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Mechanical properties of short flax fibre bundle/polypropylene composites: Influence of matrix/fibre modification, fibre content, water uptake and recycling

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Abstract

The aim of this work was to compare the effect of modification way of short flax fibre bundle/polypropylene (PP) composites on mechanical properties. Modification was carried out on fibre surface and also modifying PP matrix using several amounts of maleic anhydride-polypropylene copolymer (MAPP) as compatibilizer. The optimum doses of two different MAPP compatibilizers have been obtained. The effect of fibre bundle loading on composite mechanical properties was also analysed. The influence of water uptake on the sorption characteristics of composites has been studied by immersion in distilled water at room temperature. The effects of fibre bundle loading and also the use of MAPP modification on both water sorption and mechanical properties were also evaluated. Results showed that using MAPP as coupling agent, mechanical properties of composites improved, and water uptake rate clearly decreased. However, after long period of water immersion mechanical properties drastically decreased. On the other hand, mechanical recycling of flax fibre bundle/PP composites has been shown to be feasible.

Keywords: Flax; A. Fibres; A. Polymer–matrix composites; B. Environmental degradation; B. Mechanical properties

1. Introduction

Nowadays, ecological concern has resulted in a renewed interest in natural materials and issues such as recyclability and environmental safety are becoming increasingly important for the introduction of new materials and products [1]. Lignocellulosic fibres have many advantages as they are biodegradable, renewable and environmentally friendly. They have acceptable specific properties and comparing to glass fibres, they reduce dermal, respiratory irritation during handling as well as tool wear. However, the main disadvantage of natural fibres is their hydrophilic nature that lowers the compatibility with hydrophobic polymeric matrices during composite fabrication. They also present poor environmental and dimensional stability [1–5]. Amorphous cellulose and hemicelluloses are mostly responsible for the high water uptake of natural fibres, since they contain numerous easy accessible hydroxyl groups which give strong hydrophilic character to fibres.

Due to hydrophilic character, swelling by water uptake can lead to microcracking of the composite and degradation of mechanical properties [1]. Therefore, water uptake is one of the most serious problems that prevents a wider use of natural fibre composites [6–9], in fact, in wet conditions, mechanical performance of composites decreases [6,7,9]. The possibility for using these materials in outdoor applications makes it necessary to analyse their mechanical behaviour under the

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influence of the weathering action in the long term [6]. The generation of a stronger interface between matrix and reinforcement material could reduce the hygroscopicity of lignocellulosic-based materials [9].

In order to improve adhesion between cellulosic fibres and polypropylene (PP) matrix, coupling or compatibilizing agents can be used.

Graft copolymers of PP and maleic anhydride are known to be very effective additives for lignocellulosic/PP composites [5,10–13]. The effectiveness can be due to a better compatibility between fibres and PP matrix [14–16] as also to a better dispersion of flax fibres in PP. In the literature survey [8,17–21] different compatibilizers have been used for lignocellulosic fibre/PP composites. In a previous work [14] the influence of different flax fibre surface modifications on fibre mechanical and flax/PP interface properties has been reported. Results showed that MAPP treated fibre presented the best performances. MAPP treatment could also reduce hydrogen bonding that tends to bind fibres together [15]. The formation of covalent bonds between OH groups of cellulose and anhydride groups of MAPP [5,22], which can be confirmed by IR studies [11,23,24], is one of the reasons for strength improvement. On the other hand, entanglements between MAPP and PP chains can be created, so acting as physical cross-links [13,16]. Therefore, when stresses are applied to PP matrix, they can be transmitted to the fibre through these physical cross-links.

Two properties of maleated PPs that could influence their effectiveness as coupling agents for natural fibre/PP composites are molecular weight, which affects entanglement with the matrix chains, and acid number, which determines the functionality present in the coupling agent. To develop sufficient stress transfer properties between the matrix and the fibre, MA groups in MAPP should interact or even react with the OH groups on the fibre surface and the polymer chains of the MAPP should be long enough to permit entanglements with the PP in the interphase [13].

In this work two maleated coupling agents with different acid numbers and molecular weights were used for determining the effect of these parameters on couplen effectiveness. The objective of this work was to compare the influence of both fibre surface modification and matrix modification on mechanical properties and also to determine the optimum dose of each MAPP compatibilizer in flax fibre bundle/PP composites. After defining the optimum MAPP dose, mechanical properties of composites at different fibre bundle loadings were compared. On the other hand, the environmental behaviour of both unmodified and MAPP-modified flax fibre bundle/PP composites was evaluated by comparing water uptake and tensile properties. Finally, composites based on MAPP-modified flax fibre bundle/PP composites were grounded and reinjected in order to know the influence of number of passings through injection moulding machine on tensile properties.

2. Experimental

2.1. Materials

A commercially available PP "Eltex-P HV200" produced by Solvay with a Melt Flow Index of 10 g/10 min (at 230 °C and 2.16 kg) was used as polymeric matrix. The reinforcement was a natural flax fibre bundle obtained by a retting process, which consists in the biological action of bacteria in an aqueous medium where waxes and pectins are removed. These fibre bundles were kindly supplied by Finflax (Finland). Flax fibre bundles were first chopped to a length of approximately 30 mm and the diameter values varied from 10 to 120 μm. MAPP, Epolene E43 and G3003, kindly supplied by Eastman Chemical were used as coupling agents. Epolene E43 has a low molecular weight ($M_n = 3.900$, $M_w = 9.100$), 0.934 g/mL density and acid number of 45. On the other hand, Epolene G3003 has higher molecular weight ($M_n = 27.200$, $M_w = 52.000$), 0.912 g/mL density but lower acid number, 8, than E43 one [25].

