Effect of grafting yield and molecular weight of m-TMI-grafted-PP on the mechanical properties of wood fiber filled polypropylene composites

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ABSTRACT: m-Isopropenyl-α, α-dimethylbenzyl isocyanate (m-TMI) was grafted on isotactic polypropylene (PP) using di-cumyl peroxide as a reaction initiator under varying reaction conditions to yield m-TMI-g-PP coupling agent with four sets of grafting yield and molecular weight. Grafting yield of the synthesized m-TMI-g-PP were 1.80%, 2.01%, 9.05%, and 8.86% and molecular weight of the corresponding grafted polymer were 129,225; [Correction made here after initial online publication.] 187,240; 124,130; and 180,838, respectively. Rubberwood flour reinforced polypropylene composites were prepared using these coupling agents and tested for mechanical properties. m-TMI-g-PP coupling agent with 9.09% grafting and 124230 M_w was found to give the highest tensile and flexural strengths. Flexural modulus of the coupled composites was higher than uncoupled composites. Interfacial region of the composites characterized by scanning electron microscope (SEM) suggest effective wetting of fiber by PP in the case of coupled composites. The effect of fiber loading on composites indicates continuous increment in tensile and flexural strengths in coupled composites. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44196.

INTRODUCTION

Mechanical properties of the wood plastic composite (WPC) are largely determined by the interfacial adhesion of wood fibers with polymer matrix. Due to hydrophobic nature of plastics and hydrophilic nature of fibers and difference in their surface energies, interfacial adhesion between the two materials is one of the major concerns in such composites. Over the years, extensive research has been carried out towards improving the interfacial adhesion between nonpolar polymer matrix and polar fibrous material. One of the most common and commercially viable methods is to use a coupling agent. Coupling agent acts as a connecting bridge forming chemical bonds between hydroxyl group present on the surface of natural fibers and carbon chain of polymers. Interaction between the coupling agent and the wood fibers are generally of covalent in nature.[1] Grafting of maleic anhydride (MA) on polypropylene (PP) is one of the most studied reactions of functionalized polyolefins resulting in maleic anhydride grafted polypropylene (MAPP). MAPP, as a coupling agent, is well known to enhance interfacial adhesion between natural fibers and polypropylene and thereby improving tensile and flexural strengths.[2] Other than anhydrides, coupling agents based on isocyanates, amides, acrylates have also been used for wood filled polypropylene composites.[3]

The efficiency of coupling agent is largely determined by the functional group, grafting of such functional groups on polymeric chains and the molecular weight (M_w) of the coupling agent. Grafting yield or graft percentage represents the number of functional group available for chemical bonding with the natural fibers thereby improving interfacial adhesion and mechanical properties. High M_w of the coupling agent allows diffusion of polymer chains into the matrix supporting the chain entanglement phenomenon leading to the effective stress transfer.[4] Limited literature is available regarding grafting yield and molecular weight effect on WPC mechanical properties of coupling agent. Lu *et al.*[5] studied coupling efficiency of seven coupling agents in WPC. The coupling agent with a high molecular weight, moderate acid number, and low

Table I. Reaction Parameters for the Preparation of m-TMI-g-PP

m-TMI-g-PP coupling agent	PP (wt) g	m-TMI (wt %)	DCP (wt %)	Reaction time (min)	Reaction temperature (°C)
CA I	40	2	5	8	150
CA II	40	2.5	1	3	150
CA III	40	10	10	8	150
CA IV	40	10	5	10	150

concentration level was preferred to improved interfacial adhesion in WPC. Kim et al.[6] observed that MAPP with 1.2 maleic anhydride (MA) graft (%) and 52,000 M_w performed good in terms of improving tensile and flexural strengths. They concluded that MAPP having moderate levels of MA graft (%) and high M_w gave better mechanical properties of the composites. Sufficient MA content onto polymer chain gives strong interfacial adhesion between the natural fibers due to chemical bonds between MA and -OH groups of biofillers.[7,8] m-Isopropenyl-α, α-dimethylbenzyl isocyanate (m-TMI) is a monomer, with vinyl unsaturation and a pendant isocyanate (—NCO) functional group, that can be grafted on polypropylene chains introducing polar groups to polypropylene backbone chain.[9] Karmarkar et al.[10] synthesized m-TMI-grafted-polypropylene (m-TMI-g-PP) through melt phase functionalization and studied the effect of monomer and peroxide concentrations on degree of grafting. m-TMI-g-PP was found to be an effective compatibilizer improving interfacial adhesion between natural fibers and PP and significantly improving the mechanical properties of the composites.[11,12] This coupling agent has been reported to perform better as compared to MAPP for WPC.[13] Most of the studies with m-TMI-g-PP coupling agent have been carried out a specific grafting percentage (5.6%). Varied levels of grafting yield and molecular weight distribution of the m-TMI-g-PP can be achieved during synthesis process.[10] However, there are no reports on effect of these factors on mechanical properties of wood fiber filled composites.

In this research work, m-TMI-g-PP was synthesized in laboratory with varying reaction conditions in order to get coupling agent with high grafting-high molecular weight, high grafting-low molecular weight, low grafting-high molecular weight, and low grafting-low molecular weight. Melt phase functionalization of PP with m-TMI was carried out with different reaction time, monomer concentration, and initiator concentration to achieve the desired grafting and molecular weight. The aim of the study was to investigate effect of grafting percentage and molecular weight of m-TMI-g-PP on mechanical properties (tensile strength, flexural strength, and un-notched impact strength) of wood plastic composites. The effect of fiber content on mechanical properties was also studied with best performing coupling agent and the results were compared with the composites prepared without any coupling agent.

