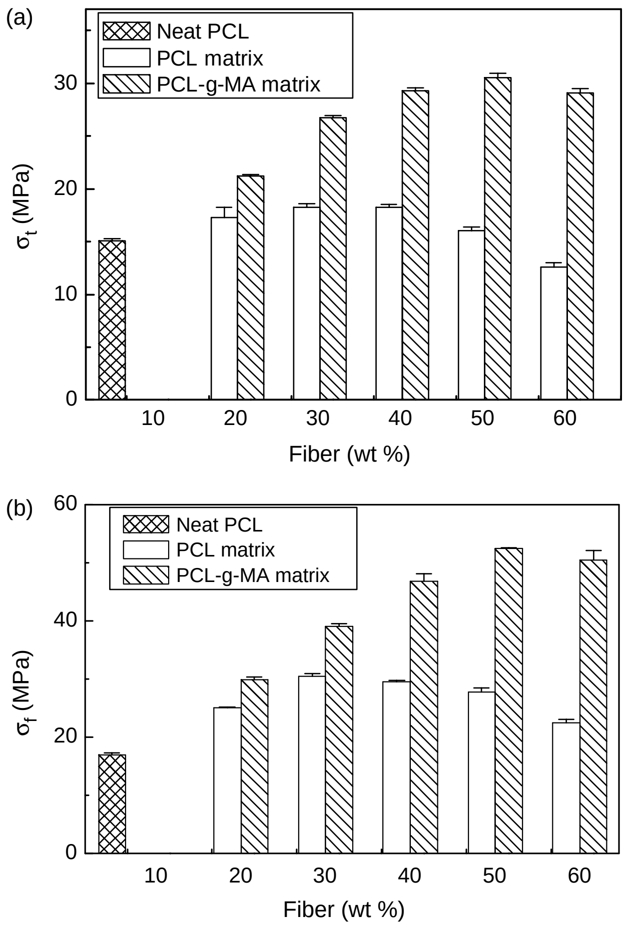
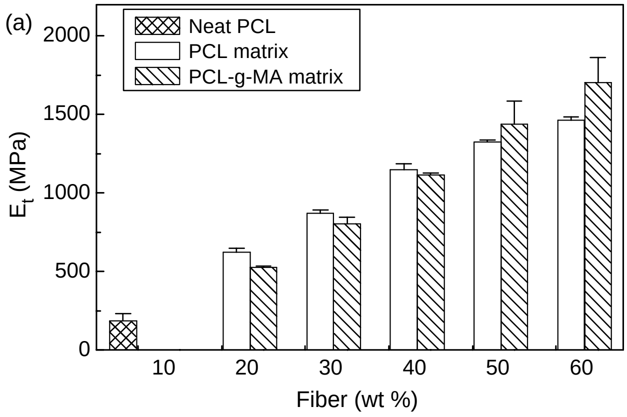


Fig. 8. (a) Tensile strength of composites as a function of fibre bundle loading and matrix type. (b) Flexural strength of composites as a function of fibre bundle loading and matrix type.

Table 2
Thermal parameters calculated from the fusion run for neat PCL, PCL-*g*-MA and composites with 30 wt% flax

Parameter	Neat PCL	Flax/PCL	2% PCL-*g*-MA	5% PCL-*g*-MA	40% PCL-*g*-MA	Flax/PCL-*g*-MA	Neat PCL-*g*-MA
T_m (°C)	63.8	64.4	64.4	64.9	64.3	64.4	64.2
ΔH_f (J/g_{sample})	76.58	71.65	63.26	69.63	75.92	82.27	116.0
ΔH_f (J/$g_{polymer}$)	76.58	102.4	90.37	99.47	108.5	117.5	116.0
X (%)	56.3	75.3	66.4	73.1	79.8	86.4	85.3



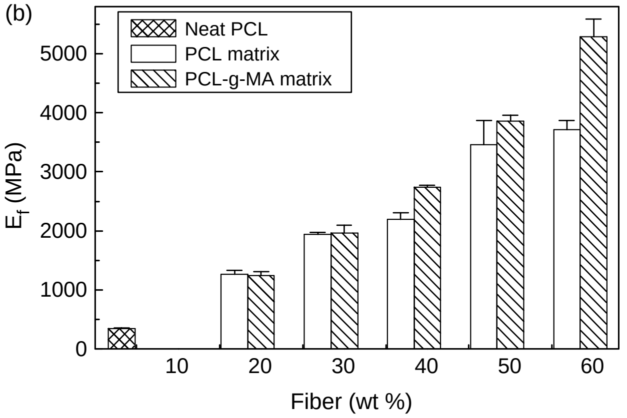


Fig. 9. (a) Tensile modulus of composites as a function of fibre bundle loading and matrix type. (b) Flexural modulus of composites as a function of fibre bundle loading and matrix type.

which could cause crack initiation, hence potential material failure (Mohanty, Khan, & Hinrichsen, 2000; Tserki et al., 2003).