2.2. Surface modification

Fibre bundles were treated with two different amounts of Epolene E43, 5 and 10 wt%. Treatment procedure was reported in a previous work [24].

2.3. Matrix modification

PP matrix was modified with MAPP. For both types of MAPP, 1, 2, 3, 4, 5, 10 and 20 wt% amounts respect to fibre bundle content were used. The amount of MAPP was fed directly into the melt mixer.

2.4. Compounding and processing

Compounding was carried out using a melt mixer (Haake Rheomix 600 with two Banbury rotors). The mixing temperature was set at 180 °C. First PP and MAPP pellets were charged and after melting dried fibre bundles were added. The systems were mixed during 5 min at 40 rpm. The loading of flax fibres varied from 0 to 60 wt%. A percent of 30 wt% of fibre bundle was used to compare the effect of amount and type of MAPP coupling agent on mechanical properties. The mixture was pelletized and kept in a vacuum oven at 100 °C for 12 h. The moulding of the dried pellets was carried out in an injection-moulding machine (Battenfeld Plus 250). Samples were moulded for tensile and flexural tests according to ASTM D638 and ASTM D790M standards, respectively.

2.5. Mechanical testing of composites

Tensile and three-point bending tests were carried out using an universal mechanical testing machine Instron, model 4206. The crosshead speeds used were 5 and 1.7 mm/min for tensile and flexural tests, respectively. The gauge length used for tensile test was 115 mm and the span for flexural test was 64 mm. At least five specimens were tested for each set of samples and the mean values are reported. On the other hand, impact test were carried out using a Rosand instrumented falling-weight impact analysis system with a "Charpy" specimen support. Following testing conditions have been used: span length was 60 mm, drop mass and drop rate were 0.7 kg and 3.29 m/s, respectively, and unnotched flexural specimens with $10 \times 4 \times 80\ mm^3$ dimensions were used. During the impact, the resistive force exerted by the sample on the striker was measured as a function of time, and stored for subsequent display and analysis. The impact energy measured only can be used for relative comparison as it does not give the accurate toughness of the material.

2.6. Fibre length and diameter measurements

Fibre length and diameter were analyzed in injection moulded specimens to investigate the effect of coupling agent and fibre content. Matrix polymer was dissolved in hot xylene and a Nikon Eclipse E600W microscopy with software analySIS® of Soft Imaging System was used for fibre length and diameter measurements. A minimum of 300 measurements were tested for each sample.

2.7. Ageing of samples

Five composite samples, with ASTM D638 standard dimensions, were immersed in distilled water at room temperature to study the kinetics of water uptake. Weight increase due to sorbed water was periodically measured. When samples were taken out from water, the wet surface of the sample was quickly dried, weighed, and then samples were again immersed in water. This process continued during 7 months. After this period, samples were mechanically tested. The water uptake at time t was calculated from Eq. (1) [26,27]

$$\Delta m(t) = \left(\frac{W_t - W_0}{W_0}\right) * 100, \quad (1)$$

where W_0 is the weight of dry specimen and W_t is the weight of wet specimen at t time. Water mass increment at equilibrium (infinite time) is represented by $\Delta m\ (\infty)$.

3. Results and discussion

3.1. Matrix modification versus fibre modification

Figs. 1(a) and (b) show the effect of modification way on both tensile and flexural properties for 30 wt% flax fibre/PP composites. When composites prepared via fibre modification or via matrix modification with MAPP are compared, both ways caused a significant increase in strength, which is agreement with other author results [12]. MAPP might act as a dispersing agent between polar fibres and apolar matrix resulting in better dispersion of the fibres [28]. Irrespective to modification way used, strength values obtained were similar. Surface modified composites show slightly higher modulus than matrix modified ones. Results have to be taken carefully as small differences in fibre content could influence them [29]. Felix and Gatenholm [11] found for cellulose/PP composites that cellulose fibre surface treatment with MAPP increased tensile strength by 80% at a fibre loading of 40 wt%. Karmaker and Youngquist [5] found for jute/PP composites that addition of 3 wt% of MAPP to the kinetic mixer at a fibre loading of 50 wt% increased tensile strength by 100%. Thus, both modification ways are valid to get a composite with higher mechanical properties than unmodified ones. However, fibre surface

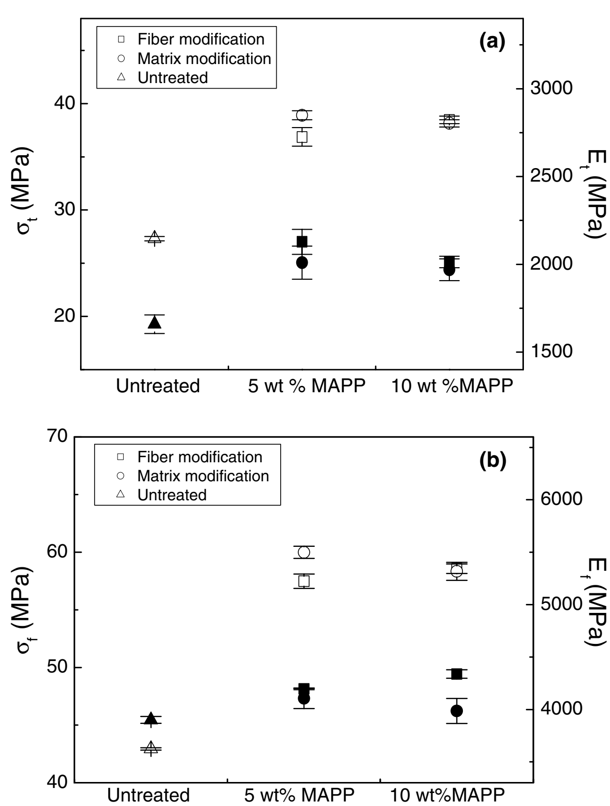

Fig. 1. Mechanical behaviour of 30 wt% flax fibre/PP composites as a function of modification way: (a) tensile; (b) flexural; strength (open symbols) and modulus (solid symbols).

modification with MAPP would probably be expensive since it involves solvent utilization, and therefore it would not be industrially practicable [12]. So that, the following results correspond to MAPP-modified PP matrix composites.

