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Performance of Different Fillers in Polymeric Methylene Diphenyl Diisocyanate (pMDI) Resin*

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Abstract

This study evaluated the possibility of using different fillers—cellulose nanocrystal, cellulose microcrystalline, wood flour, soy flour, talc, and calcium carbonate—as partial substitutes in polymeric methylene diphenyl diisocyanate (pMDI) resin. There has been concern recently regarding the use of pMDI resin due to the environmental effect of isocyanate, which is dominantly present in the resin, as well as the cost of the resin. Different fillers were used in this study as substitutes at their allowable substitution percentages. This study focused on the possibility of replacing more pMDI resin with biodegradable filler without compromising the integrity of the resin; the mechanical strength of plywood from both southern yellow pine and oak was evaluated. Fourier-transform infrared spectroscopy, scanning electron microscopy, and thermogravimetric analysis were conducted to study the effect of modification on the bond-line quality of the final product. The effects of different fillers on adhesion properties of the pMDI resin were tested on the plywood according to the American Society for Testing and Materials (ASTM D–906-64) standard. The results showed that shear strength of the modified pMDI resins ranged from 0.3 to 1.083 MPa and 0.35 to 1.178 MPa for oak and pine plywoods, respectively. The modified samples with soy flour showed significant improvement in the shear strength with 261 and 236 percent higher shear strength than the control (pMDI) for samples from hardwood and softwood, respectively. Partial substitution of pMDI resin with soy flour at 30 percent substitution substantially improves the adhesion properties of pMDI resin.

Polymeric methylene diphenyl diisocyanate (pMDI) resin is one of the synthetic resins commonly used in the wood processing industry. The use of pMDI resin in the wood industry is increasing greatly because it is free of formaldehyde emission (Frisch et al. 1983). However, its use in the plywood processing industry is limited because of its low viscosity and high cost. There is also recently a big worry about the unreacted diisocyanate, which has been reported to be a well-known dermal and inhalation sensitizer in the workplace (U.S. Environmental Protection Agency 2011, Li et al. 2017). In the past there was no focus of concern on consumer exposures to diisocyanate because of an assumption that consumers are generally exposed to products containing cured polyurethanes, which have been generally considered to be inert and nontoxic. However, there are readily available consumer products, such as adhesives that contain diisocyanate, that are not completely reacted when applied and can provide potential exposures. This exposure has been documented to cause asthma, lung damage, and, in acute situations, critical reactions (U.S. Environmental Protection Agency 2011).

One of the options that could be used to ameliorate these issues is the incorporation of fillers into the pMDI resin matrix. Fillers are solid additives that are primarily used to

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lower the cost and give body to liquid adhesives or reduce undesired flow or overpenetration into the wood. The incorporation of appropriate fillers into resins has the potential to reduce the amount and cost of glue and enhance the performance of the resin. Fillers are categorized as either organic or inorganic. Organic fillers include flour, soybean powder, wood powder, bark powder, palm kernel, starch material, etc. Inorganic fillers fall into one of three categories: metal powder, metal oxides, and minerals. They are typically used to improve compression strength and dimensionally stability of the resin (Cao et al. 2021).

The use of different fillers as a partial replacement in the adhesive formulation has been an interesting idea in the plywood production process. There have been recently numerous studies on it. The effects of silica filler on the performance of two polyurethanes adhesives containing polyglycerol- or sucrose-based polyols were examined for their application in wood bonding. It was reported that small additions of silica filler improved adhesion interactions with the substrate, reinforced polymers, and increased bond-line strengths (Mamiński et al. 2020). The potential effect of cellulose nanofibrils as a filler on the specific fracture energy of urea-formaldehyde adhesive bonds was also investigated, and the feasibility of toughening these bonds by adding cellulose nanofibrils was established. The study concluded that the combination of powdered urea-formaldehyde with untreated cellulose nanofibrils gave the best bonding performance with an up to 45 percent increase in the toughening effect when adding up to 2 percent cellulose nanofibrils (Veigel et al. 2011). Furthermore, the use of cactus waste seeds as a filler in phenol-formaldehyde (PF) adhesives in comparison with olive stones to produce wood composites were also evaluated. The study showed that incorporation of up to 20 percent cactus waste seeds and olive stones into PF resins showed higher viscosity, gel time, and solids content than with the control PF. The results also showed a reduction in the formaldehyde emission levels when compared with the control PF resin (Ait Benhamou et al., 2021). The mechanical behaviors of homopolymer polypropylene filled with calcium carbonate ($CaCO_3$) particles at different levels were also investigated. The study concluded that addition of $CaCO_3$ particles as a filler changed the elastic deformation behaviors of the manufactured composites resulting in higher moduli during tensile and flexural tests (Peng et al. 2021).

