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Blocked diisocyanates as reactive coupling agents: Application to pine fiber–polypropylene composites

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Abstract

In this paper, composites from polypropylene and Kraft pulp (from *Pinus radiata*) were prepared. Phenyl isocyanate, unblocked and phenol blocked derivatives of 4,4′-methylenebis (phenyl isocyanate) (MDI) were used as coupling agents and the mechanical properties of the obtained composites analyzed. The results showed that the addition of such compatibilizers readily improved the tensile and flexural strengths of the composites. However, no significant variation in the mechanical properties was observed for composite formulations comprising different isocyanate compounds. Accordingly, the chemical structure of isocyanate derivatives did not affect extensively the mechanical properties of MDI-coupled pine fiber reinforced composites. These results were similar to those obtained in previous studies regarding the efficiency of organosilane coupling agents. In comparison to monoreactive isocyanates, the addition of MDI increased considerably the mechanical properties of pine fiber–polypropylene composites. The mechanical anchoring of polymeric PP chains onto the irregular reinforcement surface supported this result. Non-isothermal DSC analysis showed a slowing effect of MDI on the crystallization kinetics of the coupled composites. This may have been the result of diminished polymer chain mobility in the matrix due to mechanical anchoring onto the fiber surface. Considering these results, the occurrence of strong bonds between the composite components was stated, rather than the unique existence of Van der Waals interactions among the non-polar structures.

Keywords: Blocked isocyanates; Polypropylene; Compatibility; Composites; Mechanical properties; Pine fibers

1. Introduction

It is well known that composite strength depends on the properties of the individual composite components and their interfacial interactions. In natural fiber reinforced composites, the poor dispersion and incompatibility inherent between hydrophilic natural fibers and hydrophobic polymers provide phase-separated systems, which are characterized mostly by a coarse and unstable phase morphology and poor interfacial adhesion (Bledzki & Gassan, 1999). For typical commodity polyolefins, interfacial stress transfer from the matrices to these fibers is therefore limited to relatively weak dispersion forces, resulting in weak composites (Caulfield, Feng, Prabawa, Young, & Sanadi, 1999; Hornsby, Hinrichsen, & Tarverdi, 1997). Scientists have attempted to improve the wetting and adhesive properties of natural fibers with polymeric matrices by coupling suitable chemical functional species on their surfaces. However, some typical methods for interfacial modification are usually not applicable to natural fibers for many reasons. Natural fibers cannot compete in terms of strength with synthetic fibers. However, they offer many other advantages because they are a natural renewable resource with outstanding mechanical properties, low density and low cost (Mohanty, Misra, & Hinrichsen, 2000). Aiming to improve their compatibility to hydrophobic matrices, *in situ* compatibilization by reactive processing (Liu & Baker, 1992)

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was studied by means of different reactive monomers. In this field, maleic anhydride (Maldas & Kokta, 1991) and glycidyl methacrylate (Jung, Park, Kim, & Suh, 2003) have been the monomers most frequently used.

In addition, the chemical treatment of natural fibers with isocyanates, to be used as reinforcement in composites, has been profusely studied. Polymethylene polyphenyl isocyanate (PMPPIC) (Bledzki, Reihmane, & Gassan, 1998) has been the most successfully binder in wood chemistry. Some research groups have been working on the chemical modification of commercially available isocyanates aiming to attach long alkyl chains on their structure and use them as coupling agents for natural fiber/polypropylene composites (Nair & Thomas, 2003; Trejo-O'Reilly, Cavaille & Gandini, 1997). The efficiency of such modified isocyanates, as coupling agents in natural fiber composites, is function to their electronic structure and also to their reactivity. Therefore, while alkyl isocyanates would give rise to better cohesion with non-polar thermoplastics such as polypropylene, their reactivity towards cellulose is much lower than that of aryl isocyanates (Borges, Godinho, Martins, Trinidade, & Belgacem, 2001).

Accordingly, we have been working on the derivatization of 4,4′-methylenebis (phenyl isocyanate) (MDI) to attain chemical structures electronically more compatible with polypropylene but that also preserve its high reactivity. MDI is a commodity product that, together with TDI (toluene diisocyanate), make up about 90% of the total diisocyanate in the market. The predominant use of MDI and TDI is the manufacture of polyurethanes (Allport, Gilbert, & Outterside, 2003). Recently, we reported that phenyl-blocked isocyanate can thermally de-block in the temperature range for processing polystyrene and polypropylene (170–180 °C). The use of blocked isocyanates instead of methylenebis (phenyl isocyanate) (MDI) prevented undesirable hydrolysis (Girones, Pimenta, et al., 2007). Stechiometric control of the reaction allowed the synthesis of a set of derivatives having equal reactivity towards cellulose but with a broad range of compatibility to different polymeric matrices. In this work, the effect of various isocyanate-coupling agents on the mechanical properties of pine fiber/polypropylene composites is reported.