3.2. Matrix modification with MAPP

Figs. 2(a) and (b) show the effect of MAPP type on tensile and flexural properties as a function of the amount of coupling agent used. Both MAPP lead to similar trends in composites strength. Both tensile and flexural strength increased with increasing MAPP content until a plateau region was reached. It is worth noting that, 5 and 10 wt% compatibilizer for E43 and G3003, respectively, were the optimum doses, as flexural strength increased about 40% and 60%, respectively. For tensile strength, the maximum improvement for E43 and G3003 were 42% and 58%, respectively. After adding only 1 wt% of E43 compatibilizer, composites strength clearly increased. This improvement is due to the enhanced stress transfer from the matrix to the fibre via the compatibilizer [10,22]. Further increase in the compatibilizer beyond 1 wt% of both types of MAPP increased composites strength value until a maximum. Comparing strength values of modified composites, E43 seems to be more effective until 3 wt% of coupling agent whereas beyond this percentage, G3003-modified composites showed better strength performance. As an overall trend, when MAPP was added modulus values slightly increased. This improvement could be related to better dispersion of fibre bundles on PP matrix. However, at high coupling agent concentrations (20 wt%) modulus value showed a small drop.

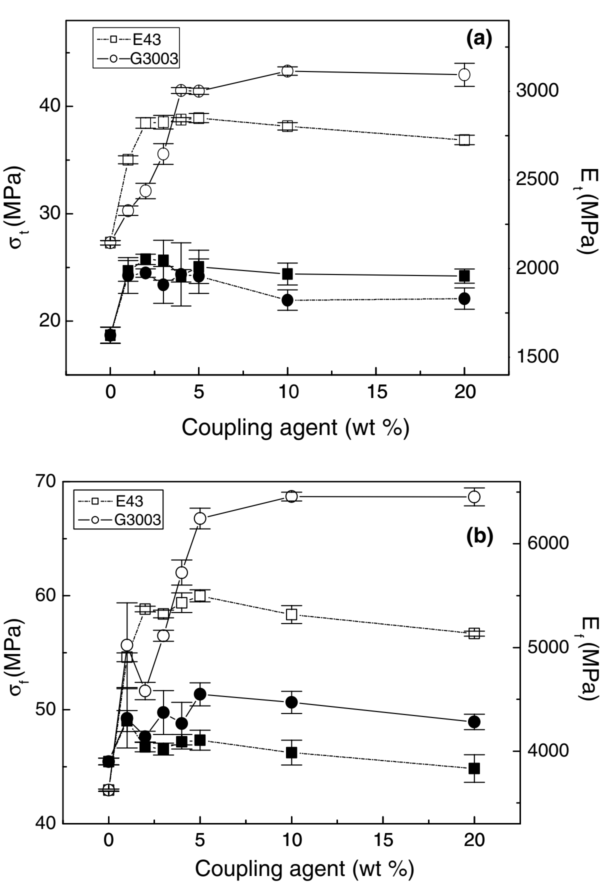

Fig. 2. Influence of MAPP type and amount on mechanical behaviour of 30 wt% flax fibre/PP composites: (a) tensile; (b) flexural; strength (open symbols) and modulus (solid symbols).

As a matter of fact, improvements on mechanical properties of composites are significantly dependent on the grafting rate and on the average molar mass of the graft copolymer coupling agent [30,31]. The behaviour of E43 and G3003-modified composites can be explained taking in account both modifier acid number and molecular weight. Acid number measures the functionality present in the coupling agent, being dependent upon MA units grafted per polymeric chain. Molecular weight is related to the ability to create entanglements between coupling agent and PP matrix [13,22]. G3003 has a lower amount of maleic groups per chain length, so at low modifier content it has not enough maleic groups to produce an optimal coupling efficiency. Beyond 3 wt% of coupling agent, G3003 has enough maleic groups to create interactions with flax fibre bundle and thus a better stress transfer from the matrix to the fibre bundle is expected. E43 has lower molecular weight, so polymer chains are shorter than G3003 ones, being the chance of entanglements with matrix lower than for G3003 one. Felix et al. [30] observed for cellulose/PP composites that using two different MAPP, with low and high molecular weight, the longer the PP chain of the modifier the better tensile properties were. They suggested that high molecular weight MAPP has more flexible PP chains which are able to diffuse deeper into the matrix. Thus, MAPP chains become more involved in inter-chain entanglements and thereby they contribute to the mechanical continuity of the system.

Fig. 3 shows the impact energy at failure of composites as a function of coupling agent content. Impact resistance decreased drastically when fibre bundles were added. Besides, composites modified with both MAPP showed similar trends as impact resistance increased upon modifier content up to a maximum was achieved. A reduction of impact strength was observed for both modifiers at 20 wt%, which can be attributed to the migration of a high amount of compatibilizer from the fibres to the matrix, causing self-entanglement among the compatibilizer chains rather than with the polymer matrix, thus resulting in slippage [10,22]. The maximum impact resistance for E43-modified composites was found between 5 and 10 wt% whilst for G3003-modified composites was at 10 wt%. These optimum values are similar to those obtained for flexural and tensile strengths. Therefore, it can be concluded that for