Presently, there is no information on the performance of different fillers in pMDI resin with regards to plywood production. This study focused on the possibility of using different fillers—cellulose nanocrystal (CNC), cellulose microcrystalline (MCC), wood flour (WF), soy flour (SF), talc, and $CaCO_3$—as partial substitutes in pMDI resin. Different fillers were used in this study as substitutes at their allowable substitution percentages. The study also focused on the possibility of replacing more pMDI resin with biodegradable filler without compromising the integrity of the resin, and the mechanical strength of the studied plywood from both southern yellow pine (*Pinus enchinata*) and oak (*Quercus rubra*) were evaluated.

Materials and Methods

Defatted SF (7B) was provided by Archer Daniels Midland (Chicago, Illinois); its dry-basis moisture content was 6.2 percent. System Three 3110S47 brown WF was purchased from System Three Resin Incorporated (USA). The pMDI resin was MONDUR 541 from Covestro. Oak and southern yellow pine veneers (2.1 and 3.4 mm, respectively) were provided by Browder and Sons Veneer Company (Thomasville, Georgia, USA). CNC was purchased from CelluForce (Canada). MCC, extra pure with an average particle size of 90 μm, and talc powder were supplied by Thermo Fisher Scientific (New Jersey, USA). The $CaCO_3$ was purchased from Research Products International (Illinois, USA).

Fourier-transform infrared spectroscopy analysis

The samples were analyzed using Fourier-transform infrared (FTIR) spectroscopy operating in attenuated total reflectance (ATR) mode. This analysis was done to monitor changes in the structure of modified samples and to establish that modification occurs. The samples were pressed against the diamond crystal surface with a spring-loaded anvil of a thermo Nicolet, NexusTM model 470/670/870 FTIR spectroscopy equipped with zinc selenide lenses. Spectra were collected in ATR mode at a resolution of 4 cm^{-1} and 32 scans per sample within the absorption bands in the region of 4000 to 650 cm^{-1}. Data collection and further processing were carried out in the Thermo Scientific Origin software.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to evaluate the thermal profile and stability of the filler-modified pMDI resin samples. The analysis of the samples was done using TGA Q 50 apparatus. Approximately 5 ± 0.5 mg of sample were placed into an aluminum crucible, which was then loaded onto the TGA pan. Using a heating rate of 10°C min^{-1}, the analysis was conducted from room temperature up to 600°C, under a nitrogen atmosphere.

Scanning electron microscopy

Scanning electron microscopy (SEM) analysis of the pMDI resins modified with different fillers was performed to study the effect of modifications on the morphological properties of the adhesives. The dried samples were mounted on aluminum stubs using double-sided conductive carbon tape, and conductivity was enhanced using carbon evaporation (Q150T ES, Quorum Technologies). The micrographs of the samples were examined using a Zeiss Merlin FE-SEM (Carl Zeiss Microscopy, Germany) operated at 5 KV and 200 pA beam current, using in-lens secondary electron (SE) and SE2 detection.

Plywood preparation and shear-strength test

The shear-strength properties of all the filler-modified pMDI resins were determined according to the ASTM D906-64 (ASTM 2004) test method. This standard measures adhesive shear strength in a plywood construction by tension loading (Instron Universal testing machine). Three-layered plywood boards were prepared from yellow southern pine and oak veneers with an average thickness of 3.4 mm and 2.1 mm, respectively. Each veneer was coated with 250 g m^{-2} of filler-modified pMDI resin. The procedure was repeated with pMDI resin only as a control. Glued veneers were hot-pressed at 180°C with a pressure of 1.6 MPa for 3 min. Ten replicates of each treatment were prepared. The test samples were placed in a conditioning

room at 65 percent relative humidity and 20°C for 96 h before shear-strength testing analysis.