EXPERIMENTAL

Materials

m-TMI was procured from Sigma-Aldrich, and was used to functionalize isotactic polypropylene (i-PP). Di-cumyl peroxide (DCP) was procured from Himedia and used as supplied, octylamine purchased from Spectrochem. Solvents of reagent grade were used as received from suppliers. Two grades of polypropylene, Repol AM120N grade having a melt flow index of 12 g/10 min at 230 °C under 2.16 kg load and H110 MA grade having a melt flow rate of 11 g/10 min at 230 °C under 2.16 kg load were procured from Reliance Industries Limited, India. AM120N grade PP granules are porous in nature with smaller bead size that helps in efficient absorption of m-TMI on to polymer. Therefore this polymer was used for synthesis of m-TMI-grafted polypropylene. H110 MA grade PP was used as the matrix polymer for composites.

Methods

Synthesis of Coupling Agent. Melt phase functionalization of polypropylene was performed in a Thermo Scientific make Haake Polylab QC torque rheometer as per the procedure described by Karmarkar.[4] For the synthesis of coupling agent, m-TMI was absorbed onto Repol AM120N i-PP granules for a minimum of 2 h. The mixing chamber was preheated to 150 °C. Then the mixture of i-PP and m-TMI was quickly added to the torque rheometer chamber at 150 °C. PP was allowed to melt for 2 min and then DCP was added. This step of adding DCP was considered as the onset of reaction. DCP and m-TMI were added by weight percent of the polypropylene. After predetermined reaction time, the reaction product was removed and quickly cooled on a steel plate at room temperature. The unreacted m-TMI and DCP from functionalized PP was removed by dissolving reaction product in the refluxing xylene followed by precipitation by cooling. The precipitated polymer was washed several times with acetone and dried in an oven at 85 °C for 6 h. Total reaction time, m-TMI concentration (by wt %), DCP concentration (by wt %) were varied during grafting to achieve different grafting yield and molecular weight distribution (Table I).

Determination of Grafting Percentage. The amount of m-TMI grafted on i-PP was determined by titration of isocyanate group of m-TMI with octylamine according to a procedure described by Braun and Schmitt.[9] 0.5 g of grafted polymer was dissolved in 50 mL of dried xylene under reflux. Then 25 mL 0.05 M n-octylamine in xylene was added. After 1 h of refluxing, solution was cooled and filtered. The purified solution was titrated to a yellow end point with 0.1 M hydrochloric acid in isopropanol using 1% bromophenol blue in dimethylformamide as the indicator.

Fourier Transform-Infrared Spectroscopy (FT-IR). Bruker make Tensor 27 model FT-IR was used to characterize the grafting of m-TMI on polypropylene. The spectra were recorded for pure PP, pure m-TMI, m-TMI-g-PP, and composite material with a co-addition of 64 scans at a spectral resolution of 4 cm^{-1}.

Gel Permeation Chromatography (GPC). Molecular weight distribution of m-TMI-grafted-PP was determined at Product

Table II. Grafting Percentage, Molecular Weight, and Melt Flow Index of Coupling Agents

m-TMI-g-PP coupling agent	Grafting (%)	M_w	M_n	Polydispersity (PD)
CA I	1.80	129,225	48,130	2.68
CA II	2.01	187,240	72,530	2.58
CA III	9.05	124,130	46,100	2.69
CA IV	8.86	180,838	95,925	1.88

and Application Development Centre, Gharda Chemicals Ltd (GCL), Mumbai. High temperature GPC system with refractive index (RI) detector was used. Analysis was carried out at 140 °C using two mixed bed columns. After stabilization system was calibrated using narrow molecular weight polystyrene sample having polydispersity between 1.01 and 1.1. Polymer sample was dissolved in trichloro benzene (TCB) to get concentration of 1 mg in 10 mL of TCB. Mobile phase used for analysis was TCB. Total run time of the sample was 30 min. Molecular weight (M_w, M_n) were calculated using Cyrus software installed with the machine.

Wood Pulverization and Sieving. Untreated Rubberwood (*Hevea brasiliensis*) was procured from local market. The wood material was converted into chips using a small scale wood chipper. The chips were dried in an oven for 24 h and then pulverized. The pulverized wood powder was further sieved using a gyrator sieve shaker and segregated into different particle sizes with standard BSS meshes. Segregated mesh size of −80 +100 wood powder was oven dried at 105 °C for 24 h and used for compounding of Rubberwood filled polypropylene composites.

Preparation of Composite. Compounding of Rubberwood filled plastic composites was done using a 28 mm co-rotating twin screw extruder. The extruder had six heating barrels. Temperature profile was kept from 150 °C to 165 °C throughout the experiments. Extruder system was started with pure PP at 110 rpm. After reaching steady conditions, feed was replaced with premixed mixture of PP granules, wood powder, and the coupling agent. The product was recovered as strands of composite, passed through water bath, and subsequently fed to palletizer to obtain 3 mm length granules. Palletized granules were oven dried at 85 °C for 24 h to remove moisture. The dried granules were then injection molded according to ASTM standards for determining the mechanical properties

Composites with all the four m-TMI-g-PP coupling agents were blended at 30% and 50% reinforcement of Rubberwood (Table I). All coupled composites contained 5% coupling agent based on wood content. The control was Rubberwood powder and polypropylene composites without the coupling agent. After the blending, samples were injection molded and tested for the mechanical properties. Among the four coupling agents, the best performing formulation in terms of mechanical properties was further used to study the effect of fiber loading. Composites with wood content varying from 10 to 50 wt % were prepared and tested for mechanical properties.