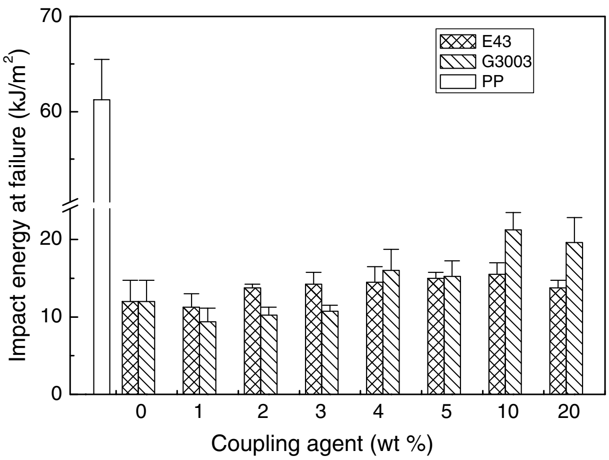

Fig. 3. Influence of MAPP type and amount on impact energy of composites with 30 wt% flax fibre.

different MAPP coupling agents, there is an optimum dose which results in the best improvement on mechanical behaviour of flax fibre bundle/PP composites. Similar observations were made by Qiu et al. [32] for fibrous cellulose/PP composites. They observed that tensile strength highly increased with an increase in the MAPP content, showing a maximum around 10 wt% beyond which tensile property decreased. They suggested that there is a critical amount of compatibilizer at which MAPP exhibits the strongest interactions with cellulose fibres as well as with PP matrix, which is similar to that observed in our work. Keener et al. [33] found for lignocellulosic fibre/PP composites, with 30 wt% fibre content, that 3% of maleated PP Epolene G3015, which acid number and molecular weight are intermediate provided optimal performance. Mechanical results seem to indicate that coupling of MAPP anhydride groups on flax fibre surface, but also a higher extent of physical entanglements with PP matrix because of increase on MAPP molecular weight, do have an important contribution on fracture toughness.

All results reported below are related to the optimal doses of MAPP.

3.3. The effect of fibre bundle loading

Figs. 4(a and b) and 5(a and b) show both tensile and flexural properties of composites as a function of fibre bundle loading and MAPP type. For unmodified composites tensile strength decreased as fibre bundle content increased whereas it showed similar flexural strength values than for neat PP. This is in agreement with the trend observed in other unmodified lignocellulosic fibre-reinforced composites [10–12,27,32]. This behaviour suggests that there was small stress transfer from the matrix to the fibres irrespective of the amount of fibre present [10,22]. When MAPP was added, modified composites showed higher strength values than those for unmodified ones and neat PP as MAPP addition increased fibre/matrix adhesion [14,16,34,35]. The highest strength improvement was obtained when G3003 coupling agent was used. The effect of MAPP modification became more pronounced with an increase of fibre bundle content [10–12]. At a fibre bundle loading of 60 wt%, the flexural strength increased by 93% and 118% for E43 and G3003-modified composites, respectively. In the case of a 20 wt% fibre bundle content the increase was 26% and 27% for E43 and G3003-modified composites, respectively. Strength of MAPP-modified systems increased with the amount of fibre bundle present, probably as a consequence of both improved fibre bundle dispersion in the matrix and better fibre/matrix adhesion, which is in agreement with other works [10,36].

Addition of MAPP, as mentioned above, slightly increased modulus values. However, other authors reported [5,11,22,37] that coupling agent addition has not significant effect on tensile and flexural modulus. As expected, increasing of fibre bundle content resulted in higher modulus values. Similar observations were reported by other authors [11,22,37] for other lignocellulosic based PP composites.

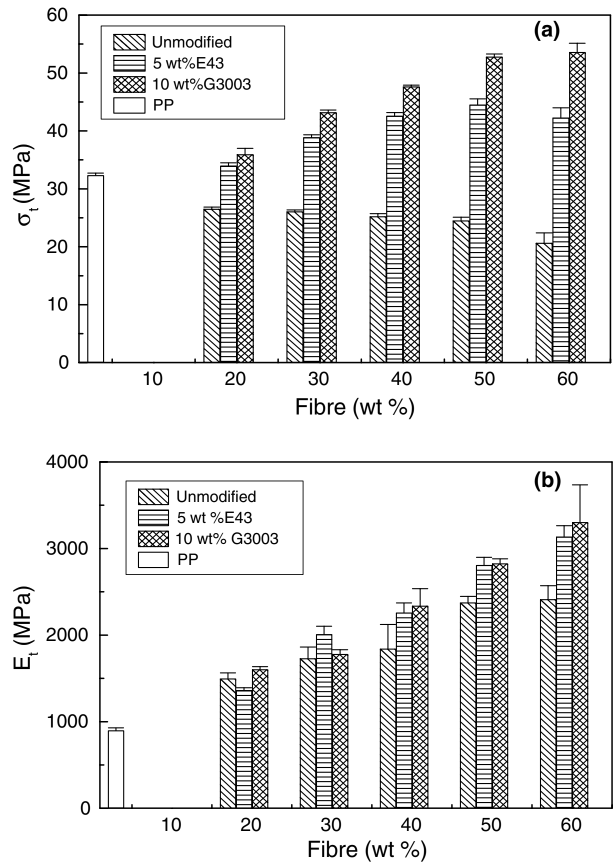

Fig. 4. Tensile behaviour as a function of fibre loading and MAPP type: (a) strength; (b) modulus.