Statistical analysis

The statistical analysis was performed using Statistica software (Statsoft v13). The data were analyzed by one-way analysis of variance to determine if the formulation parameters had significant effects on the measured properties. Multiple means were compared with a post-hoc Fisher LSD test to evaluate if there were significant differences among the panels.

Results and Discussion

The notations for each panel sample are indicated in Table 1 for convenience purposes, and the allowable substitution ratio of different fillers in pMDI resin used in this study are presented in Table 2.

FTIR spectroscopy analysis

FTIR was employed to monitor changes in the structure of pMDI resin upon modification with different fillers and to evaluate variations in the molecular structures of the modified samples. Figure 1 illustrates the FTIR spectra of filler-modified samples. The emergence of peaks at 1512, 1431, 1412, and 1297/1287 cm^{-1}, which correspond to N–O stretching, O–H stretching, S=O stretching, and C–O stretching, respectively, in the $CaCO_3$–MDI modified resin established the modification process for this sample (Hosseinpourpia et al., 2018, Alawode et al. 2020b). The newly emerging peaks in the modified MCC–MDI at 1434 and 1413 cm^{-1}, which correspond to O–H bending of a carboxylic acid compound and S=O stretching of a sulfate compound, respectively, also established the occurrence of a chemical reaction between microcrystalline powder and the pMDI resin (Zhang et al. 2013).

For CNC–MDI resin, the emergence of peaks at 987 and 898 cm^{-1}, which correspond to C=C bending of alkene compound and C–H bending, respectively, prove the efficiency of the modification process (Kalami et al. 2017). The emergence of the following peaks in the SF–MDI-modified sample at 1637, 1435, and 1309 cm^{-1}, which were attributed to the C=N bending of imine/oxime compound, O–H bending of a carboxylic acid compound, and S=O stretching of sulfone compound, respectively, established that there was a chemical interaction between SF and MDI resin. For WF–MDI-modified resin, the peaks at 1414 and 692 cm^{-1}, which indicated S=O stretching of sulfate compound and C=C bending of alkene compound, respectively, also established the structural variation. And finally, for the modified talc–MDI sample, the emergence of the following absorption bands, 1638/1604, 1435/1309, 1232/1181, and 1412 cm^{-1}, which correspond to C=C stretching of an alkene compound, O=H bending of a carboxylic acid compound, C=O stretching corresponds to alkyl aryl ether/tertiary alcohol compound and S-O Stretching of sulfate compound respectively, validate the efficient modification procedure for this modified samples (Alawode et al. 2019, Govender et al. 2020). For all the modified samples the spectra for the peaks between 2240 and 2267 cm^{-1}, which correspond to isocyanate (N=C=O stretching), in the MDI resin still emerged but with reduced intensity (Hashim et al. 2011).

Table 1.—Formulation descriptions of the samples.

Sample notation	Descriptions
pMDI	Polymeric methylene diphenyl diisocyanate resin
WF–MDI	Wood flour substituted in pMDI resin
SF–MDI	Soy flour substituted in pMDI resin
Talc–MDI	Talc powder substituted in pMDI resin
$CaCO_3$–MDI	$CaCO_3$ powder substituted in pMDI resin
MCC–MDI	Microcrystalline cellulose substituted in pMDI resin
CNC–MDI	Cellulose nanocrystal substituted in pMDI resin

Table 2.—Fillers allowable substitution ratio and notation for each panel sample.

Fillers[a]	Allowable substitution ratio	pMDI ratio	Panel notation[b]	
			Oak	Pine
pMDI	N/A	N/A	HMDI	SMDI
WF–MDI	10	90	HWF	SWF
SF–MDI	30	70	HSF	SSF
Talc–MDI	30	70	HTalc	HTalc
$CaCO_3$–MDI	50	50	$HCaCO_3$	$SCaCO_3$
MCC–MDI	10	90	HMCC	SMCC
CNC–MDI	50	50	HCNC	SCNC

[a] See Table 1 for filler definitions.
[b] H = hardwood; S = softwood.