2. Experimental

2.1. Materials

Polypropylene homopolymer (Isplen® PP070-G2M by Repsol YPF) was used as thermoplastic matrix for the preparation of composites. The PP matrix was injection-molding grade with a melt flow index of 12 g/10 min (at 230 °C and 2.16 kg). Bleached Kraft pulp (from *Pinus radiata*) supplied by Torraspapel SA (Spain) was used as reinforcement. Before compounding, fiber sheets were dispersed in a 1:3 water/diethylenglycol dimethyl ether (diglyme) solution using a Pulper. After being vacuum filtered, fibers were dried in an air-circulating oven at 80 °C. 4,4′-Methylenebis (phenyl isocyanate) (MDI) and phenyl isocyanate, as well as anhydrous phenol, butanol and dodecanol were all supplied by Sigma–Aldrich and used as received. MDI derivates were synthesized in our laboratory according to previous work (Girones, Pimenta, et al., 2007). An amount of 4,4′-methylenebis (phenyl isocyanate) (5 g, 20 mmol) was put into a round bottom flask with 100 ml of anhydrous butyl acetate solvent. The flask was fitted with a pressure equalizing funnel under nitrogen atmosphere at 40–45 °C. The required amount of alcohol, and dibutyltin dilaurate as catalyst, were diluted in butyl acetate and placed into an addition funnel. After purging with nitrogen, the solution was added dropwise during 15 min. After that, the reaction was completed as assessed by FTIR (disappearance of the NCO absorption signal at 2250–2270 cm^{-1}). The derivatization with phenol was kept for 2 h. Products were recovered by solvent evaporation at room temperature, washed with 2-propanol and dried in an oven at 60 °C.

2.2. Preparation of composites

The material compounding was carried out using an intensive melt mixer Brabender Plastograph™ (Duisburg, Germany). The mixing temperature was set at 180 °C. In order to ensure an equal dispersion and fiber content for all samples, a large amount of a 30 wt% pine fiber reinforced polypropylene (PP) was prepared. The blended material was milled and screened using a 10 mm mesh (SM100 from Retsch GmbH, Haan, Germany). Afterwards, 5% by weight of coupling agents (Fig. 1), with respect to the fiber content, was added to the composite and the ingredients were mixed in the Brabender for 4 min. Finally, the mixture was pelletized and kept in an oven at 80 °C for at least 24 h. Composite specimens from the dried pellets were obtained using an injection-molding machine (35-ton Mateu & Solé, Barcelona, Spain). The mold used was made in steel according to ASTM D3641 standard.

2.3. Mechanical characterization

Mechanical properties were evaluated by using an Instron 1122 universal testing machine. Test specimens were stored in a climate chamber at constant temperature (25 °C) and humidity (50%) for over a week before measurement. All mechanical tests were conducted according to ASTM standard specifications, D638 for tensile tests and D790 for flexural tests. Results were the average taken from at least seven specimens for each composite blend and mechanical property.

2.4. Scanning electron microscopy (SEM) analysis

The fractured surfaces of tensile test specimens and cryogenic fractured surfaces of composites were analyzed using scanning electron microscopy in order to evaluate