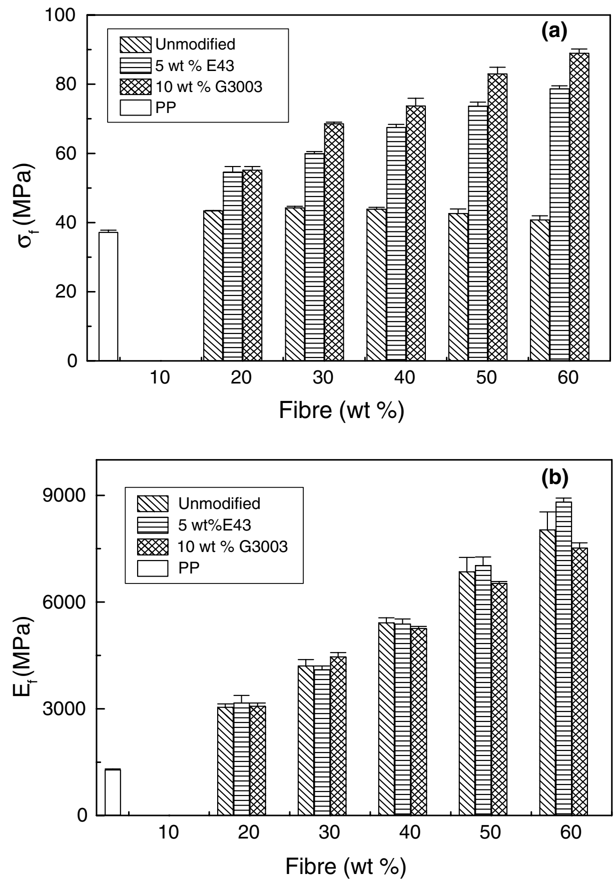

Fig. 5. Flexural behaviour as a function of fibre loading and MAPP type: (a) strength; (b) modulus.

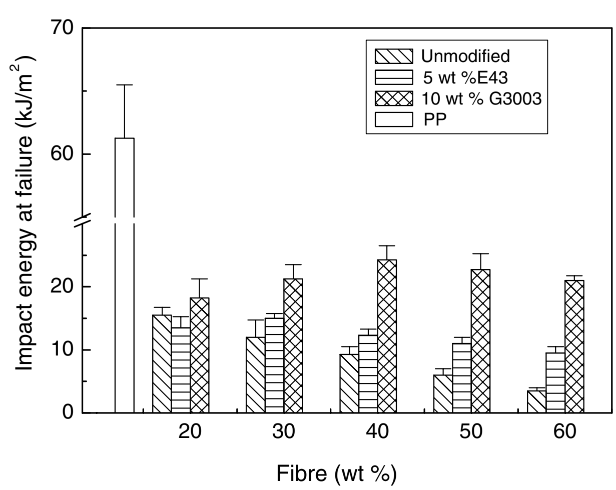

Fig. 6. Impact energy as a function of fibre loading and MAPP type.

Fig. 6 shows impact energy as a function of fibre bundle loading and MAPP type. All composites showed lower impact energy than neat PP because the addition of the fibre bundles creates regions of stress concentrations that require less energy to initiate cracking [10]. The impact energy of unmodified composites decreased when increasing fibre bundle content. However, modified composites showed a maximum, thereafter decreasing. For E43 and G3003-modified composites, the maximum impact energy was obtained at 30 and 40 wt% fibre bundle contents, respectively. Thus, improving fibre/matrix adhesion and fibre bundle dispersion through use of MAPP increases the resistance to crack initiation at the fibre/matrix interface, and the fall in impact strength with the addition of fibre bundles is not as dramatic [10]. As for tensile and flexural strength, G3003-modified composites showed the highest impact energy due to the important contribution on impact behaviour of the higher amount of entanglements with respect to the E43-modified ones.

3.4. Fibre breakage analysis

Processing affects the final fibre aspect ratio and thus the mechanical properties of the product [38]. Processing techniques such as internal mixing and injection moulding can cause a high fibre attrition [5,39] owing to the strong shear stresses acting in the viscous molten polymer [40]. Fibres can be broken into smaller fibres if the hydrodynamic forces exceed the fibre strength and/or the cohesive forces between the individual fibres [39]. Natural fibres have weak links as natural and artificial flaws as well as kink bands [14]. These weak links are the most probable rupture points along the fibre length when the fibre is mechanically stressed [5,40].

The final diameter (*d*), fibre length (*L*) and aspect ratio (*L*/*d*) values of the fibres extracted from composites are reported in Table 1. After injection molding, fibre diameter decreased and for all system the final fibre diameter is around 20 μm, which means that the used fibre bundles have been separated through processing. Besides, the original fibre length drastically decreased as higher fibre content was. This fact led to a reduction of around 30% in the aspect ratio for all composites when the fibre content was raised from 20 to 60 wt%.

Joseph et al. [41] found for sisal/PP + MAPP composites that viscosity increases with fibre loading. Therefore higher melt viscosity resulted in a reduction of aspect ratio. Using MAPP the average fibre length is slighthly higher than that for unmodified composites for all fibre contents. One of the reasons may be that MAPP has a low molecular weight compared to PP matrix, so MAPP could act as a lubricating agent. Thereby a reduction of shearing among fibres and molten PP could occur [5]. The slight higher aspect ratios but above all the improvement of fibre/matrix adhesion provide a considerable reinforcing effect, as discussed above.

3.5. Water uptake

Joly et al. [34,42] found for different MAPP that the grafting extent corresponding to covalently bonded compatibilizing agent on the cellulose fibre (degree of

Table 1
Fibre characteristics after processing as a function of fibre content and coupling agent

Fibre content (wt%)	Unmodified			E43			G3003		
	d (μm)	*L* (μm)	*L*/*d*	*d* (μm)	*L* (μm)	*L*/*d*	*d* (μm)	*L* (μm)	*L*/*d*
20	19 ± 9	158 ± 75	8.3	20 ± 10	197 ± 105	9.9	25 ± 10	236 ± 108	9.4
30	18 ± 7	154 ± 77	8.6	20 ± 7	203 ± 109	10	21 ± 5	194 ± 96	9.2
40	20 ± 8	146 ± 76	7.3	18 ± 7	155 ± 68	8.6	22 ± 8	155 ± 73	7.0
50	18 ± 7	135 ± 69	7.5	18 ± 6	150 ± 67	8.3	18 ± 6	147 ± 65	8.2
60	19 ± 8	118 ± 59	6.2	20 ± 8	141 ± 68	7.0	20 ± 6	122 ± 43	6.1

crystallinity was 65%) was very low (∼1% or less), only celluloses one OH group out of 19.000 to 45.000 reacted with MAPP. So that slight differences in water uptake should exist between unmodified and MAPP-modified composites.