Sample Preparation. Composites were moulded into standard ASTM type specimen (ASTM D638 for tensile and D790 for flexural tests) using a 60 ton L&T Demag make microprocessor controlled, closed loop injection molding machine. The prepared specimens were stored in desiccator for a minimum of 24 h before testing.

Mechanical Testing. Mechanical tests (tensile and flexural) were performed using a Shimadzu make universal testing machine (model AGIS10, 10 KN). Tensile tests were conducted in accordance with ASTM D638-94b, using specimen type I (dimension—165 mm ×13.2 mm × 3.2 mm). Crosshead speed was 50 mm/min. Flexural strength was determined as per ASTM D790-92 with a support span of 100 mm and a crosshead speed of 2.8 mm/min. Specimen for the flexure tests had the dimension 127 mm × 13.2 mm × 6.4 mm. For each test, five replicates were tested. Un-notched impact strengths were measured according to ASTM D256 on a Ceast make impact tester. For un-notched impact strengths, 5.4 joule hammer was used. Ten replicates for each composition were tested for impact strength.

Surface Morphological Study of the Wood Plastic Composites. Morphology of fracture surface of the composites was analyzed using FEI make Scanning electron microscopy (SEM) with tungsten source and everhart thornley detector (ETD) to examine the interfacial adhesion between wood fiber and PP matrix.

RESULTS AND DISCUSSION

Synthesis and Characterization of Coupling Agents

The reaction conditions during the grafting of m-TMI on polypropylene were selected in a manner to obtain coupling agent with low grafting low molecular weight, low grafting high molecular weight, high grafting low molecular weight, and high grafting high molecular weight. The grafting percentage and molecular weight of the obtained coupling agents are shown in Table II. Among the four coupling agents, CA-I and CA-II were characterized with low grafting but distinctly different molecular weight. CA-III and CA-IV exhibited high grafting percentage and different molecular weights. The difference in grafting percentage and molecular weight observed for m-TMI-g-PP can be explained based on the reaction mechanism of m-TMI with PP (Scheme 1) as described by Karmarkar.[4] Since m-TMI molecule has a vinyl unsaturation and a pendant isocyanate group which is not conjugated with aromatic ring [Scheme 1(a)], therefore both functional groups can react independently.

It is well known that in presence of heat, di-cumyl peroxide breaks down to form free radicals. Reaction will follow two different paths in presence of free radical. One is the free radical
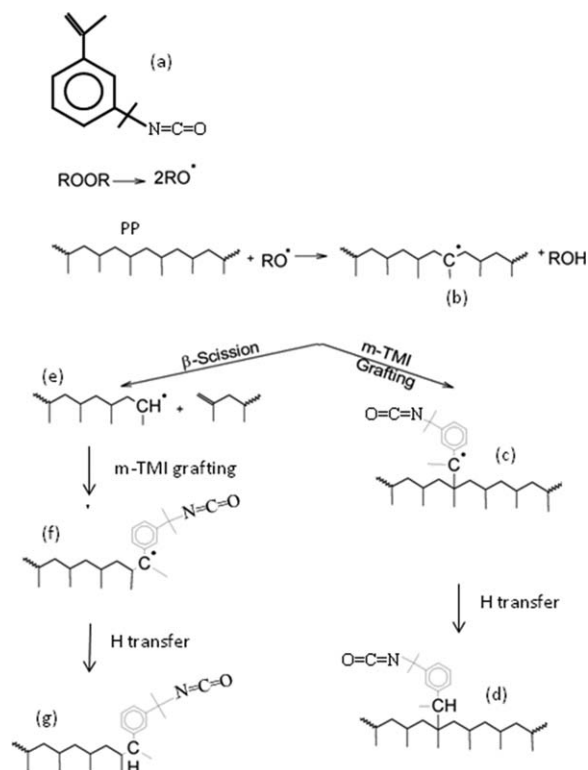
Scheme 1. Grafting mechanism of m-TMI on PP (redrawn from Karmarkar.[4])

specifically abstracts hydrogen, bonded to tertiary carbon of polymer chain than hydrogen bonded to secondary or primary carbon atom due to the thermodynamic stability of tertiary free radical more than primary and secondary carbon [Scheme 1(b)]. The free radical thus produced in polymer chain attack on methylene (—CH2—) group of m-TMI molecule to give again a tertiary free radical which abstracts hydrogen from tertiary carbon of neighboring polymer chain to give m-TMI grafted PP. The reaction cycle repeats to give m-TMI grafted PP until whole of free radical is consumed [Scheme 1(c,d)]. In the alternate path, the free radical produced in polymer chain mentioned above is sufficiently not long lived or cannot find a m-TMI molecule, then β scission occurs i.e. the bond between free radical carbon and carbon atom in β position breaks to give a chain scission product of low molecular weight alkene polymer and secondary free radical at polymer chain [Scheme 1(e)]. The free radical thus produced reacts with m-TMI to give m-TMI grafted PP of reduced molecular weight [Scheme 1(f,g)]. Synthesizing coupling agent with high grafting percentage without significant loss of molecular weight is critical to the coupling agent.

