

Blocked isocyanates as coupling agents for cellulose-based composites

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Abstract

In this work, the stability of blocked isocyanates has been evaluated and the reactivity of different urethanes with the hydroxyl groups of natural cellulose fibres has been studied during the preparation of composites. The thermal dissociation of carbamate groups studied by TGA was function of the nature of the carbamate bond. According to this, the elimination of alcanol groups took place between 280 and 300 °C, while the elimination of phenolic groups was found at 170–180 °C. Because this last range of temperatures is the commonly used for polypropylene and polystyrene processing, aryl blocked isocyanates were chosen as reactive isocyanate groups for the preparation of natural fibre composites. The reaction of microcrystalline cellulose with such derivatives was evaluated resulting in the formation of new carbamate bonds assessed by FTIR and elemental analysis. Therefore, isocyanates and blocked isocyanates were used as coupling agents during the preparation of pine fibre/polystyrene composites. The addition of MDI or phenol blocked MDI derivative to pine reinforced polystyrene composites gave similar improvements of the mechanical properties of their composites. Consequently, it was stated that these coupling agents could be used for blending natural fibres with other matrices by means of a reactive mixing process.

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1. Introduction

The mechanical properties of cellulose fibres and its application as reinforcing agent for thermoplastic materials have being largely studied (Eichhorn et al., 2001; Lu, Wu, & McNabb, 2000; Mohanty, Misra, & Hinrichsen, 2000). The use of agro-industrial residues as reinforcement of polymer matrices gives rise to natural fiber-reinforced composites with improved strength and toughness, eventually more competitive from an economic point of view compared to the original plastic material (Herrera-Franco & Valadez-Gonzalez, 2004). The technical studies suggest that natural fibre composites have the potential to compete with composites reinforced with inorganic fibres (Zafeiropoulos, Williams, Baillie, & Matthews, 2002). However, the mechanical properties of composites reinforced with high

performance inorganic fibres have still not been reached (Hornsby, Hinrichsen, & Tarverdi, 1997). This situation can be explained by the non-effective bonding between the natural reinforcement and the conventional polymers at fibre–matrix interface. In this sense, the development of better compatibility between the hydrophilic cellulose fibres with the typically non-polar thermoplastic matrices is one of the main objectives of the current research (Bledzki, Reihmane, & Gassan, 1996). One of the aims of our research (Mutjé, Gironès, López, Llop, & Vilaseca, 2006) is the application of cheap treatments onto cellulose fibres to improve its compatibility with polymer matrices. The surface chemical modification of natural fibres is a typical approach for changing the surface polarity of cellulose fibres. In this field, many studies have been focused on the reaction of cellulose with different isocyanates (Nair & Thomas, 2003; Trejo-O'Reilly, Cavaille, & Gandini, 1997). However, the use of totally anhydrous solvents and special care to prevent any spurious inlet of moisture is required to avoid the hydrolysis of the reagents (Botaro & Gandini, 1998). Furthermore,

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natural fibres are highly hygroscopic, with a great tendency to absorb water until the equilibrium state is reached, so that its complete dehydration is fairly difficult. Therefore, whilst the low cost of the natural fibres is one of their main advantages against the use of inorganic fibres, this kind of modification stands for an increase in the total cost of the final composite. This fact leads to non-competitive products from an economical point of view if the improvements on the mechanical properties of the corresponding composites are considered (Joseph, Thomas, & Pavithran, 1996).

For all these reasons, the use of blocked isocyanates during the preparation of cellulose-based composites is proposed. Blocked isocyanates would prevent the hydrolysis of the reagents and the thermal released isocyanate groups would allow the cellulose derivatization directly in the extruder, avoiding the use of anhydrous organic solvents and consequently reducing the cost of the modification process.

The chemistry of the urethane bond, based on the reaction of isocyanates with alcohols, has been largely investigated. Different studies have demonstrated the reversibility of the urethane bond and its thermal dissociation (Joel & Hauser, 1994). Actually, the instability of these linkages at high temperatures is of great concern in the thermoplastic polyurethane (TPU) works. Under these conditions, the released isocyanate groups remain highly reactive towards most common functional groups, as indicated by the many molecular rearrangements that take place in processed TPU (Lu, Hoye, & Macosko, 2002).