Taking into account both acid number and amount of compatibilizer used in MAPP modified composites, it is clear that E43 modified composites should present more chance to block more fibre hydroxyl groups than G3003 modified composites ones, thus being a better candidate for decreasing water uptake. Therefore the study on water uptake has been performed only for E43-modified composites.

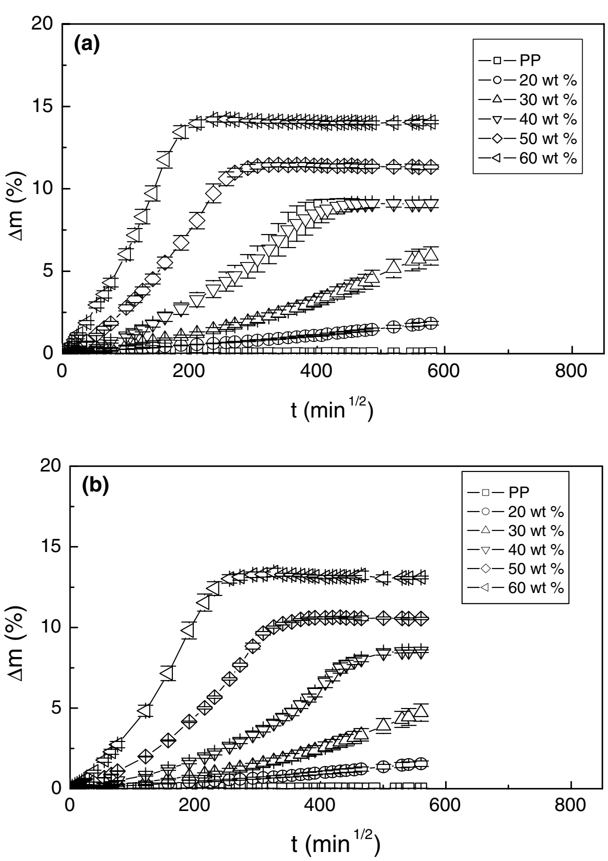

Fig. 7. Water uptake for composites as a function of square root of immersion time for different fibre loadings: (a) unmodified; (b) 5 wt% E43-modified.

Figs. 7(a) and (b) show water uptake evolution for unmodified and 5 wt% E43-modified composites, respectively, as a function of square root of immersion time for different fibre bundle loadings. After aging period, not all samples had reached a saturated moisture level. Composites that have reached a saturated moisture level exhibit a similar pattern of water uptake, being the shape of curves similar to that observed by other authors [1,9,43,44]. Initially, water uptake was linear until plateau or equilibrium state was achieved. On the other hand, PP only showed very small amount of water after aging for 7 months at room temperature. PP is hydrophobic, so that, water uptake of the composites was entirely due to the presence of natural fibres, being the contribution of the hydrophobic thermoplastic matrix negligible, which is in agreement with other works [9,26,43–45].

Both initial rate of water uptake and equilibrium water uptake values of composites increased with fibre bundle content [32,46]. For other lignocellulosic thermoplastic composites, it has been demonstrated that water uptake is proportional to fibre loading as sorption of thermoplastic matrices, such as polyethylene or PP, can be neglected [27,45,47]. Diffusivity was analysed with the hypothesis of a Fickian mechanism. One-dimensional approach was followed for the determination of the diffusion coefficient, *D*, which can be calculated as [48–51]

$$D = \pi\left(\frac{d\theta}{4\Delta m(\infty)}\right)^2, \tag{2}$$

where θ is the slope of the linear portion of the sorption curves and d the initial sample thickness. Since the specimens were of finite dimensions, a correction for the effect of diffusion through the edges can be made according to Eq. (3) for rectangular specimens

$$D_c = D\left(1 + \frac{d}{h} + \frac{d}{w}\right)^{-2}, \tag{3}$$

where D_c is corrected diffusion coefficient and h and w are sample length and width, respectively. This equation is based on the assumption that the rates of diffusion are the same in all directions [52]. Although tensile samples are not rectangular because they have grips that lead to water absorption, for simplicity tensile specimens were considered as rectangular with 10 and 150 mm width and length, respectively. Diffusivity and equilibrium uptake values with different fibre bundle loadings for unmodified and 5 wt% E43-modified composites are given in Tables 2 and 3, respectively. The results for the diffusion coefficient are similar to the values reported by other authors [51,53]. Use of MAPP remarkably reduced diffusion coefficient, being higher when fibre bundle loading was increased, whilst water uptake at equilibrium slightly decreased. Similar observations were found by George et al. [44] for pineapple-leaf fibre/low density polyethylene composites. Peijs et al. [1] found that the use of MAPP lowers the diffusivity for flax fibre mat in combination with PP matrix. For improved adhesion between matrix and fibres, rate of the diffusional processes decreases since there are fewer gaps in the interfacial region and also more hydrophilic groups as hydroxyls are blocked by the coupling effect [53].