In case of CA- I, as the concentration of m-TMI (2%) was much lower than DCP (5%), the β−scission of PP chains becomes prominent leading to m-TMI-g-PP with low grafting (1.8%) and low M_w (129,225). The synthesis reaction of CA-II was carried out for a very short period (3 min) along with small quantity of DCP (1 wt %) and m-TMI (2%) with respect to PP. This has resulted in low grafting (2.01%) but high

molecular weight (M_w, 187,240) as the small quantity of initiator controls the β-scission of polymer chain.

In case of CA- III, 10% of m-TMI absorbed on PP was added to torque rheometer maintained at 150 °C. When the polymer melts completely, 10% of DCP was added at once. In this case the grafting percentage was 9.06 with M_w of 124,230. High m-TMI content during the reaction resulted in high grafting. At the same time high DCP content, the formation of free radical in polymer chain increases with probability of β scission reaction. The secondary free radical produced on polymer chain after undergoing scission mechanism reacts with m-TMI to give the grafted product (high grafting) with loss in molecular weight.

The procedure mentioned in methods section is followed in all cases, except for CA-IV (Table I). In this case DCP was added in two equal volumes. After first 2 min, 2.5% DCP was added and the reaction was allowed to take place for 5 min. After this, remaining 2.5% of the DCP was added and reaction was continued for further 5 min. Thus total reaction time was 10 min. In this case, it is observed that the obtained grafted PP had a high grafting percentage (8.96) along with high M_w. The possible reason may be that for every molecule of DCP which dissociates, it produces two molecule of di-cumoxyl free radical. Since DCP is added in two stages the formation of free radical in polymer chain is controlled and the probability of reacting m-TMI with PP carbon chain increases with low level of β scission reaction, which is the main cause of loss in molecular weight in PP during grafting.

FT-IR spectrum of grafted polypropylene is shown in the Figure 1. The spectrum band at 2260 cm^{-1} which is characteristic of —NCO group is clearly evident in grafted product. The absorption band at 1698 cm^{-1} characteristic of C=C stretching vibration, in the pure m-TMI is seen to diminish due to grafting. This confirms with mechanism of grafting. The grafting takes place via vinyl unsaturation of m-TMI whereas the —NCO group (peak at 2260 cm^{-1}) remains available for reaction with hydroxyl group present in wood. The FT-IR spectrum of the four coupling agents reflects the differences in the peak height of the absorption band at 2260 cm^{-1} (Figure 2). The peak height for the coupling agent with low grafting percentage (CA I and CA II) are much lower as compared to the peak height with high grafting percentage (CA III and CA IV).

Effect of Grafting Percentage and Molecular Weight Distribution of m-TMI-g-PP on Mechanical Properties of the Composite

The main aim of synthesizing coupling agents with different grafting percentage and molecular weight was to study the influence of these two parameters on mechanical properties. The use of coupling agent improves the interfacial adhesion between the polymer matrix and the wood fibers. Part of polymer matrix surrounding wood fiber is called as interfacial region. The interface region is important, which exhibits different properties than the whole matrix. Mechanical properties of the composite depend largely on the effective interfacial adhesion between the fibers and polymer matrix. The coupling agent acts a connecting bridge between these two materials, improving
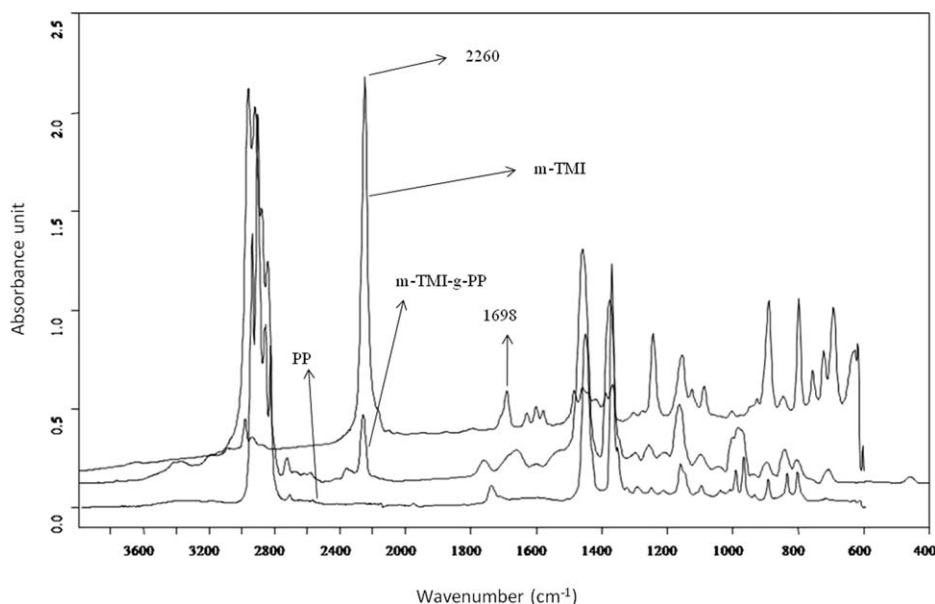
Figure 1. FT-IR spectra of (a) m-TMI, (b) PP, (c) m-TMI-*g*-PP.

the interfacial adhesion. The isocyanate (—NCO) functional group of the m-TMI-*g*-PP reacts with hydroxyl group on wood fibers to form carbamate ester linkages whereas the PP chain entangles with the matrix polymer. The FT-IR spectra (Figure 3) clearly demonstrate the formation of ester bond (peak at 1720 cm^{-1}) in the composite material. This indicated the reaction between —NCO group in m-TMI-*g*-PP and —OH groups present in wood. The reaction mechanism of m-TMI-*g*-PP with wood has been described in detail by Karmarkar *et al.*[11] Applied stresses applied on the composite material are transferred from matrix to fibers through covalent bonds at interface region. Thus, number of bonding sites also affects the properties of the composite.