Many potential blocking agents for isocyanates have been reported (Nasar, Subramani, & Radhakrishnan, 1999; Sultan Nasar, Shrinivas, Shanmugam & Raghavan, 2004), being phenols the most particularly studied. Thus, blocked isocyanates have been extensively reviewed (Wicks & Wicks, 2001, 1999). However, as far as our knowledge is concerned, while many works are dealing with the use of diisocyanates as coupling agents (Joseph et al., 2003; Nair & Thomas, 2003) no attempts have been made to the application of blocked isocyanate derivatives during the extrusion of natural fibres and thermoplastic matrices. In this work, the thermal stability of 4,4'-methylenebis (phenyl isocyanate) (MDI) derivatives with different alcohols has been studied by thermogravimetric analysis. The obtained products have been characterized by ^1H NMR spectroscopy and by Fourier Transformed Infrared Spectroscopy equipped with Attenuated Total Reflectance (FTIR-ATR). The reactivity of the released isocyanate groups with cellulose pine fibres and its influence on the mechanical properties of the corresponding composites has been also evaluated.

2. Experimental

2.1. Materials

Sheets of bleached pine fibres were supplied by Torrapapel S.A. (Sarrià de Ter, Spain) with an 8–10% moisture content. The average fibre length was 2.2 mm measured by

means of a Kajaani FS-100 analyzer. Before compounding, the sheets were dispersed in a diglyme:water mixture (3:1), vacuum filtered and dried in an air circulating oven at 80 °C. 4,4'-Methylenebis (phenyl isocyanate) (MDI) was provided by Sigma–Aldrich in a technical grade and used as received. Its NCO content (wt.%) was regularly analyzed. Methanol, butanol, octanol, dodecanol, hexadecanol and anhydrous phenol supplied by Sigma–Aldrich in analysis grade were used as blocking agents. Alcohols were dried and kept in molecular sieves before use. Microcrystalline cellulose Avicel® PH-101 from Fluka Chemicals was used to verify the reactivity of MDI derivatives with cellulose alcohols. DMSO- d_6 analysis grade from Sigma Aldrich was used as solvent for the ^1H NMR characterization. Polystyrene from BASF was used as thermoplastic matrix for the preparation of composites.

2.2. Characterization methods

Products were characterized by means of infrared spectroscopy (IR), elemental analyses (EA) and thermogravimetric analysis (TGA). Infrared spectra were recorded using a Mattson Satellite FTIR spectrometer equipped with a MKII Golden Gate Reflection ATR System. A Shimadzu TG-50 apparatus was used to determine the thermal stability of samples from room temperature to 450 °C at a heating rate of 10 °C/min in a nitrogen flow of 20 ml/min. MDI and its derivatives were also characterized by ^1H NMR in DMSO- d_6 using a Bruker DPX-200 spectrometer.

2.3. Experimental procedures

2.3.1. Synthesis of blocked MDI

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 or phenol) and 1 ml of dibutyltin dilaurate as catalyst (Mormann & Michel, 2002; Ni, Nash, Worden, & Soucek, 2002) were diluted in butyl acetate (total volume of 50 ml) and placed into an addition funnel. After purging with nitrogen, the solution was added dropwise during 15 min. Since aromatic isocyanates are extremely reactive with primary alcohols, vigorous stirring was kept during the addition. After 15 min, the reaction was completed as assessed by FTIR (disappearance of the NCO absorption signal at 2250–2270 cm^{-1}). As the reaction with phenol occurs slowly, the derivatization was kept for 2 h to ensure the full conversion. Products were recovered by solvent evaporation at room temperature, washed with 2-propanol and dried in an oven at 60 °C.

2.3.2. Treatment of microcrystalline cellulose with blocked MDI (Ph–M–Ph)

Oven dried Avicel® (2.0 g) and 1 g of Ph–M–Ph was placed in a round bottomed flask and soaked with the

appropriated volume of toluene. After refluxing for 2 h, the urethane treated microcrystalline cellulose was recovered by filtration, purified by Soxhlet extraction in toluene and finally oven dried until constant weight was achieved.