TGA analysis

Figure 2 shows the individual TGA and derivative thermogravimetry (DTG) curves comparing the thermal stability and decomposition properties of all filler-modified samples after subjecting them to a heating program from room temperature to 600°C. The influence of incorporating different fillers in pMDI resin as partial substitutes on the thermal stability of these biodegradable fillers was investigated through analysis of TGA and DTG curves. Table 3 presents the thermal properties of all modified samples obtained from TGA and DTG curves. From the TGA curves, the initial weight loss of the modified samples ranged from 1.4 to 4.4 percent, with $CaCO_3$–MDI having the lowest values and MCC–MDI having the highest values. This loss is associated with the loss of water and volatiles (Amini et al. 2013). The maximum decomposition temperatures of 217.4°C, 348.9°C, 368.0°C, and 345.1°C were recorded for pMDI, WF–MDI, talc–MDI and SF–MDI-modified resin samples, respectively, whilst 280.73°C, 222.05°C, and 274.4 °C were recorded for MCC–MDI, CNC–MDI, and $CaCO_3$–MDI samples, respectively. This indicates that the incorporation of fillers in the pMDI resin has a marked influence on the thermal property of the modified resins.

SEM analysis

The SEM analysis of all filler-modified pMDI resins and the unmodified (control) are presented in Figure 3. This analysis was conducted to show any morphological changes in the surface properties of modified resin samples. It is clearly shown that the smooth surfaces of pMDI (control) changed and became completely rough after modification with different fillers. A comparable observation has been reported by different authors (Hosseinpourpia et al. 2018, Alawode et al. 2020a). Furthermore, resin particles were