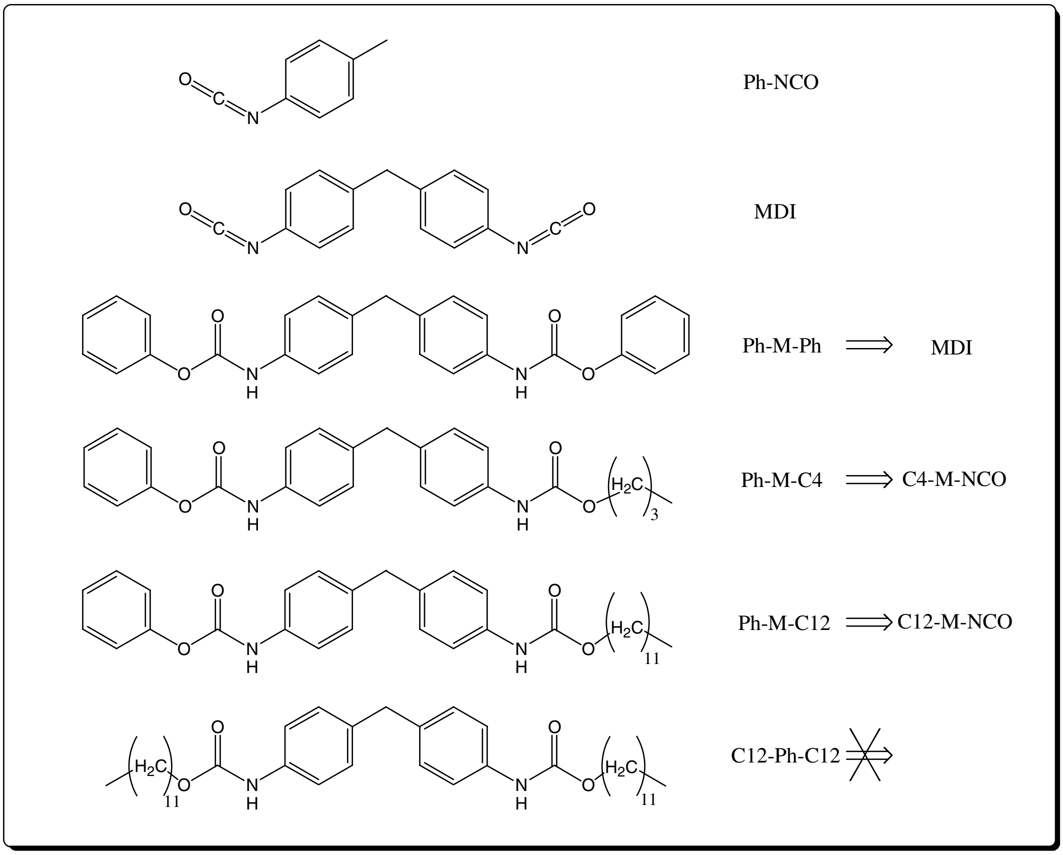

Fig. 1. The coupling agents used in this work. The phenol groups in the MDI derivatives are thermally released at 170–180 °C regenerating the isocyanate functions.

the degree of adhesion, and for morphological and fracture behavior studies. A Zeiss DSM 960 microscope operating at 25 kV was used. Fibers were laid down on the aluminum stub using a conductive adhesive tape and were sputter-coated with gold (K550 from Emitech, Ltd., Ashfort, UK).

2.5. Crystallization behavior by differential scanning calorimetry

DSC measurements were performed with a Perkin-Elmer Thermal Analysis DSC 8230-B differential scanning calorimeter. DSC measurements were carried out under nitrogen atmosphere from 210 °C to room temperature at a cooling rate of 10 °C/min and a heating rate of also 10 °C/min.

3. Results and discussion

Table 1 shows the effect of the different coupling agents on the mechanical properties of pine reinforced polypropylene. It is known that there is a close relationship between the tensile property of a composite and its interfacial adhesion. In all cases, tensile modulus increased for coupled composites. This enhancement might be assigned to a better dispersion and orientation of the reinforcement fibers into the matrix. Noticeably, treatment with C_{12}–M–C_{12} reported slightly lower increments than the rest of the analyzed coupling agents.

Even though thermal dissociation of urethanes linkages have been detected, even at 150–160 °C (Joel & Hauser, 1994), TGA analyses of C_{12}–M–C_{12} indicated no major weight loss occurred below 250 °C (Girones, Pimenta, et al., 2007). Therefore, at polypropylene processing tem-

Table 1
Effect of treatment with isocyanate coupling agents on tensile properties of pine fiber reinforced composites

	Neat PP	30% wt pine fiber reinforced composite coupled with					
		Uncoupled	C_{12}–M–C_{12}	C_{12}–M–Ph	C_4–M–Ph	PhNCO	MDI
Young modulus (GPa)	1.28 ± 0.04	1.89 ± 0.08	2.03 ± 0.08	2.14 ± 0.07	2.30 ± 0.07	2.35 ± 0.13	2.24 ± 0.08
Strain (%)	>20	3.4 ± 0.3	3.9 ± 0.4	4.5 ± 0.2	4.3 ± 0.2	4.0 ± 0.3	3.8 ± 0.3
Tensile strength	29.1 ± 0.2	28.9 ± 0.7	30.2 ± 0.5	31.4 ± 0.3	32.0 ± 0.2	32.3 ± 0.5	38.2 ± 0.7
Flexural modulus (GPa)	1.31 ± 0.04	2.26 ± 0.08	2.45 ± 0.03	2.49 ± 0.07	2.54 ± 0.04	2.68 ± 0.05	2.47 ± 0.03
Flexural strength	45.2 ± 0.8	51.4 ± 0.8	51.7 ± 0.9	53.5 ± 0.6	53.8 ± 0.6	55.7 ± 0.5	62.8 ± 1.1

peratures (from 180 up to 200 °C) the number of C_{12}–M–C_{12} reactive isocyanate groups should be negligible and, consequently, it was expected to act as a dispersing agent rather than coupling agent.