2.3.3. Preparation of composites

Composites were prepared using a Plastograph Brabender™ intensive melt mixer. The mixing temperature was set at 180 °C. In order to get a better homogeneity and dispersion, polystyrene (PS) and pine fibres (30 wt.%) were pre-mixed during 4 min at 80 rpm. The mixture was then granulated by means of a blade mill equipped with a nominal 10 mm mesh. Afterwards, composites were blended in the Brabender for 4 min with the corresponding coupling agent. Finally, the mixture was pelletized and kept in an oven at 80 °C at least 24 h before the injection-moulding. The specimens were moulded using a 35-Ton Mateu&Solé injection machine (Barcelona, Spain) with a steel mould according to ASTM D3641 standard. The samples were conditioned according to ASTM D618 standard before testing.

2.3.4. Mechanical characterization

All mechanical tests were performed according to ASTM D638 standard for tensile tests and ASTM D790 for flexural tests. Mechanical properties were evaluated using an Instron 1122 universal testing machine. At least seven specimens were tested for each composite.

3. Results and discussion

Blocked isocyanates were obtained by classical reaction of MDI with the proposed alcohols using dibutyltin dilaurate as catalyst. Fig. 1 illustrates the chemical reactions that took place, also considering the formation of diarylureas due to any trace of water in the system (Lapprand, Boisson, Delolme, Mechin, & Pascault, 2005). In Fig. 1 the N—H assignment peaks of ^1H NMR for the different species are also shown. Diarylureas were detected for the appearance of a peak at 8.5 ppm in the ^1H NMR spectra. Additionally, an absorption band at 1635 cm^{-1} in the FTIR spectra due to the stretching vibration of the urea bond was found. Fig. 2 shows the FTIR spectra of Ph-M-Ph and Bu-M-Bu.

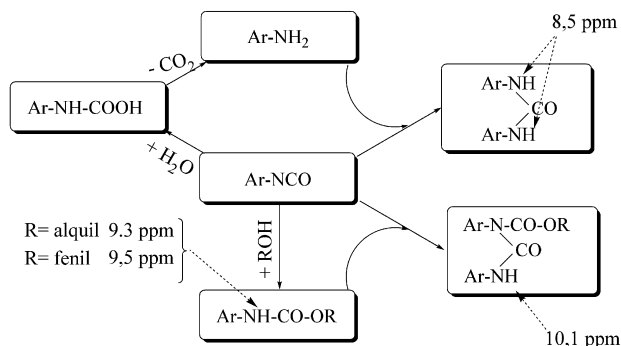


Fig. 1. Schematic reactions involving isocyanate compounds.

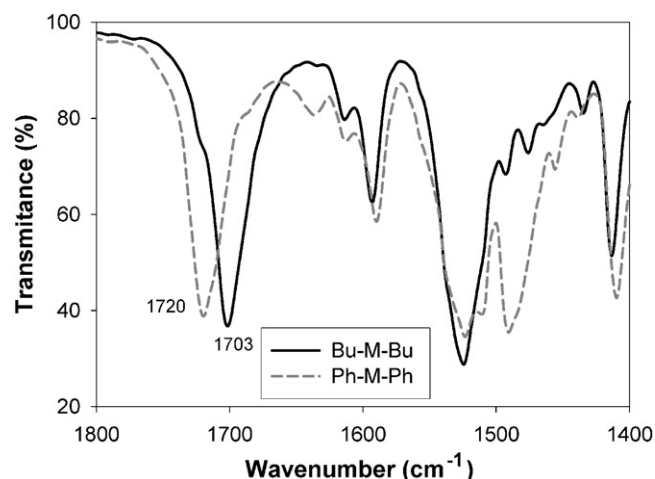


Fig. 2. FTIR spectra of Bu-M-Bu and Ph-M-Ph.