Use of MAPP slightly reduced equilibrium water uptake for MAPP-modified samples, this small reduction being attributed to the improved interfacial adhesion [9,26,44] that avoid an easy penetration of water molecules into the modified composites [9] and reduced water accumulation in the interfacial voids which prevents water from entering the natural fibre [26]. Rana et al. [22] mentioned that the decrease of water uptake using MAPP might be attributed to some of fibre hydrophilic –OH groups reacting with maleic anhydride to form ester linkages and thereby giving slightly lower water-uptake values.

Table 2
Equilibrium uptake, diffusion coefficient and corrected diffusion coefficient values with different fibre bundle loadings for unmodified composites

Fibre (wt%)	Δm (∞) (%)	$D * 10^9$ (cm^2/s)	$D_c * 10^9$ (cm^2/s)
30	5.92	1.52	0.75
40	9.09	4.73	2.32
50	11.36	9.72	4.78
60	13.96	17.45	8.57

Table 3
Equilibrium uptake, diffusion coefficient and corrected diffusion coefficient with different fibre bundle loadings for 5 wt% E43 modified composites

Fibre (wt%)	Δm (∞) (%)	$D * 10^9$ (cm^2/s)	$D_c * 10^9$ (cm^2/s)
30	–	–	–
40	8.53	1.88	0.92
50	10.56	3.95	1.94
60	13.08	11.8	5.80

3.6. Effect of water immersion on mechanical properties

After aging in distilled water at room temperature for around 7 months, tensile properties of all types of samples show significant drop (Fig. 8(a) and (b)). Mechanical properties decreased because water molecules changed the structure and properties of fibres, matrix and interface between them. When fibre/matrix interface is accessible to moisture from the environment, the cellulosic fibres tend to swell, thereby developing shear stresses at the interface, which favours ultimate debonding of the fibres, which in turn causes a reduction in tensile strength [51]. It is also seen that tensile properties for MAPP-modified systems were better than for unmodified ones. Similar observations for bamboo-glass reinforced PP composites were observed by Thwe and Liao [26]. In contrast, for Kenaf/PP composites, Caulfield et al. [54] found that after water exposure, no clear distinction was observed between unmodified and MAPP-modified samples. George et al. [44] investigated the variation of tensile strength for pineapple leaf fibre/LDPE composites after water immersion for different periods of time, finding that as immersion time increased, composite tensile strength decreased. Singh

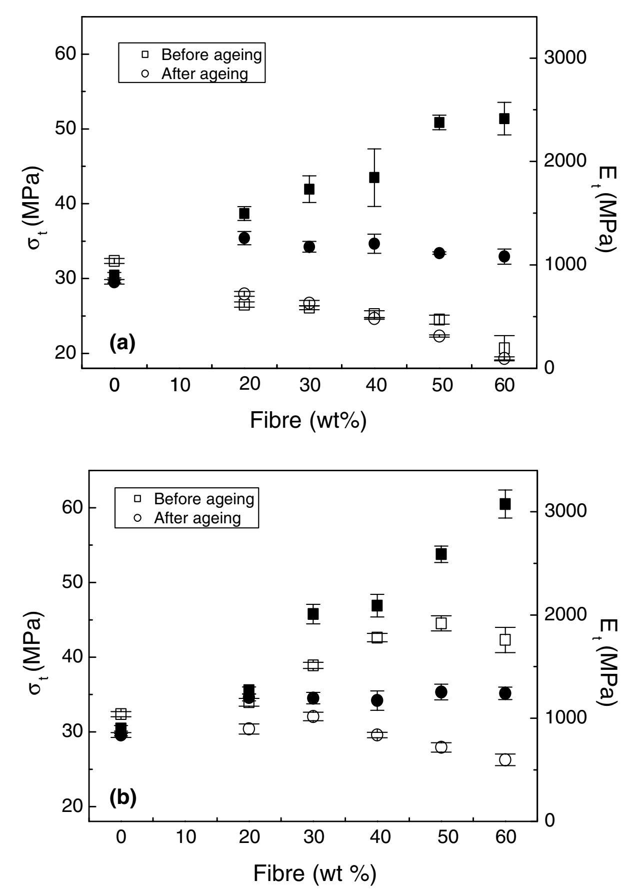

Fig. 8. Variation of tensile strength (open symbols) and modulus (solid symbols) of composites with different fibre contents before and after ageing in distilled water: (a) unmodified; (b) 5 wt% E43-modified.

et al. [55] found that the reduction in strength for jute/phenolic composites with increasing humidity levels is expected to depend on the amount of moisture/water which disturbs the mechanical integrity of composites by affecting the matrix, the fibres and the fibre/matrix interface simultaneously.

After water immersion, the stress–strain behaviour for composites containing different fibre loadings was examined (Fig. 9). Curves extended into the nonlinear region in all cases. Modulus, which was determined from the initial slope of the stress–strain curve, was similar for both fibre loadings. This trend is in contrast with results obtained previously with composites before ageing, suggesting that after water immersion composites fibres degraded and subsequently composites modulus was irrespective to fibre content. Sreekala and Thomas [56] observed for oil palm fibres that in the swollen stage the strength and modulus were found to decline. Joseph et al. [51] observed that after exposure sisal/PP composites in boiling water for 7 h, composites modulus decreased due to plasticization effect. That is, the absorbed water molecule reduces the intermolecular hydrogen bonding between cellulose molecules in the fibre and establishes intermolecular hydrogen bonding between cellulose molecules in the fibre and water molecules, thereby reducing the interfacial adhesion between the fibre and the matrix, and as a result decreasing composites mechanical properties. Espert et al. [53] observed that after water absorption of lignocellulosic/PP composites, SEM micrographs clearly showed the degradation of the fibres and the loss of adhesion between fibre and matrix. Stamboulis et al. [7] concluded that rather than the result of interface failure or matrix cracking, the mechanical degradation of the composites at relatively long immersion times is most likely the result of fibre degradation.