The strength properties determined at 30% and 50% wood content are shown in Table III. The percent change values in the table are based on the increase in strength values of coupled composites compared to composite prepared without any coupling agent. At 5% coupling agent concentration for all the blends, composite prepared with CA-III coupling agent exhibited the highest strength properties. Tensile strength at 30% fiber reinforcement was 40.01 N/mm^2 and flexural strength 53.51 N/mm^2 representing 38.06% and 26.86% increase respectively with respect to composites without coupling agent. At 50%, there was 80.61% and 54.67% increase in tensile and flexural strength, respectively. The impact strength at 30% and 50% fiber reinforcement increased by 25.35% and 47.15%, respectively. Composite prepared with CA-IV (high grafting and high molecular weight) also showed significant increase in strength properties but were slightly inferior than CA-III coupled composites.

Composites prepared with CA-I and CA-II, which were characterized with low grafting, suggest that there were very few functional sites available for covalent bonding with wood and therefore the improvement in the properties is marginal as compared to control composites. Among these two agents, the molecular weight of CA-II was higher but the strength of the composites was the lowest among the four coupling agents. Though the coupling agent CA-IV had a grafting percentage as high as 8.86% and high molecular weight of 180,838, composites prepared with CA-III were better in strength properties suggesting that there is a combinational effect of both grafting percentage and molecular weight of m-TMI-*g*-PP on interfacial adhesion between wood fiber and PP. Low grafting leads to low properties but at the same time too high molecular weight of the coupling agent resulted in lowering the strength which is in contrast to the general perception that high molecular weight coupling agent is the most efficient in transferring the stresses from matrix to the polymer and thereby improving the strength.[5,14] However, most of the studies relating molecular weight of coupling agent with strength are with MAPP and the maximum M_w is reported be 60,000 to 80,000. Keener *et al.*[15]
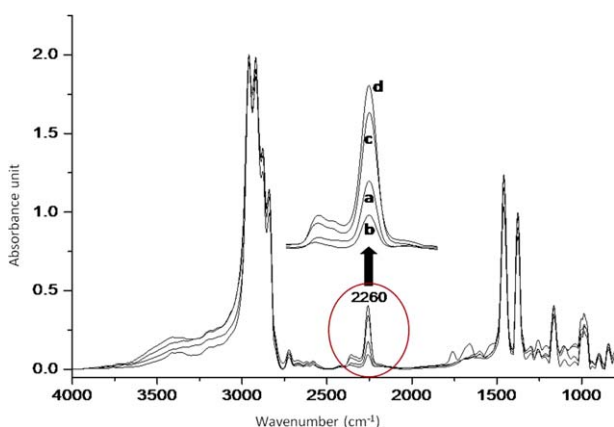

Figure 2. FT-IR spectrum of the synthesized coupling agents with different grafting levels (a) CA-II, (b) CA-I, (c) CA-IV, (d) CA-III. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
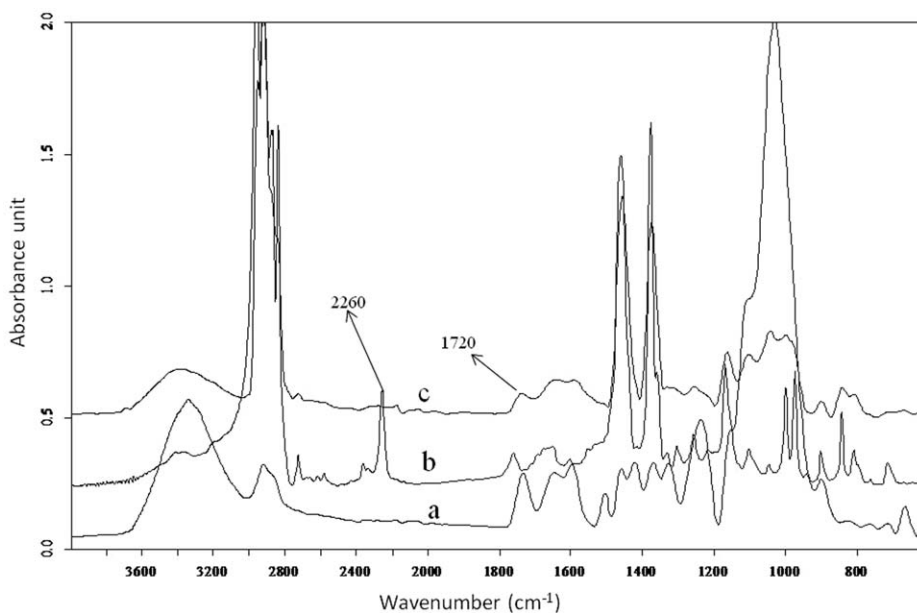
Figure 3. FT-IR spectrum of (a) wood, (b) m-TMI-*g*-PP, (c) composite.

suggested a balance in molecular weight and functionality in coupling agent for its effectiveness. The effectiveness of the coupling agent depends on its ability to form chemical linkages with wood surface along with entanglement of coupling agent chain with the polymer matrix. During the kneading and blending of composites, the chains of coupling agent get entangled with whole polymer matrix whereas ─NCO group in the chain reacts with the hydroxyl groups available at the fiber surface thus forming an interface region. For short polymer chains i.e. coupling agent with too low M_w hardly any entanglement take place. However, too high M_w of the coupling agent may not allow the functional groups to reside at the interface.[15] In this case, M_w of about 1,20,000 was found to be ideal to achieve enough chain entanglement for effective stress transfer from one chain to another. Further increase in molecular weight is not found to have any positive influence on the mechanical properties. It was very evident in difference in strengths with similar

grafting percentage (CA I vs. CA II and CA III vs. CA IV). The improvement in mechanical property demonstrates that the grafting percentage and molecular weight attained in CA III was found to be optimum for m-TMI-*g*-PP coupling agent.