The carbonyl signals of the carbamate bonds were clearly distinguished. Thus, the C=O stretching vibration corresponding to the phenylcarbamate bond appeared at $1720\text{--}1725\text{ cm}^{-1}$, while the alkylcarbamate peak was observed at $1695\text{--}1705\text{ cm}^{-1}$. For the R-M-Ph derivatives, both signals were appreciated, confirming the existence of the two different functionalities in the MDI structure. Absorption frequencies of N—H stretching and carbamate bond appeared at 3325 and 1535 cm^{-1} , respectively. Fig. 3 represents the typical ^1H NMR spectrum of the synthesized diurethanes. The characteristic peak at 9.5 ppm was common to all prepared dialkylurethanes, while a signal at 9.3 ppm was observed in the spectrum of diphenylurethane. For R-M-Ph compounds, both peaks were detected. The conservation of the 1:1 ratio between both peaks was indicating the formation of the two carbamate bonds in an identical proportion. The formation of urea compounds due to the non-totally anhydrous systems was revealed by signals at 8.5 ppm. Moreover, the formation of allophanate compounds could be followed by the appearance of a peak at 10.1 ppm. However, when the reaction temperature was kept below 50 °C almost no allophanate compounds were observed.

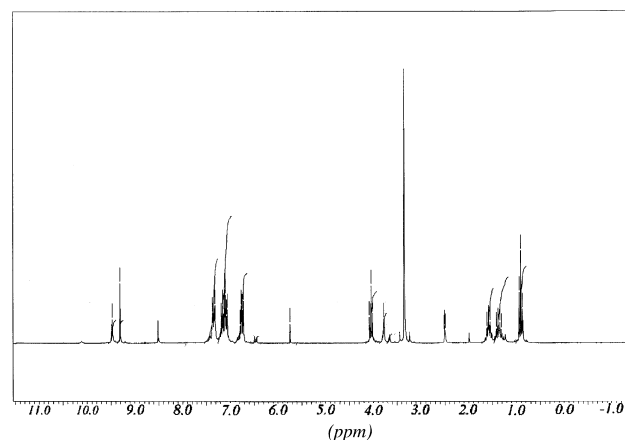


Fig. 3. ^1H NMR spectra of Bu-M-Ph compound.

Thermogravimetric analysis of blocked isocyanates was developed in order to characterize the thermal behaviour of those obtained blocked diisocyanates. The TGA thermograms of diphenyl, dialkyl and phenyl-alkylurethanes obtained from room temperature to 450 °C are shown in Fig. 4. In the figure, three weight loss steps can be identified at 170–180, 270 and 360 °C corresponding to the decomposition of phenyl carbamates, alkyl carbamates and phenylureas, respectively. The thermogravimetric curve of diphenyl carbamate showed a first weight loss step around 180 °C attributed to the elimination of phenyl groups and another one from 270 to 360 °C ascribed to the decomposition of the regenerated MDI (first) and to the decomposition of phenylureas (secondly), produced due to non-totally anhydrous conditions during the synthesis. For the thermogram of dibutyl carbanilate, no major weight loss was observed until 270 °C confirming the high thermal stability of alkyl urethane bonds. In some TGA, a small weight loss could be observed at 360 °C. This weight loss temperature was independent to the nature of the alcohol introduced in the MDI structure, suggesting again its relationship with the presence of ureas.

In order to determine the reactivity of phenyl MDI derivatives with the hydroxyl groups of cellulose, a mixture of Avicel® and Ph-M-Ph was refluxed for 2 h in toluene. Elemental analysis of the recovered and purified Avicel® derivate showed the presence of an appreciable amount of nitrogen, which was assigned to the presence of carbamate bonds in its structure (Table 1). Additionally, the FTIR spectrum of the recovered Avicel® showed a peak at

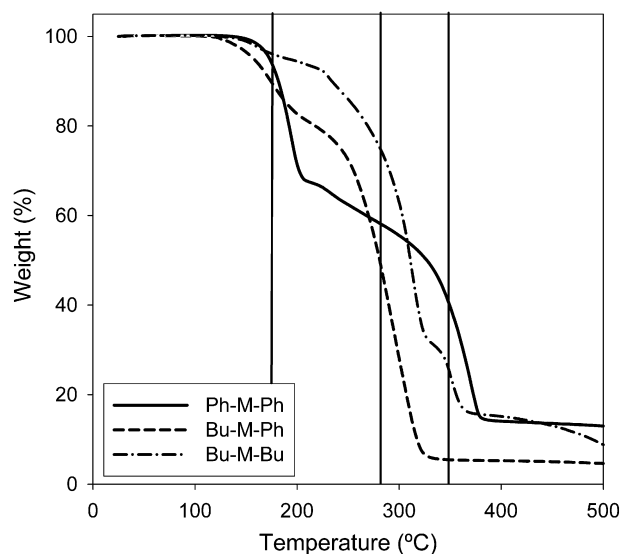


Fig. 4. TGA of various MDI carbamates.