This was confirmed by SEM observations performed on fractured surfaces of pine reinforced polypropylene composites before and after coupling (Fig. 2). Uncoupled pine composites show no evidence of interfacial bonding between fiber and matrix phases. Many voids can be observed around the fibers. In addition, many cavities are present on the composite due to fiber pull out. Coupling with C_{12}–M–C_{12} did not produce any detectable modification on the composite superficial appearance.

By the opposite, as reported elsewhere (Girones, Pimenta, et al., 2007), the thermal release of phenol in Ph–M–R derivatives proceeds readily at 170–180 °C. Then, under processing temperature conditions, deblocking should take place readily, regenerating the isocyanate groups. The further reaction of the released isocyanate groups with superficial hydroxyl groups presents on the fiber surface would increase its compatibility with the polymeric matrix resulting in an increase on tensile modulus, as observed. The chemical structure of the phenyl protective group, electron rich, is far different to that of the matrix. During the reactive mixing process, this can prevent its evacuation from the fiber surface, its diffusion through the matrix and final elimination. A complex system would appear where reaction of isocyanate groups with the fiber superficial hydroxyl groups would compete with its thermal degradation and the regeneration of the previous urethane bound (Fig. 3). Occurrence of reaction between blocked isocyanates and cellulosic fibers was corroborated by FTIR analysis of fibers extracted from the prepared composites (Girones, Pimenta, et al., 2007).

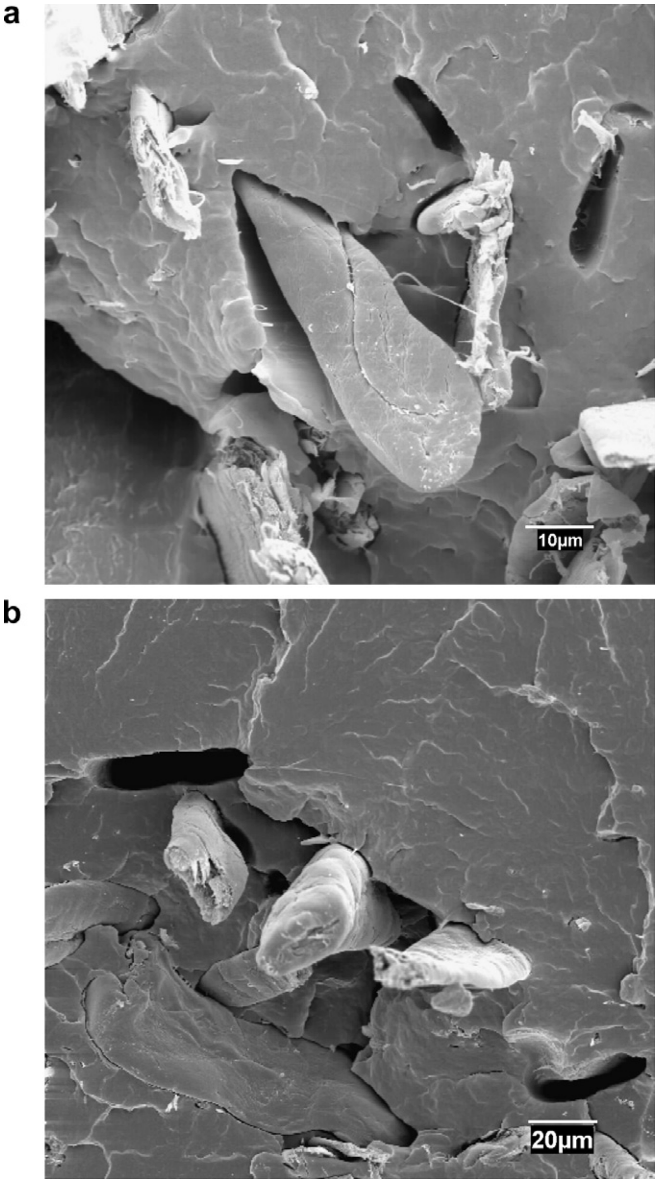

Fig. 2. SEM observations on fractured surfaces of uncoupled pine reinforced polypropylene composites (a) and C_{12}–M–C_{12} coupled (b).

Considering the experimental values obtained regarding tensile strength (Table 1), once more the treatment with C_{12}–M–C_{12} was the less effective. No major differences were observed among the agents with reactive isocyanate groups applied.