Although after water immersion tensile strength drop, composites containing MAPP still showed higher strength.

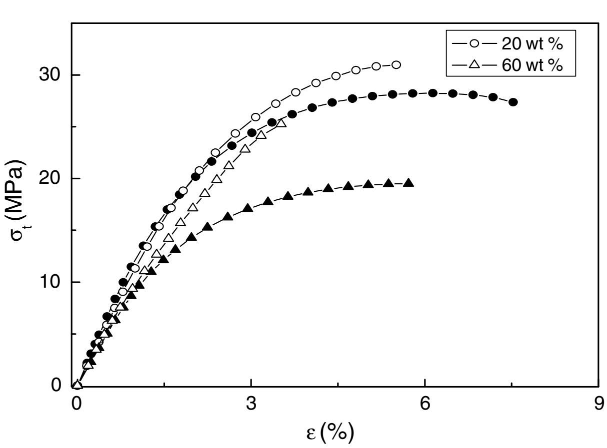

Fig. 9. Tensile stress vs. deformation curves for unmodified (solid symbols) and 5 wt% E43-modified (open symbols) composites with 20 and 60 wt% flax fibres after water immersion.

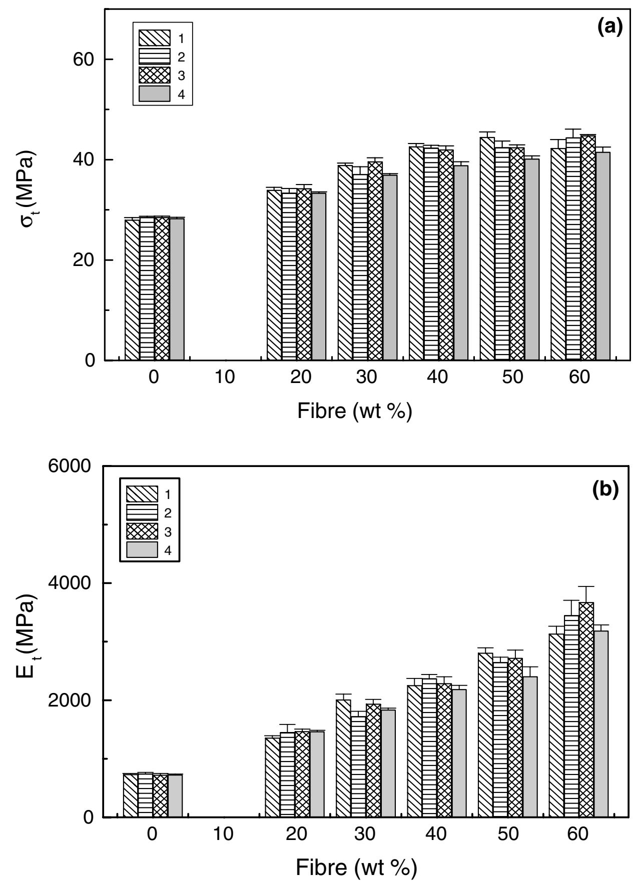

Fig. 10. Tensile behaviour of 5 wt% E43-modified composites as a function of fibre loading and number of passings: (a) strength; (b) modulus.

3.7. Mechanical recycling

Figs. 10(a) and (b) show the effect of number of passings through injection moulding machine on tensile properties at different fibre bundle loadings. After passing 4 times, tensile properties only showed a small decrease. A similar trend was shown by Joseph et al. [57] for 20 wt% sisal fibre/LDPE matrix composites. It is worth noting that after passing 3 times mechanically recycled composites through injection moulding machine, tensile properties were similar to those for unrecycled materials. So that, mechanical recycling of flax fibre bundle/PP composites is possible as mechanical properties only slightly changed.

4. Conclusions

The influence of MAPP amount and type on mechanical properties of flax fibre bundle/PP composites has been investigated. The effects of MAPP addition on both water uptake and rate have also been studied. Use of MAPP as coupling agent improved mechanical properties of composites by enhancing the adhesion between flax fibre bundles and PP. Besides, fibre bundle surface treatment with MAPP or matrix modification with MAPP had similar effects on mechanical properties of composites.

Both acid number and molecular weight of MAPP are important parameters in order to determine its effectiveness. Results suggest that there is a critical amount of compatibilizer, dependent upon its constitution and molecular weight, at which the strongest interactions between lignocellulosic fibres and PP matrix occur. Mechanical properties showed that 5 and 10 wt% compatibilizer are the optimum doses for E43 and G3003, respectively. Besides, the improvement in mechanical properties was higher for composites modified with G3003 than for those with E43 since G3003 higher molecular weight can lead to more entanglements between MAPP chains and PP matrix.

Stiffness of unmodified and MAPP-modified composites increased as fibre bundle content higher was, being MAPP-modified composite modulus slightly higher. However, the strength for unmodified flax fibre bundle/PP composites decreased with flax fibre bundle content, as a consequence of a poor interfacial adhesion, while for MAPP-modified composites the opposite trend was observed.

Water uptake increased with fibre bundle content. MAPP-modified composites exhibited a remarkable reduction in water uptake rate. Besides, due to a better interfacial bonding between flax fibre bundle and PP matrix, the equilibrium water uptake showed a small reduction. Although the use of MAPP slightly decreases composite affinity to water, long period of water immersion degrades fibres mechanical properties and subsequently composites properties. Therefore, flax fibre bundle/PP composites should not be used in applications where water uptake is of critical importance.

After passing MAPP-modified flax fibre bundle/PP composites several times through injection moulding machine, mechanical properties only slightly changed. So that, mechanical recycling of flax fibre bundle/PP composites is one feasible option to re-use this type of material.

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