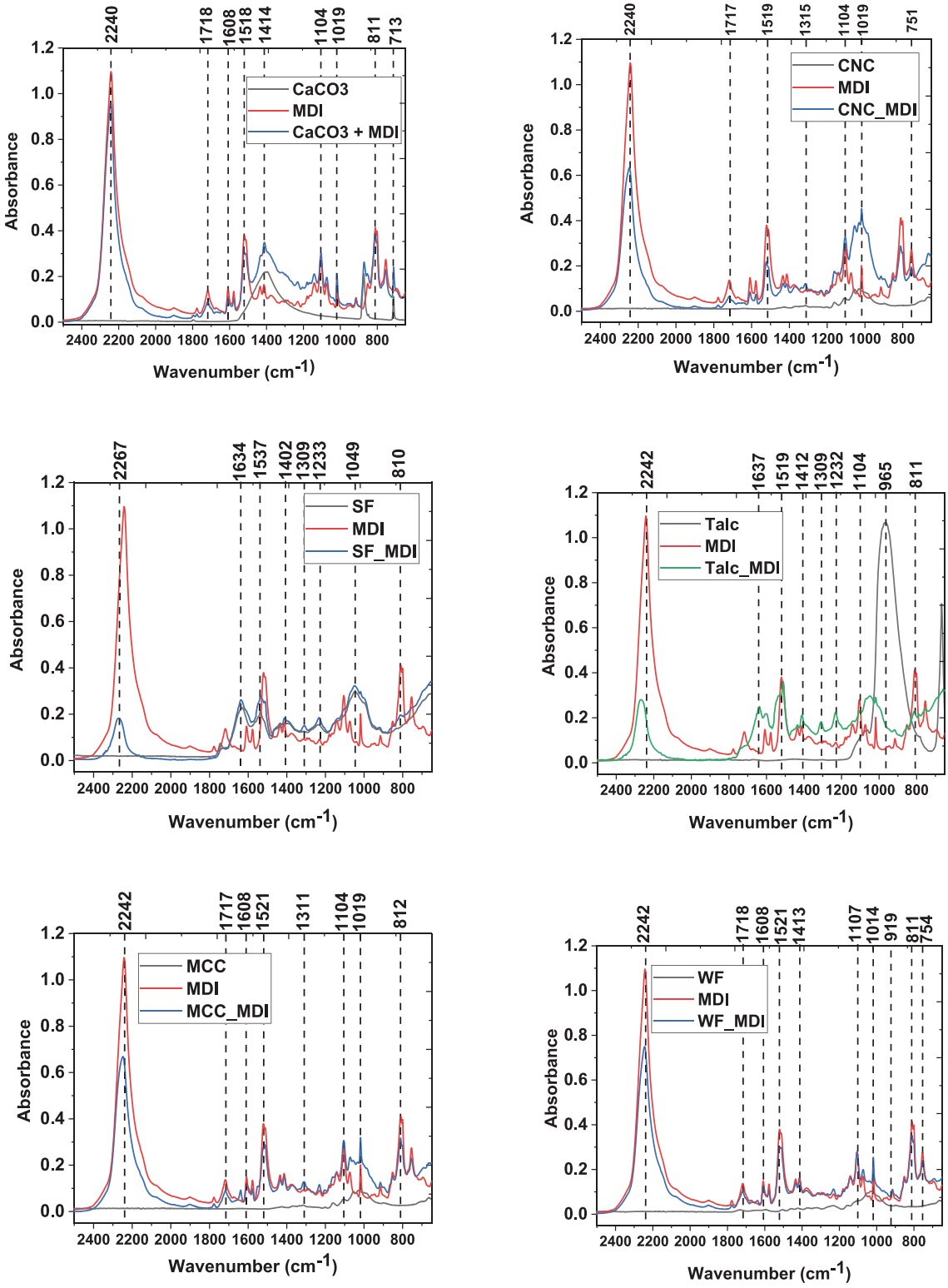

Figure 1.—Attenuated total reflectance–Fourier-transform infrared spectra of samples. SF = soy flour; MDI = methylene diphenyl diisocyanate, MCC = cellulose microcrystalline; WF = wood flour.

coated with coarse films for all filler-modified samples. This may be due to the existence of fillers, which resulted in possible blending and side reactions between control and fillers. The coarseness seen in MCC–MDI and WF–MDI samples was not as rough as other samples. This could be because of a lower allowable substitution ratio. The SEM also established that the fillers were evenly distributed within the pMDI resins matrix. The SEM micrographs proved the visual agreement of effective modification of the pMDI resin.