The evolution of the obtained values seems to indicate that the improvements on the mechanical properties are not effected by the chemical structure of the coupling agents and its compatibility to the matrix. Otherwise, the tensile strength would follow the trend C_{12}–M–Ph > C_4–M–Ph > Ph–NCO.

Assuming the usual amount of accessible OH groups on fiber surface (0.1–1%) (Rowland & Roberts, 1972), the coupling agent concentration (5 wt%) represents a large excess. In fact, for many different types of natural fiber composites, studies have indicated an optimum amount of diverse coupling agents being around 3% (Maldas, Kokta, Raj, & Daneault, 1988; Pickering & Ji, 2004; Rozman, Lai, Ismail, & Mohd Ishak, 2000).

However, when comparing the results of the different coupling agents it seems that the tensile strength does not depend on its structure, but on the concentration of the available reactive isocyanate groups. The improvement in both strength and modulus showed the following trend Ph–NCO > C_4–M–NCO > C_{12}–M–NCO ≫ C_{12}–M–C_{12}. It is worth noting, however, that the differences between Ph–NCO, C_4–M–NCO and C_{12}–M–NCO were slightly perceptible.

This apparent lack of effect of the alkyl chain in the R–NCO coupling agent efficiency is in agreement with results reported regarding the utilization of other coupling agents such as silanes and ketenes (Girones, Mendez, Boufi, Vilaseca, & Mutje, 2007) and is assigned to the low energy related with the hydrophobic interactions taking place in the fiber–matrix interface.

In addition, the differences observed among composites coupled with Ph–NCO and MDI are noticeable. Since having homologous molecular and electronic structures, reactivity of Ph–NCO does not differ to great extent from that of MDI (Fig. 4). Furthermore, its lower steric hinderance should allow a higher degree of substitution. There-

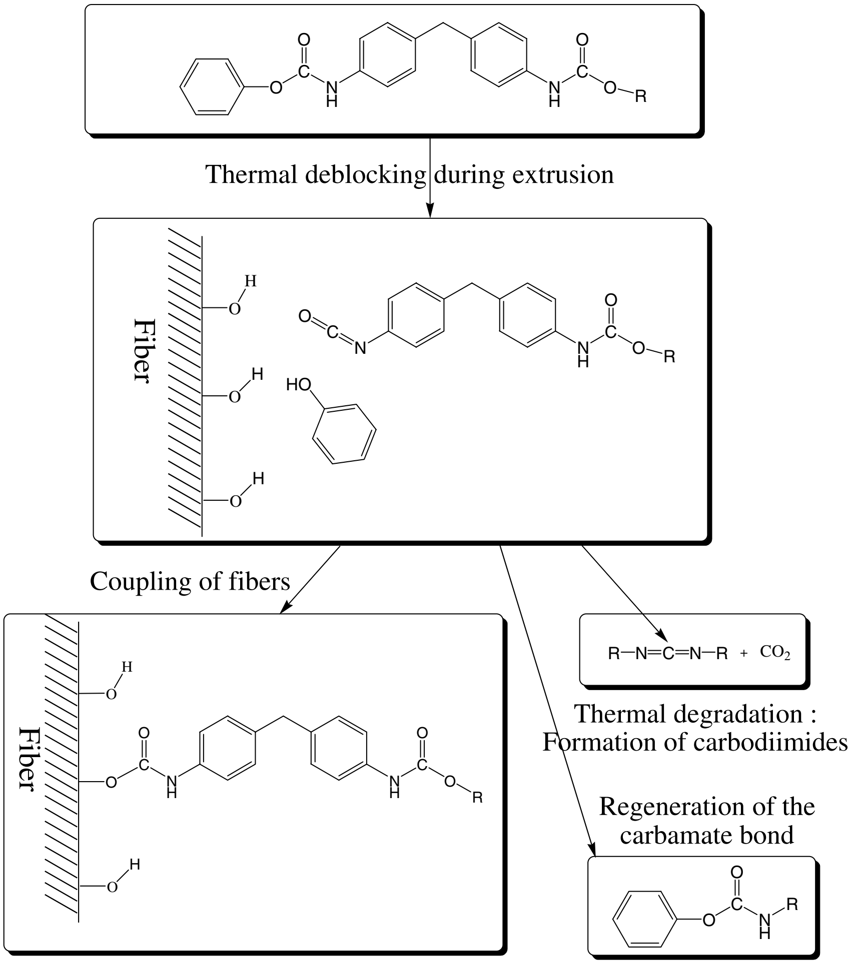

Fig. 3. Coupling and side-reactions during melt processing.