On the other hand, all composites showed higher tensile and flexural modulus than neat PCL. Both types of composites showed the same trend, increasing fibre bundle content resulted in higher modulus values. Similar observations were reported by other authors (Lee & Ohkita, 2003; Shibata et al., 2003; Tserki et al., 2003) for other lignocellulosic fibre/biodegradable matrix composites. Taken in account the error bars and the small differences in fibre content (Arbelaiz, Fernández, Cantero et al., 2005), for the same fibre content composites based on PCL and PCL-*g*-MA composites showed similar modulus values. Therefore, modulus remains nearly unaffected by matrix modification.

3.4. Analysis of tensile properties

An iterative method has been used varying k_S and k_E values in Eqs. (1) and (3) to obtain the best fitting between theoretical and experimental values. Fig. 10 compares the theoretical and experimental tensile strength of flax/PCL and flax/PCL-*g*-MA composites. For flax/PCL composites, a k_S equal to 0.040 for tensile strength, model gives a good fitting up to 0.2 fibre volume fraction. However, above this volume fraction strength values deviate from theory. It seems that short fibre bundles act more like flaws in the structure rather than as reinforcement agent (Dong, Sapieha, & Schreiber, 1993). This could be the reason for the large deviation of strength values. For flax/PCL-*g*-MA composites tensile strength, the model shows a reasonable agreement with experimental values up to high fibre loadings for k_S equal to 0.075. Furthermore, in composites based on PCL-*g*-MA matrix k_S is higher compared to that for flax/PCL composites.

Fig. 11 compares the theoretical and experimental tensile modulus of flax/PCL and flax/PCL-*g*-MA composites. Tensile modulus increased linearly as higher the amount of fibres was. A good correlation between theoretical and experimental results was seen for k_E equal to 0.0075. Ali et al. (2003) found that the strength efficiency factor and modulus efficiency factor for long glass fibre/PCL composites were in the range of 0.0037–0.1124 and 0.0550–0.1906, respectively. So that, our strength efficiency factor value is in the range of those reported

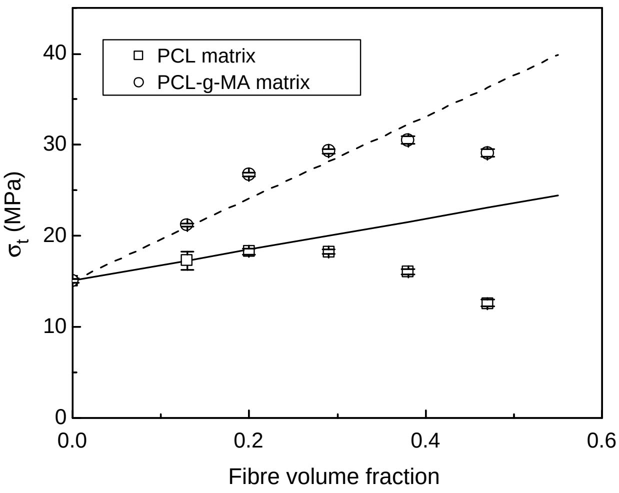


Fig. 10. Theoretical (line) and experimental (open symbols) tensile strength of flax/PCL and flax/PCL-*g*-MA composites.

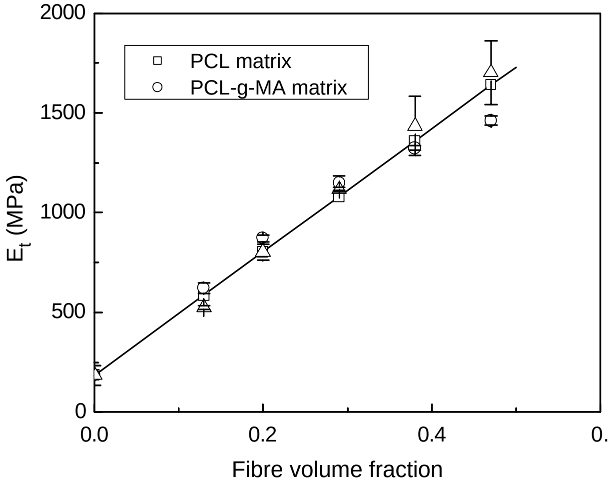


Fig. 11. Theoretical (line) and experimental (open symbols) tensile modulus of flax/PCL and flax/PCL-*g*-MA composites.

values, but our modulus efficiency factor are far from those reported values.