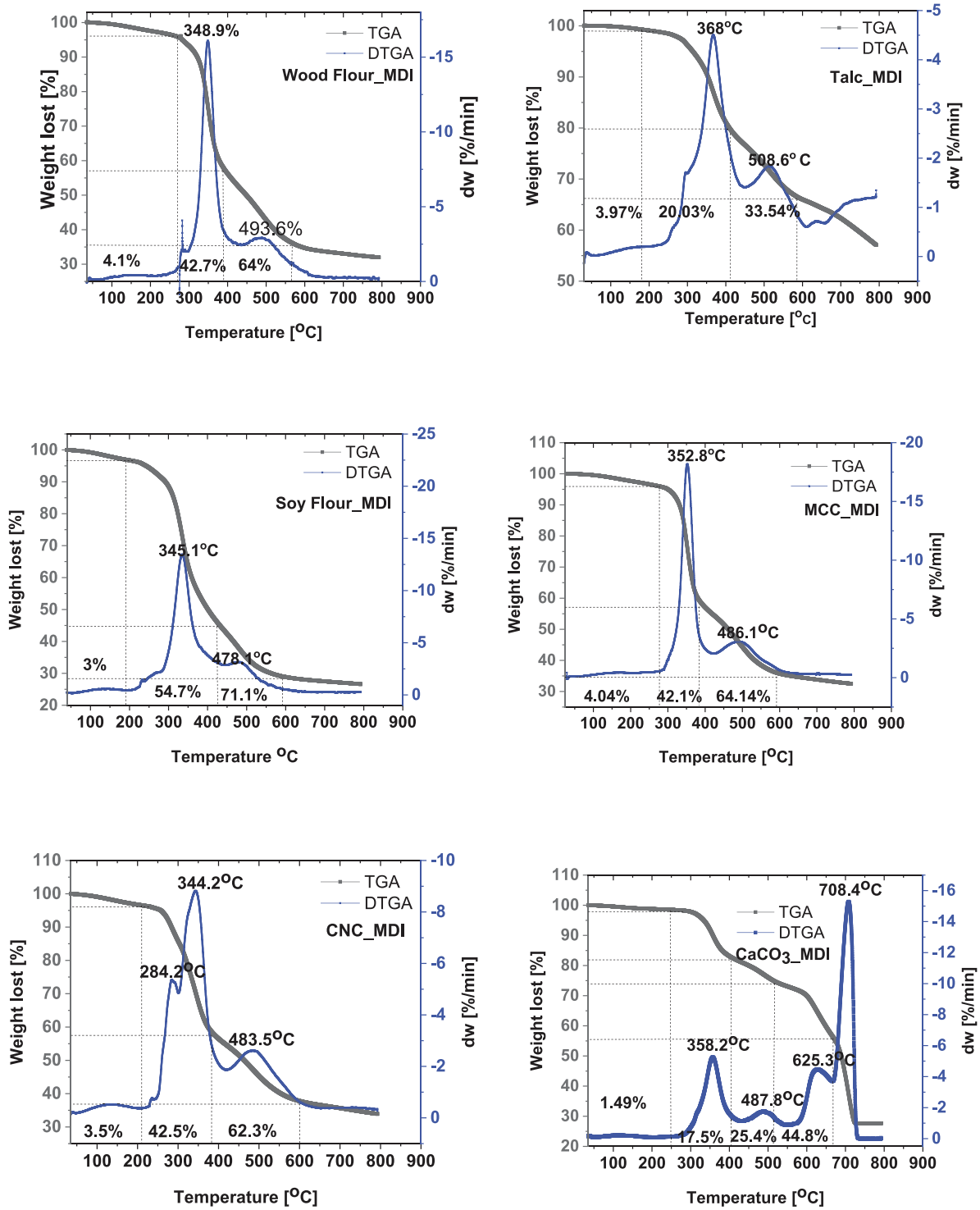

Figure 2.—Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTGA) curves of samples. MCC = cellulose microcrystalline; CNC = cellulose nanocrystal.

Shear-strength test (oak)

The results presented in Figure 4 show the mean values of shear strength for the panels made from oak veneers using different filler-modified pMDI resins; their performance was compared with panels made with pMDI resin only as a control. Hardwood SF (HSF) panels had the highest shear strength of 2.178 MPa, while pMDI panels had the least shear strength values, 0.20 MPa. This could be because of the low viscosity of pMDI resin, which usually caused starved bond joints in the panels during pressing. Similarly, the resin was usually observed to bleed through veneer surfaces and bonding joints during plywood production. This established our assertion of why pMDI is not currently being employed in the plywood industry. Furthermore, the results showed there was a significant difference between the HSF panels and the