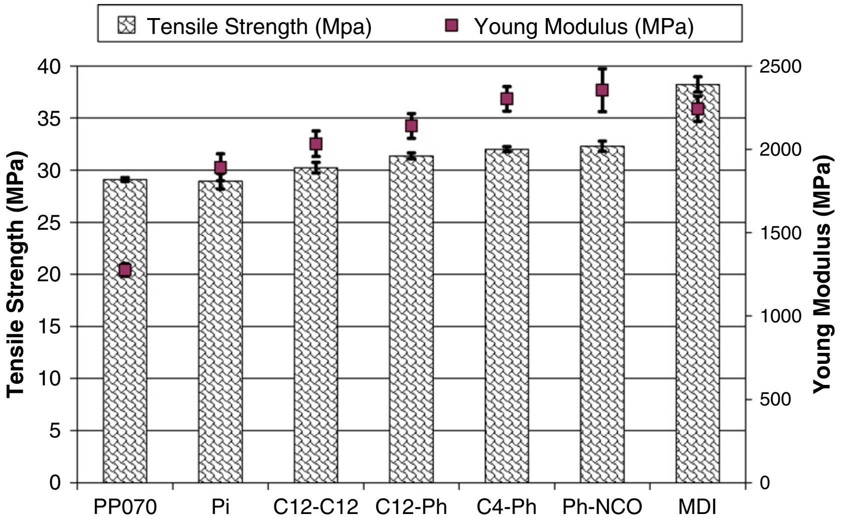

Fig. 4. Tensile behavior of 30% pine reinforced polypropylene as a function of coupling agent.

fore, for same reaction extent, the hydrophobicity imparted to the fibers should be similar, and the improvement on the mechanical properties of the final composite should be comparable.

The tensile strength enhancement for the composite formulation comprising MDI doubled that obtained with all other isocyanate-coupling agents, reaching values up to 35% higher than that of uncoupled composites. The interfacial improvement provided by MDI treatment was clearly visible on the SEM observations performed on the fractured specimens (Fig. 5). Presence of PP grafted onto the fiber surface can be observed and no cavities are present

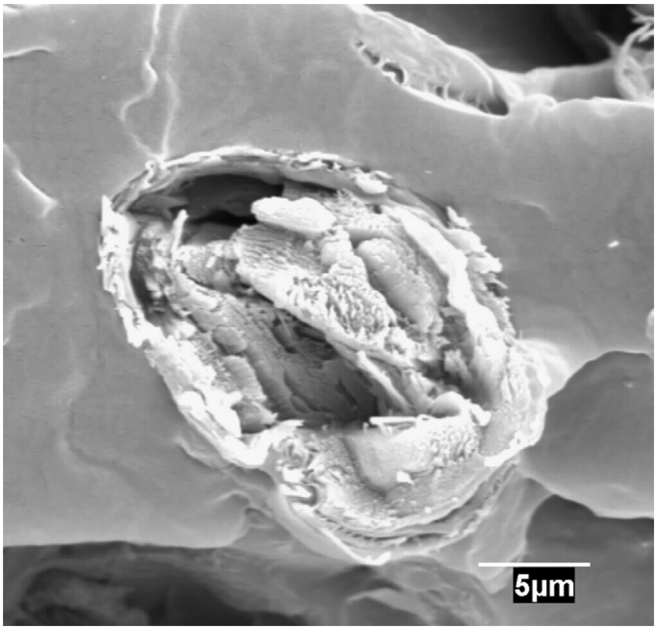

Fig. 5. SEM microphotography of a tensile fractured surface of MDI coupled pine reinforced polypropylene composite.

on the fiber–matrix interface. The coupled fibers adhered well to the polymer matrix and undergo breaking during tensile failure instead of being pulled out from the matrix.

The different behavior of MDI compared to other isocyanates suggested the importance of polyreactivity for the coupling agents' efficiency. In fact, according to the literature, the coupling agents with higher impact on the mechanical properties of natural fiber composites are polyfunctional agents, such as maleic anhydride-grafted polypropylene (MAPP) or polymethylene polyphenylene isocyanate (PMPPIC). By the opposite, monofunctional compounds, such as many silanes (Tung, Yamamoto, Matsuoka, & Fujii, 2004), monoisocyanates (Vazquez, Dominguez, & Jenny, 1999), ketenes (Quillin, Caulfield, & Koutsky, 1992) and others, despite enhancing the compatibility with the matrix provided limited improvements on the strength of the composites.