Effect of Fiber Reinforcement on Physical Properties WPC. In order to study the effect of fiber loading percentage on physical and mechanical properties of WPC; composites were blended at varying wood content ranging from 10 to 50 wt % using CA-III coupling agent. Coupling agent concentration was kept at 5 (wt %) to the weight of the fibers. Formulations used for making composites are showed in the Table IV. Properties were compared to composites without any coupling agent. Tensile strength, flexural strength, flexural modulus and un-notched impact strength of composites at different fiber loading are shown in Figures 4 to 7.

Table III. Strength Properties (±1 SD) of the Composites Prepared with m-TMI-*g*-PP Coupling Agent Having Different Grafting Percentage and Molecular Weight
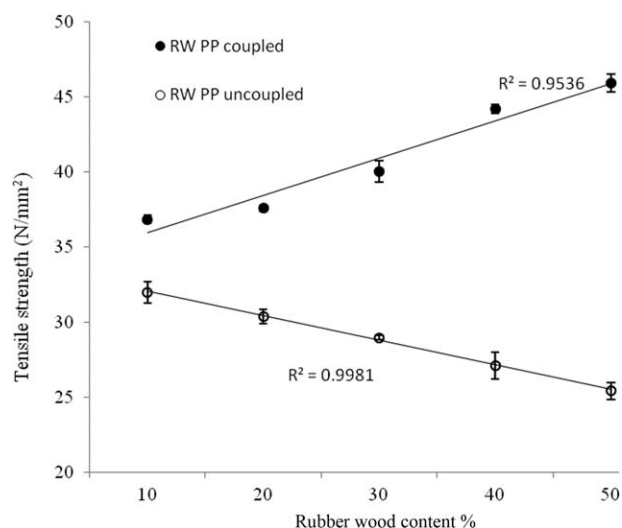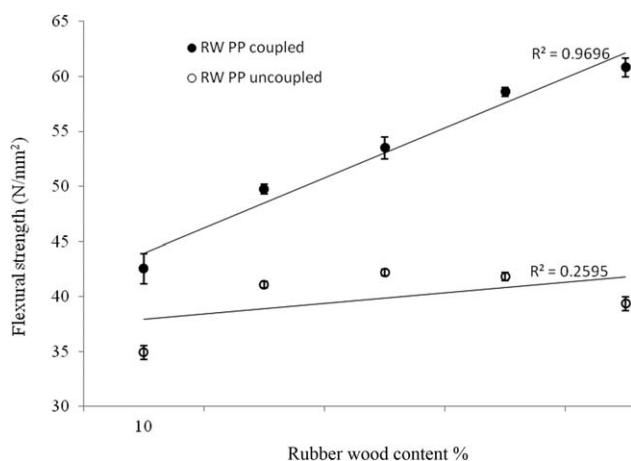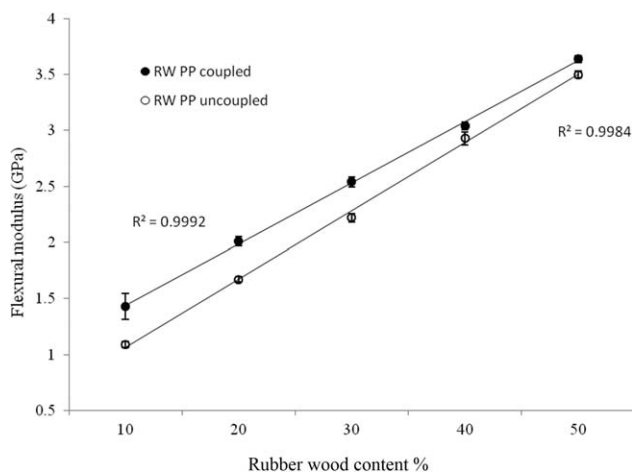
	Tensile strength (MPa)		Flexural strength (MPa)		Unnotched impact strength (J/m)	
m-TMI-*g*-PP	30% wood	50% wood	30% wood	50% wood	30% wood	50% wood
CA-I	35.93 ± 0.22 (23.98%)	35.28 ± 0.22 (38.73%)	47.03 ± 0.39 (11.64%)	47.66 ± 0.58 (21.14%)	153 + 1.33 (0.64%)	115 ± 1.25 (14%)
CA-II	32.20 ± 0.44 (11.11%)	29.23 ± 0.99 (14.94%)	45.53 ± 0.67 (7.94%)	42.68 ± 1.07 (8.49%)	145 ± 11.40 (−4.97%)	93 ± 4.78 (−8.76%)
CA-III	40.01 ± 0.71 (38.06%)	45.93 ± 0.60 (80.61%)	53.51 ± 0.99 (26.86%)	60.85 ± 0.85 (54.67%)	191 ± 6.35 (25.35%)	149 ± 17.20 (47.15%)
CA-IV	37.84 ± 0.16 (30.57%)	42.35 ± 0.79 (66.53%)	49.46 ± 0.56 (17.25%)	56.73 ± 0.51 (44.20%)	191 ± 9.90 (25.28%)	146 ± 11.00 (44.89%)
Uncoupled	28.98 ± 0.14	25.43 ± 0.56	42.18 ± 0.28	39.34 ± 0.62	152 ± 22.66	101 ± 1.67