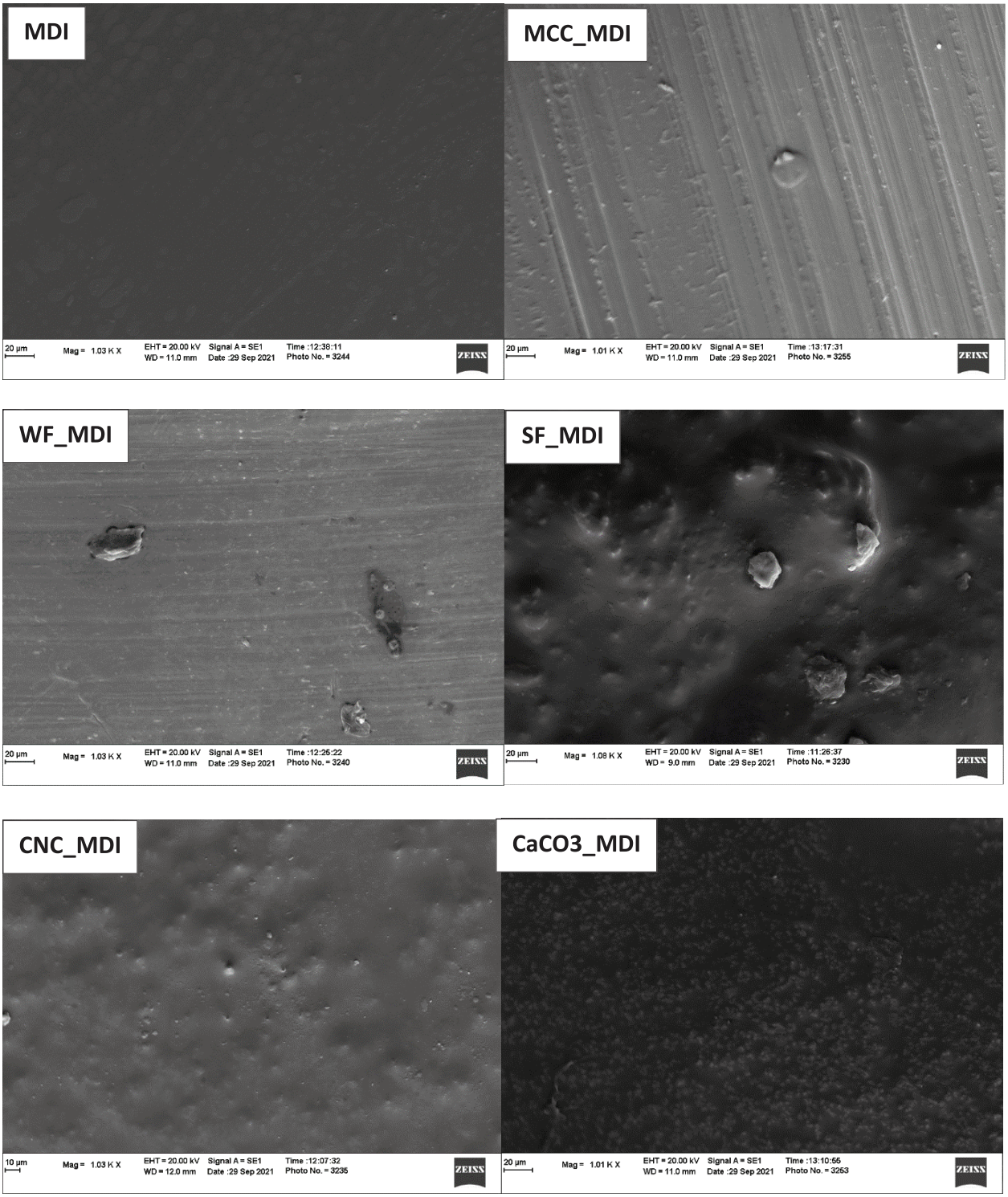

Figure 3.—Scanning eletron micrographs of samples. MDI = methylene diphenyl diisocyanate; WF=wood flour; CNC = cellulose nanocrystal.

other panels. There was also a significant difference between the HCNC panels and the other panels. From the results, we could also deduce that there was no significant difference among panels $HCaCO_3$, HMCC, HTalc, HMDI, and HWF. The panels made with a SF–MDI-modified sample showed significant improvement in the shear strength with 261 percent higher shear strength than the control (pMDI) for samples made from hardwood (oak). Finally, according to the results presented in Figure 4, only panel HSF exceeded the minimum requirement of 1 MPa for characteristic shear strength for cross-layer bond lines according to EN 16351 (European Standards 2015).

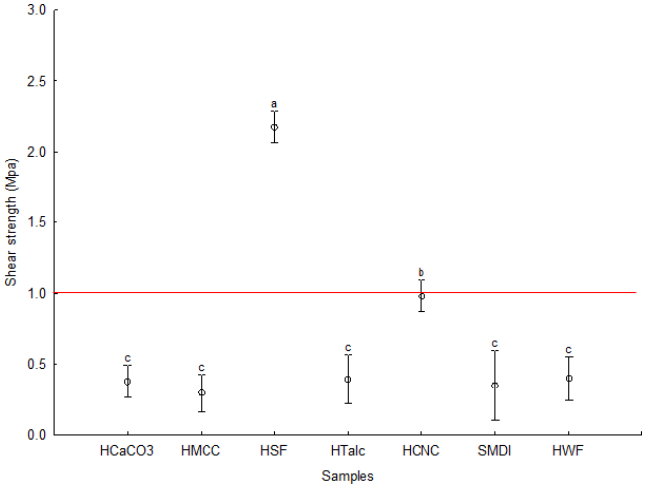

Figure 4.—Shear strength of plywood made with oak veneers using different resin formulations. The error bars indicate standard deviation of the average shear-strength values of 10 plywood samples' measurements. The means that do not share a letter are significantly different ($P < 0.05$; Fisher LSD test). H = hardwood; MCC = cellulose microcrystalline; SF = soy flour; CNC = cellulose nanocrystal; MDI = methylene diphenyl diisocyanate;WF = wood flour; S =softwood.