Table 1
Elemental analysis of Avicel® and Avicel® derivatives

Raw material	Grafting agent	%C	%H	%N	%S
Avicel®	–	44.40	8.30	0.00	0.00
Avicel®	MDI	45.25	6.49	1.16	0.00
Avicel®	Ph-M-Ph	44.24	6.60	0.54	0.00

1708 cm⁻¹ corresponding to the stretching vibration of alkylic urethane bonds. Since the unique existing hydroxyl groups belong to cellulose, the signal was attributed to the formation of new carbamate linkages between Avicel® and the unblocked isocyanate (Fig. 5). Moreover, the FTIR spectra showed an absorption peak at 1538 cm⁻¹ corresponding to the amide —NH—C=O symmetric stretching vibration and a signal at 1597 cm⁻¹ associated to the benzene rings of MDI structure. Absorption at 1640 cm⁻¹ is commonly assigned to absorbed water (Colom, Carrasco, Pages, & Cañavate, 2003). Other peaks appearing on FTIR spectra are summarized and assigned in Table 2.

Finally, blocked isocyanates were used as coupling agents of pine fiber/PS composites. These coupling agents were added during the extrusion process, as described in Section 2. The mechanical properties of composites comprising 30 wt.% of pine fibre modified with different grafting agents are summarized in Table 3. Namely, the mechanical properties of pine fibre/PS composites containing unmodified technical grade MDI, phenyl blocked MDI (Ph-M-Ph) and dibutyl MDI derivative (Bu-M-Bu) are shown. Additionally, the mechanical properties of non-reinforced polystyrene and reinforced with un-modified pine fibre are also shown. The mechanical properties of non-reinforced polystyrene were enhanced by the incorporation of 30 wt.% of pine fibre. Thus, the tensile strength increased by 14% and

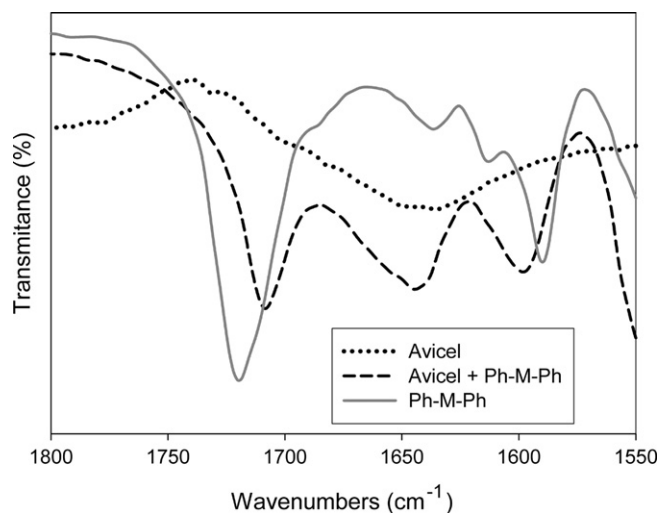


Fig. 5. FTIR of Ph-M-Ph and Avicel® before and after treatment with Ph-M-Ph in boiling toluene.

Table 2
Characteristic signals of the infrared spectra

Wavenumber (cm ⁻¹)	Assignment
2270–2230	N=C=O asymmetric stretching
1720–1695	C=O stretching (amide: —NH—CO—O—)
1660–1640	C=O stretching (urea: —NH—CO—NH—)
1650–1635	Absorbed water
1600	C=C aromatic stretching
1535–1540	—HNCO— symmetric stretching
1465	CH ₂ sym bending pyran cycle
1425	CH ₂ cellulose
1230–1250	C—N stretching