Values in parentheses are the percent improvement in the respective strength properties with respect to uncoupled composites.
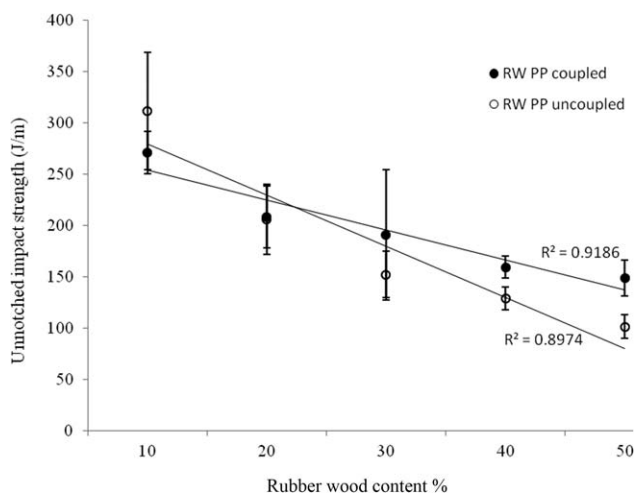
Table IV. Formulations for Composites Preparation

Composite (%)	Polypropylene (g)	Rubber wood (g)	Coupling agent (m-TMI-g-PP) (g)
10	720	80	4
20	640	160	8
30	560	240	12
40	480	320	16
50	400	400	20

Both tensile and flexural strengths of the composites with coupling agent increased with the increase in Rubberwood content. Whereas, in case of uncoupled composites, as the fiber content increased tensile strength declined sharply at 50% fiber to 25.43 N/mm^2, from 31.99 N/mm^2 at 10%. A 54.67% increase in flexural strength was observed with respect to composites without

Figure 6. Flexural modulus of Rubberwood-PP coupled and uncoupled composite.

any coupling agent at 50% wood content. Similar results were also observed by the Chauhan et al.[13] and Aggarwal et al.[16] In absence of coupling agent, Rubberwood fibers are not contributing in improvement of strength properties. The tensile strength is an indicator of the interfacial adhesion between fibers and the matrix. The loss in tensile strength properties in uncoupled composites indicates the poor interfacial adhesion between fibers and polypropylene. However, with coupling agent, tensile strength increased continuously with increasing fiber concentration. The interfacial adhesion between fiber and matrix in both coupled and uncoupled composites was analyzed from the fractured surface by SEM (Figure 8). Impact fractured surfaces of 40% fiber filled composites were examined under SEM operated at 10 kV, both with coupling agent and without coupling agent. In case of uncoupled composite the failure from the fiber-matrix interface is clearly evident [Figure 8(A)]. Whereas in coupled composites, the majority of fibers are coated with matrix polypropylene [Figure 8(B)]. The —NCO functional group present on coupling agent is highly reactive with —OH groups present on the surface of fibers, which yields

Figure 4. Tensile strength of Rubberwood-PP coupled and uncoupled composite.

Figure 5. Flexural strength of Rubberwood-PP coupled and uncoupled composites.

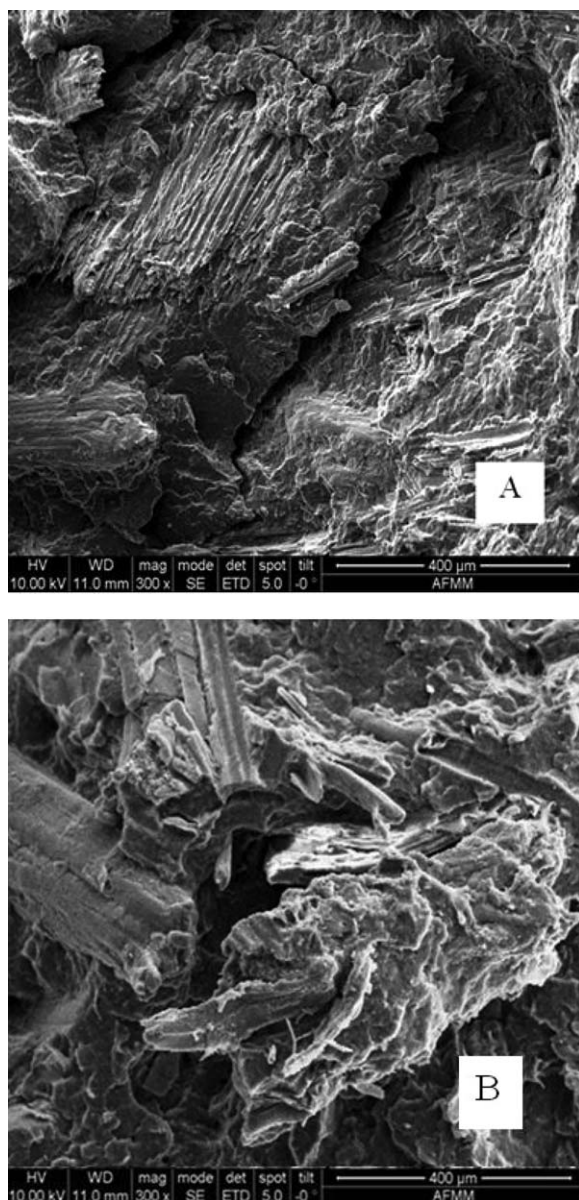**Figure 7.** Un-notched impact strength of Rubberwood-PP coupled and uncoupled composites.