Shear-strength test (southern yellow pine)

The mean values of shear strength for the panels made from southern yellow pine veneers for both filler-modified and control samples are presented in Figure 5. The adhesives' shear strength varies with modification fillers and followed a similar trend as reported above with the panels made with oak veneers. The shear strength for panels made with southern yellow pine ranged from 0.35 to 2.33 MPa. Panels produced with SF–MDI-modified resin had the highest shear strength of 2.33 MPa among all samples

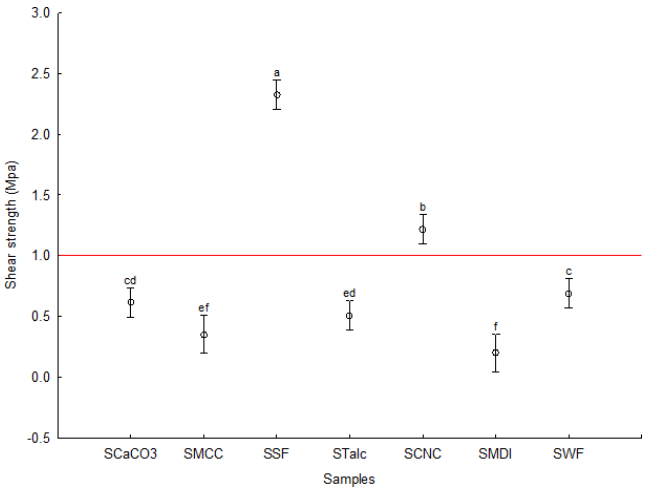

Figure 5.—Shear strength of plywood made with southern yellow pine veneers using different resin formulations. The error bars indicate standard deviation of the average shear-strength values of 10 plywood samples' measurements. The means that do not share a letter are significantly different ($P < 0.05$; Fisher LSD test). S = softwood; MCC = cellulose microcrystalline; SF = soy flour; CNC = cellulose nanocrystal; MDI = methylene diphenyl diisocyanate; WF = wood flour.

Table 3.—Thermal properties of modified samples.

Fillers[a]	IDT[b] (°C)	MRDT (°C)	Residue (%)	$D_{1/2}$ (°C)
pMDI	217.4	279.7	55.74	737.7
WF–MDI	266.8	348.9	32.02	448.5
SF–MDI	222.0	345.1	26.4	401.1
Talc–MDI	223.5	368.0	57.1	N/A
$CaCO_3$–MDI	274.4	708.4	27.7	689.0
MCC–_MDI	280.7	352.8	32.5	462.1
CNC–MDI	222.1	344.2	33.9	463.4

[a] See Table 1 for filler definitions.
[b] IDT = initial decomposition temperature; MRDT = maximum rate of decomposition; $D_{1/2}$ = 50% weight decomposition.

including the control (pMDI). The lowest shear-strength mean values were shown by panels made with MCC–MDI and pMDI (control) resins with a shear strength of 0.35 MPa. Furthermore, the results showed that there were significant differences between the panels softwood SF and CNC (SSF and SCNC) compared to other panels. And there was no significant difference among the panels $SCaCO_3$, SMCC, STalc, SMDI, and SWF. The results also showed that only panels SSF and SCNC exceeded the minimum requirement of 1 MPa for characteristic shear strength for cross-layer bond lines according to EN16351 (European Standards 2015). Finally, the panels made with the SF–MDI-modified resin showed significant improvement in the shear strength with 236 percent higher shear strength when compared with panels made with the control resin (pMDI).

Conclusion

This study evaluated the possibility of using different fillers as partial substitutes in pMDI resin. The modified samples with SF showed significant improvement in the shear strength with 261 and 236 percent higher shear-strength values than the control (MDI) for samples made from hardwood and softwood veneers, respectively. This could be due to the reactions between isocyanates and hydroxyl-containing compounds in the SF resulting in the formation of urethane groups. It could also be as a result of immediate reactions between amine groups in the SF and isocyanates to form a substituted urea (Frisch et al. 1983). Partial substitution of MDI resin with SF at 30 percent substitution substantially improves the adhesion properties of MDI resin. This excellent performance of SF-modified samples could be due to the reaction of the isocyanate group in the pMDI with amines group in the SF which led to the formation of allophanate and biuret linkages by reaction with urethanes (Frisch et al. 1983). With regards to the shear-strength performance of both species, only panels made with SF- and CNC-modified pMDI resin exceeded the minimum requirement of 1 MPa for characteristic shear strength for cross-layer bond lines according to EN16351 (European Standards 2015). In conclusion, the use of SF as a filler in pMDI resin has great potential in the plywood industry.

Acknowledgment

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