Table 3
Mechanical properties of pine fibre/PS composites

Material	Grafting agent	Tensile strength (MPa)	Tensile strain (%)	Young's modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)
PS	–	41.4 ± 0.8	2.05	2335 ± 81	79.9 ± 1.2	3053 ± 68
PS + pine	–	47.1 ± 0.3	1.63	3489 ± 357	83.3 ± 1.1	5241 ± 119
PS + pine	MDI	49.3 ± 0.8	1.77	3621 ± 210	87.9 ± 1.2	5133 ± 188
PS + pine	Ph–M–Ph	49.1 ± 0.8	1.75	3644 ± 181	86.9 ± 3.4	5248 ± 174
PS + pine	Bu–M–Bu	47.4 ± 1.1	1.76	3547 ± 318	83.4 ± 4.1	5062 ± 177

the Young's modulus by 48%, although the strain to break decreased by 20% due to the stiffening of the composites. These results agree with those established by several authors for wood fibre/polystyrene composites (Maldas, Kokta, Raj, & Daneault, 1988; Nair & Thomas, 2003).

Moreover, the addition of MDI (5 wt.%) to the pine fibre/PS composite during the extrusion process resulted in an additional increase of the mechanical properties, in agreement with results reported for similar natural fibre composites (Bledzki, Reihmane, & Gassan, 1998; Joseph, Joseph, & Thomas, 2002; Maldas et al., 1988). The occurrence of covalent bonds between MDI and the surface hydroxyl groups of cellulose could explain the enhancement, as well as the strong interactions between the π -electrons of the benzene rings of both MDI and polystyrene matrix. It is also worth noticing that the tensile strain was not reduced due to the presence of MDI, but slightly increased. This phenomenon indicated that MDI was affecting not only the rigidity of the composite but also the affinity, dispersion and adhesion of the pine fibres to polystyrene matrix. These increases in the mechanical properties were assigned to the effectiveness of MDI as coupling agent. At this point, it is important to remind the effect of the good compatibility at fibre–matrix interface, which mostly affects the tensile stress but not the rigidity (elastic modulus) of the system. Similar results were obtained for pine fibre/PS composites coupled with Ph–M–Ph. This fact pointed out the appropriate elimination of phenol groups and the good regeneration of isocyanate functions during the mixing process.

For this type of composites, the improvement on the mechanical properties induced by the use of MDI or Ph–M–Ph compounds should be explained by means of the formation of covalent bonds between the coupling agent and the cellulose fibre or by the existence of electronic interactions between them. In order to distinguish the main effect, pine fibre/polystyrene composites were modified using Bu–M–Bu coupling agent. Considering its thermal stability, no major isocyanate release was expected at the extrusion temperature. According to this, any significant improvement on the mechanical properties of pine fibre/PS composite was observed for the formulation containing Bu–M–Bu coupling agent. The thermal release of isocyanate groups did not occur at the processing temperature and no covalent linkage with the cellulose fibres could take place. FTIR was applied to extracted fibres from treated composites as shown in Fig. 6. The figure illustrates the FTIR of the extracted fibres from untreated composites and MDI and

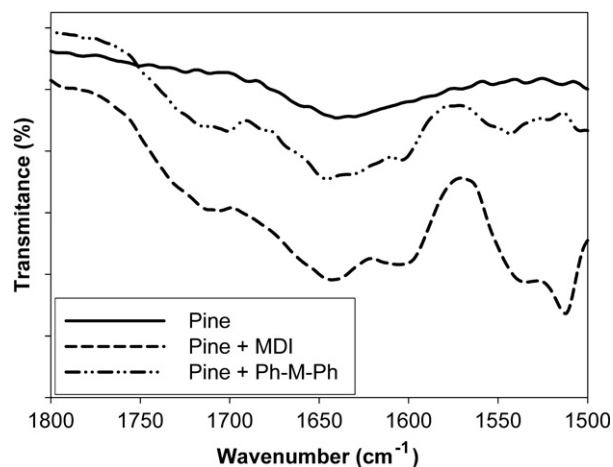


Fig. 6. FTIR of extracted fibres from treated and untreated pine fibre/polystyrene composites.