3.5. TG analysis

Thermograms of flax fibre, neat PCL, flax/PCL and flax/PCL-*g*-MA composites are shown in Fig. 12 a and b. TG curve for flax fibres shows three weight loss stages which is in agreement with other studies reported (Gañán & Mondragon, 2002; Joseph et al., 2003; Van de Velde & Baetens, 2001). Flax fibres normally contain sorbed moisture due to their hydrophilic character. The first weight loss peak (102.5 °C) is related to the release of 8–9 wt% water present in the fibre. Taken in account that during moulding process temperature up to 150 °C was achieved, the evaporation of water could cause porosity in the matrix (Felix & Gatenholm, 1991), so leading to a worsening of mechanical properties, it becomes evident that flax fibres have to be predried before processing (Cantero, Arbelaiz, Mugika, Valea, & Mondragon, 2003). The second peak is related to the degradation of cellulose, hemicelluloses (Van de Velde et al., 2001) and pectins. This second peak (391.5 °C) shows a shoulder at 320 °C which corresponds with the pectins and hemicelluloses content. The third peak (503 °C) has been attributed to the further breakage of decomposition products of stage 2 (Joseph et al., 2003). Thermograms do not show changes in the degradation mechanism due to fibre adding and matrix modification. These results indicate that fibre addition and matrix modification slightly reduced the thermal stability of PCL, which is in agreement with the results reported by Ruseckaite and Jiménez (2003) for composites with sisal fibres and PCL matrix.

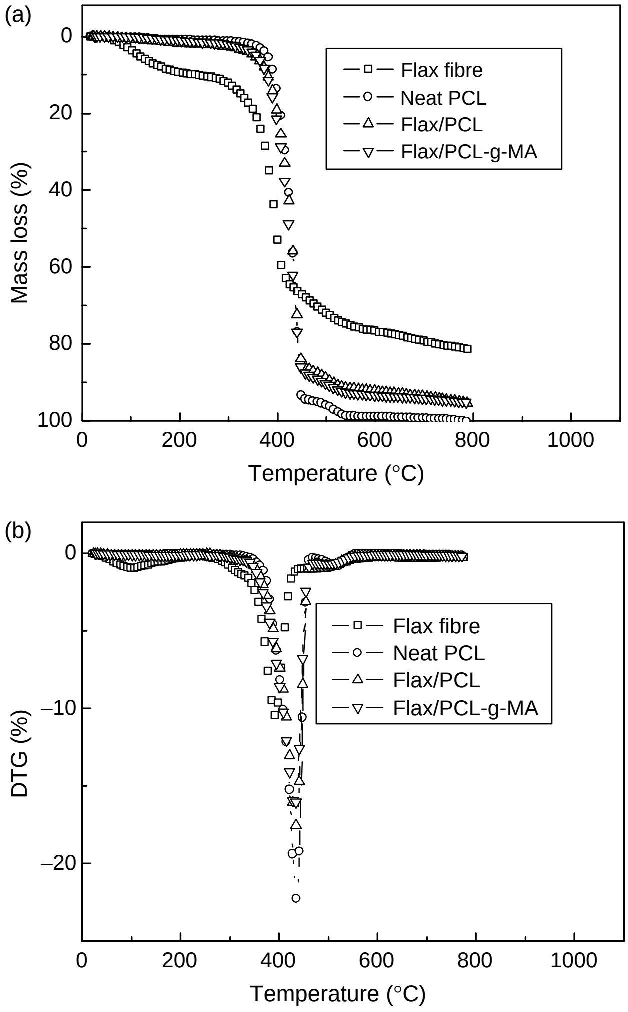


Fig. 12. (a) The mass loss percent curves of different samples. (b) The derivative curves of different samples.

4. Conclusion

The objective of this study was to prepare PCL-*g*-MA coupling agent and to study the mechanical properties of flax fibre bundles/PCL composites with different amounts of synthesized PCL-*g*-MA coupling agent and fibre content.

Both mechanical properties and crystallinity of composites decreased with the addition of small amounts of PCL-*g*-MA coupling agent. Crystallinity reduction seems to be the possible reason for lower mechanical properties. Increasing coupling agent amount, in addition to major crystallinity, composites show better mechanical performance. The highest crystallinity and thus the best mechanical properties were obtained when flax/PCL-*g*-MA composites were prepared. The improvements obtained for tensile and flexural strength are 54 and 44%, respectively. SEM confirmed adhesion improvement between flax fibre bundles and PCL-*g*-MA matrix. A good correlation exists between theoretical and experimental values except to unmodified strength values. For flax/PCL composites, above 0.2 fibre volume fraction experimental values are lower than predicted value ones as a consequence of lack of adhesion between flax fibre and PCL matrix. The results obtained by TG indicated that fibre addition and matrix modification slightly reduce the thermal stability of PCL.

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