Some high molecular weight bireactive-coupling agents may be able to establish covalent bridges between two or more different fibers or structures. Such unions between the single fibers may allow the creation of higher structures that would act as a network and whose work would become much more efficient. Recently Malchev observed that kind of structures in fiberglass reinforced polyethylene/polyamide-6 blends (Malchev, David, Picken, & Gotsis, 2005). However, considering its dimensions, the formation of such structures seems unlikely for MDI derivates coupling agents. In addition, the volumetric percentage of fibers into the matrix seems too low to allow fiber–fiber interactions. Mechanical anchorage of the PP molecules may be an alternative.

During the first stage (mixing of the uncoupled fibers and matrix), the PP chains may penetrate into the fiber holes and valleys presents onto the irregular fiber surface.

Successive addition of the diisocyanate may form covalent linkages with the fiber hydroxyl groups, enclosing the molecules of PP and thus locking them onto the fiber structure (Fig. 6). Since such kind of interactions should have some effect onto the mobility of the polymeric matrix, the crystallization behavior of the composites was analyzed by DSC.

In Table 2, the thermal parameters of PP and PP composites are summarized. In general, fiber reinforcements use to act as nucleating agent (Arroyo, Lopez-Manchado,

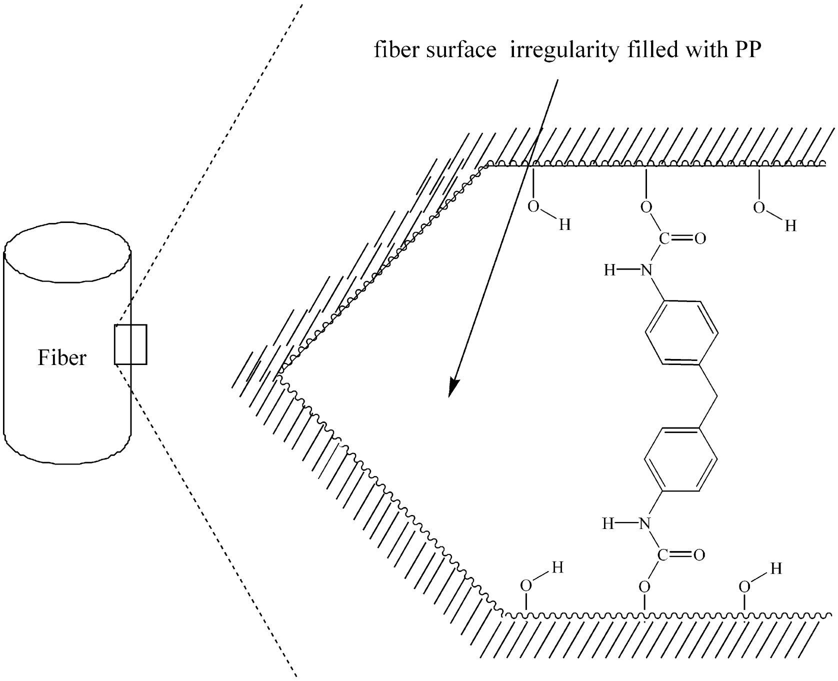

Fig. 6. Proposed model for the interaction between MDI and cellulose polymer chain in a single fibre.

Table 2
Thermal properties of the materials obtained by DSC

Material	Reinforcement (30%)	Grafting agent	T_m(°C)	ΔH_m (J/g)[a]	T_c(°C)	$-\Delta H_c$ (J/g)[a]	ΔT_α(°C)
PP	–	–	169.2	50.4	113.7	104.2	55.5
PP	Pine	–	166.8	85.2	124.6	107.4	42.2
PP	Pine	C_{12}–M–C_{12}	165.9	80.1	124.0	105.6	41.9
PP	Pine	Ph–NCO	167.0	88.5	123.0	111.1	44.0
PP	Pine	MDI	166.8	88.4	119.4	105.1	47.4

[a] ΔH_m is expressed in Joules per gram of polypropylene.

& Avalos, 1997) and this has an important effect on crystallization rate (Amash & Zugenmaier, 2000). In previous works, the addition of pine fibers to the PP caused very slight variation on melting temperature (T_m) (Girones, Pimenta, et al., 2007). The difference to neat PP was more important when the crystallization temperature (T_c) was compared. As pointed out by Joseph et al. (2003) the fiber-polypropylene composites showed higher T_c than that of PP. However, in opposition to other investigations (Joseph et al., 2003; Qiu, Zhang, Endo, & Hirotsu, 2003), the chemical coupling of pine composites produced a decrease on their T_c. This was particularly evident for MDI coupled composites, as shown in Fig. 7. This result suggested a reduction on the nucleation effect of the fibers in the presence of MDI (Quillin, Yin, Koutsky, & Caulfield, 1994). Physical anchoring of PP chains into fiber surfaces' irregularities may explain the decrease on fibers' nucleating capacity after coupling with MDI. The lower mobility of the polypropylene chains due to its grafting should difficult their orientation and consequently would cause a diminishing of their crystallization kinetics.