Figure 8. SEM micrograph of impact fractured specimens of 40% wood fiber filled composites. (a) Without any coupling agent, (b) with m-TMI-*g*-PP coupling agent.

urethane linkage, and therefore isocyanate is chemically linked to the wood fibers. Therefore m-TMI-*g*-PP effectively improves the interfacial adhesion between the natural fibers and PP.[17]

Flexural modulus exhibited an increasing trend with the increase in fiber content in both coupled and uncoupled composites unlike strength properties. The increase in the modulus with increasing wood content in both types of composites is due to the increased proportion of high-modulus wood fibers in the low-modulus polypropylene matrix. However, the modulus values for coupled composites were higher than uncoupled composites at all fiber content. Higher modulus in coupled composites may be attributed to the alterations in crystal morphology of the polypropylene chains near the fiber-matrix

interface.[18–20] With the addition of coupling agent, a transcrystalline layer is reported to form around the fiber which is characterized by high elastic modulus that can increase the modulus contribution of the polymer matrix to the composite modulus.[21]

Un-notched impact strength of the composite material declined with increasing fiber content in both coupled and uncoupled composites (Figure 7). Presence of wood fibers in polymer matrix act as a stress concentration points and crack initiation starts from these points. Another reason for decrease in impact strength may be the stiffening of polymer chains due to bonding between wood fibers and matrix.[11] For high impact properties, in fact, a slightly weaker adhesion between fiber and polymer is desirable, as it would result in a higher degradation of impact energy, supporting the so-called fiber pull-out. Good adhesion on the contrary results in abrupt fiber fracture with a minor energy degradation.[22] The improvement in mechanical (tensile and flexural) properties of the composites can be attributed to high strength and modulus of natural fibers and improved interfacial between matrix and fibers.

CONCLUSIONS

The results suggest that the coupling agents can be synthesized with desired molecular weight and grafting levels by modifying the reaction conditions. There were significant differences in tensile and flexural strengths of composites with different coupling agents. The grafting percentage of about 9% and molecular weight of about 120,000 of the m-TMI-*g*-PP coupling agent was found to give the best mechanical properties in the composites. The strength properties increased with the fiber content in coupled composites which indicate the effective wetting of fiber with polypropylene during compounding.

REFERENCES

1. Li, Q. *J. Thermo. Compos. Mater.* **2003**, *16*, 551.

2. Karmaker, C.; Youncquist, J. A. *J. Appl. Polym. Sci.* **1996**, *62*, 1147.

3. Moad, G. *Prog. Polym. Sci.* **1999**, *24*, 81.

4. Karmarkar, A. Ph.D. Thesis, Indian Institute of Science, Bangalore, **2007**.

5. Lu, J. Z.; Wu, Q.; Negulescu, I. I. *J. Appl. Polym. Sci.* **2005**, *96*, 93.

6. Kim, H. S.; Lee, B. H.; Choi, S. W.; Kim, S.; Kim, H. J. *Compos. A* **2007**, *38*, 1473.

7. Kim, H. S.; Yang, H. S.; Kim, H. J. *J. Appl. Polym. Sci.* **2005**, *97*, 1513.

8. Baroulaki, I.; Karakasi, Q.; Pappa, G.; Tarantili, P. A. *Compos. A* **2006**, *37*, 1613.

9. Braun, D.; Schmitt, M. W. *Polym. Bull.* **1998**, *40*, 189.

10. Karmarkar, A.; Aggarwal, P.; Modak, J.; Chanda, M. *J. Polym. Mater.* **2003**, *21*, 101.

11. Karmarkar, A.; Chauhan, S. S.; Modak, J. M.; Chanda, M. *Compos. A* **2007**, *38*, 227.

12. Nandi, A.; Kale, A.; Raghu, N.; Aggarwal, P. K.; Chauhan, S. S. *J. Ind. Acad. Wood Sci.* **2013**, *10*, 62.

13. Chauhan, S. S.; Aggarwal, P.; Karmarkar, A. *J. Compos. Mater* **2015**, DOI: 10.1177/0021998315622050.

14. Dányádia, L.; Janecskac, T.; Szabóc, Z.; Nagyc, G.; Móczóa, J.; Pukánszkya, B. *Compos. Sci. Technol.* **2007**, *67*, 2838.

15. Keener, T. J.; Stuart, R. K.; Brown, T. K. *Compos. A* **2004**, *35*, 357.

16. Aggarwal, P. K.; Raghu, N.; Karmarkar, A. *Mater. Des.* **2013**, *43*, 112.

17. Guo, C. G.; Wang, Q. W. *J. Appl. Polym. Sci.* **2008**, *109*, 3080.

18. Maldas, D.; Kokta, B. V.; Daneaukt, C. *J. Appl. Polym. Sci.* **1989**, *37*, 751.

19. Maldas, D.; Kokta, B. V.; Daneaukt, C. *J. Appl. Polym. Sci.* **1989**, *38*, 413.

20. Simonson, J.; Rials, T. G. *J. Thermo. Compos. Mater.* **1999**, *9*, 292.

21. Sanadi, A. R.; Caulfield, D. F.; Jacobson, R. E. Agro-Fiber Thermoplastic Composites; Lewis Publishers: Boca Raton, FL, **1997**; p 377.

22. Mueller, D. H.; Krobjilowski, A. J. *Ind. Text.* **2003**, *33*, 111.