Ph–M–Ph treated pine/PS composites. The analysis of the spectra for treated composites showed the presence of peaks arising at 1705 and 1600 cm^{-1} , corresponding to the stretching vibration of amide carbonyl groups and C=C aromatic rings respectively. This result indicated the formation of covalent bonds between the fibres and the coupling agents. Additionally, the tensile fractured surfaces of untreated and MDI treated pine/PS composites were evaluated by SEM analysis. In Fig. 7, two patterns of the tensile fractured surfaces of untreated pine/PS composites (Fig. 7a and b) and two of MDI treated pine/PS composites (Fig. 7c and d) are shown. It can be observed better interfacial for those composites containing MDI coupling agent. Thus, a huge gap between at fibre–matrix interface was found for pine fibre/PS composites without coupling agent while better fibre–matrix interaction can be stated for composites containing MDI coupling agent.

It is worth noting that, although the mechanical enhancement was moderate, enough evidences of the interfacial interaction caused by the presence of MDI or phenol-blocked MDI were found. All these results emphasize the potential of phenol blocked isocyanate compounds as grafting agents when added directly during the mixing process, avoiding the use of organic solvents for the fibre surface modification.

4. Conclusions

In the current study, various blocked MDI adducts were synthesized and their deblocking temperatures were

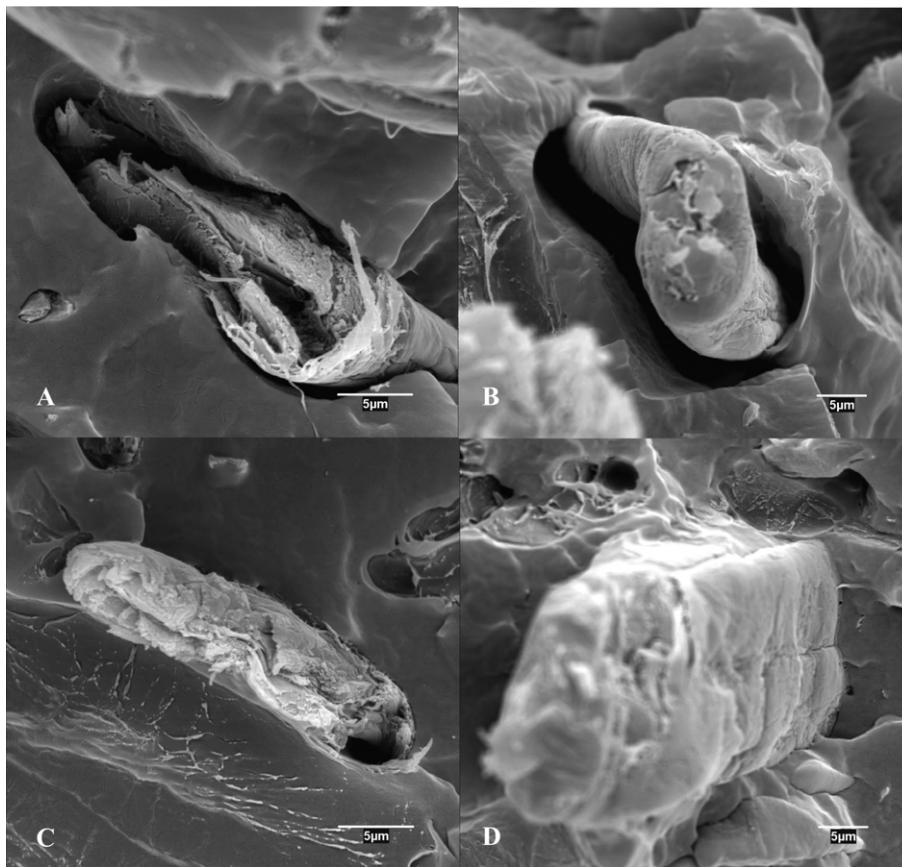


Fig. 7. SEM microphotographs of untreated pine fibre/PS composites (A, B) and MDI treated pine fibre/PS composites (C, D).

investigated. TGA have demonstrated that at the PS and PP processing temperatures (170–180 °C) the deblocking process of the MDI-phenol adducts occurs satisfactorily, preserving the integrity of the MDI-primary alcohol urethane bond. Reactivity at high temperature of microcrystalline cellulose with blocked diisocyanate has been corroborated by elemental analyses and infrared spectroscopy. The addition of blocked and unblocked MDI during the processing of pine fibre/polystyrene composites resulted in an increase of both tensile and flexural strengths of these materials.

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