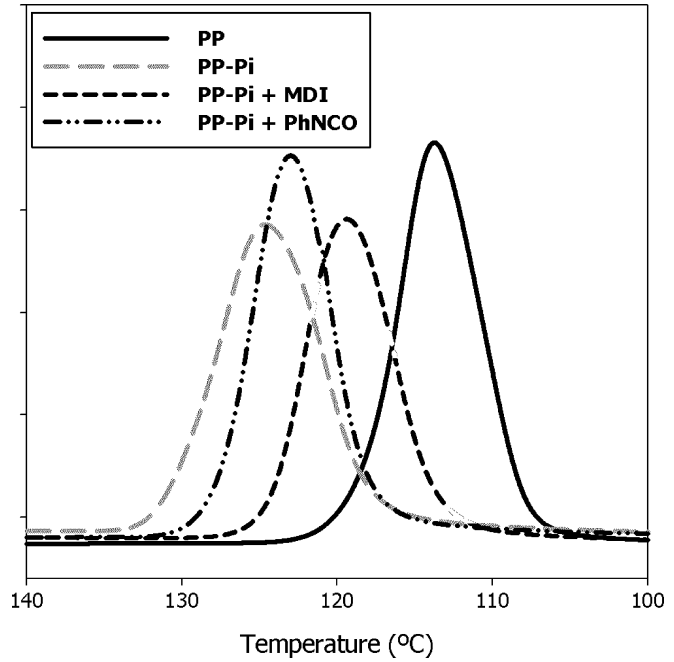

Fig. 7. Crystallization temperature (T_c) of PP, pine-PP composite and its MDI couple-pine composites obtained from DSC analysis.

The tendencies mentioned on the analysis of tensile mechanical properties can be applied to flexural properties (Fig. 8). Compared to uncoupled pine reinforced composites, the addition of monoisocyanates caused improvements in flexural strength varying from 4 to 8%. Meanwhile, coupling with MDI caused the highest increment of 22% with respect to uncoupled pine, which represent an increment of almost 40% with respect to unfilled PP. Apart from for Ph–NCO coupled composite (with slight higher flexural modulus) no major differences were observed between the different coupled composites; all of them with higher values than those of uncoupled pine/PP.

4. Conclusions

Coupling with phenol-blocked isocyanates during intensive mixing process does occur as corroborated by FTIR

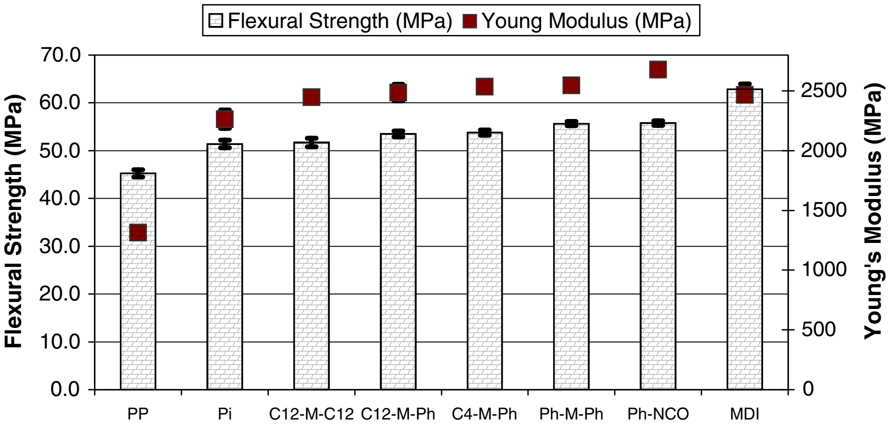

Fig. 8. Flexural behavior of 30% pine reinforced polypropylene as a function of coupling agent.

analysis of extracted fibers. Despite some enhancements are detected compared to untreated composites, no significant changes are observed among the mechanical properties of composites treated with the diverse mono- and modified diisocyanates analyzed. The low energy associated with the hydrophobic interactions established in the fiber–matrix interface can explain the lack of impact on mechanical properties of the pine fibers surface modification. By the opposite, composites coupled with an untreated diisocyanate (MDI) displayed much better mechanical performances than those treated with monoisocyanates. Formation of physical entanglements, resulting in mechanical anchoring of the matrix onto the reinforcement, during addition of MDI is proposed. For composites coupled with MDI, DSC analysis showed a decrease in their crystallization temperature, which is assigned to the reduction of the polymeric matrix chains mobility. This result may indicate polyreactivity being a required feature for an efficient coupling agent.

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