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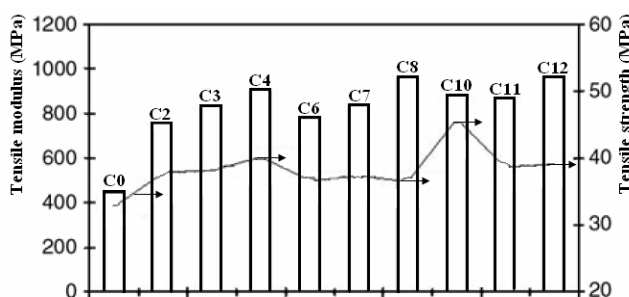
EFFECT OF AN ORGANICALLY MODIFIED NANOCCLAY ON THE PROPERTIES OF SOME COMPATIBILIZED PP-WOOD COMPOSITES

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Polypropylene/clay/wood flour nanocomposites were prepared through melt blending, using a compatibilizing agent, as well. Their thermal and mechanical properties were investigated by the means of TGA and DSC, and mechanical tests, respectively. The effect of addition of the organically modified clay (Cloisite 20A) and compatibilizer (MAPP) on the composites properties was the main purpose of this study. Experimental results indicated an improved thermal stability for all samples, while tensile strength and modulus increased, but only up to a certain content of wood (20%). Over this amount, the composite samples displayed lower values, but still higher than those for composites without clay. For the wood flour, a granulometric study was performed in order to assess the influence of particle size on composites properties.



INTRODUCTION

Thermoplastic wood-polymer composites (WPCs) are a group of materials that have attracted much attention from the academic and industrial media due to their versatility and tunable properties. A wide range of thermoplastics, such as polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and various polyesters, along with diverse lignocellulosic materials, including wood flour, sawdust, bark, paper, paperboard, sawmill waste, rice straw, cotton, hemp and other agricultural wastes, are used to produce WPCs for different applications ranging from housing, decking and interior design to sporting goods, automotive and aerospace industry, etc.¹⁻⁶

Wood and lignocellulosic materials, compared to other reinforcement agents, have many

advantages: lower density, moderate strength, high specific modulus, low relative friction and fiber surface modification ability, as well as wide availability. These are also more cost-effective than other reinforcing materials and can be successfully used in applications where cost saving prevails over the product strength. The main disadvantages of these fillers are as follows: hydrophilic/hydrophobic incompatibility with the polymer matrix, thermal degradation at temperatures over 160°C, poor dispersion during processing without appropriate shear stress, and water sorption that affects dimensional stability and mechanical properties.

Concerning the compatibility between matrix and filler, two approaches are widely applied: the use of (1) a compatibilizing agent, *e. g.*, maleated oligo-olefins, or (2) chemically modified wood.

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Furthermore, combining these approaches enables the preparation of composites with improved characteristics.⁷⁻¹¹

New opportunities occurred along with the development of the nanotechnology and nanostructured materials which have opened new research directions in interdisciplinary studies at nanoscale. One of them is the use of layered silicates (nanoclays) as component of various composite formulations, including WPCs, yielding in new materials with significantly improved properties.¹²⁻¹⁶ Silicates, such as montmorillonite, hectorite, and saponite, have a layered structure that upon exfoliation leads to composites with very high stiffness and strength. Small amounts of nanoclays (usually, 1-5%wt) added to WPC formulations entailed not only increase in the modulus, strength, and heat resistance, but also gas permeability reduction, decreased flammability and enhanced moisture resistance.

Nature of clay (raw or modified), particle size, dispersion quality, intercalation/exfoliation, processing type and parameters are only a few factors affecting the material performance. Another factor of the same importance is the order of mixing. In a multicomponent material, various linkages may be formed or destroyed during compounding of different components, with direct influence on the final material properties. It was proven that the experimental protocol leading to the best results is the melt mixing/blending, in a one-step or two-step procedure.¹⁶⁻²¹ Basically, the one-step one-pot procedure evolves as follows: the polymer matrix is initially melt blended with the compatibilizing agent and the clay (raw or organically modified) and the wood is added afterwards. In the two-step procedure,¹² polymer-

compatibilizer-clay hybrids are compounded and pelletized first, and then the wood is compounded with hybrids into an extruder. Another approach is to prepare a master batch of compatibilizer and clay in preset ratios, and then to add the corresponding amounts of polymer and wood.²⁰

In the last decade, studies were conducted on polymer-clay-wood composites obtained by melt compounding, emphasizing the beneficial effect of clay on the material properties and the synergetic action of clay and compatibilizer. There are many commercially available compatibilizing agents (maleated HD- or LD- polyolefins, such as PE-g-MA or MAPE, PP-g-MA or MAPP) having various degrees of grafting and different molecular weight. Studies¹⁶ indicated that HDPE-based MAPEs result in higher thermal and mechanical properties of wood/polyethylene composites, compared with their counterparts with lower molecular weight. This effect is expected to be retrieved in polymer-Compatibilizer-clay-wood hybrids.

This study was intended to assess the combined effects of an organically modified montmorillonite (Cloisite 20A) and a compatibilizer (MAPP) on the properties of some polypropylene-wood composites. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and stress-strain tests were used to evaluate composite properties evolution upon addition.

RESULTS AND DISCUSSION

Composites formulation and their sample codes are presented in Table 1.

Table 1

Composites sample codes and their formulation

Sample code	PP	MAPP	CI20A	Wood chips
C0	100	0	0	0
C1	100	3	1	0
C2	100	3	1	10
C3	100	3	1	20
C4	100	3	1	30
C5	100	5	3	0
C6	100	5	3	10
C7	100	5	3	20
C8	100	5	3	30
C9	100	10	5	0
C10	100	10	5	10
C11	100	10	5	20
C12	100	10	5	30

Granulometric study of wood particles

We employed in composites two different types of granulated fillers: clay, with particle size distribution $<15\mu\text{m}$ (90%), and wood particles with size in the range 0.1-7 mm. Therefore, a granulometric study of the wood component is required. The wood particles were separated on vibrosieves with size fractions of ≤ 0.2 , 0.2–0.5, 0.5–1, 1–2, 2–3, 3–5, 5–7, and 7–10 mm (hereafter, the size of the fraction is marked by its upper limit). The yield of each fraction was defined by weighing with a microbalance. A packing factor (F), specific for the wood filler, was defined and its values were determined by vibrational compacting of the wood chips in a glass measuring cylinder, according to the literature,²² as well as the density of the wood filler particles, ρ_f . The granulometric distribution (percentage) of wood chips is presented in Table 2 and Fig. 1. The yield of each fraction was defined by weighing.

Table 2

The granulometric distribution of wood particles

Fraction (mm)	Distribution (%)
< 0.2	6
0.2-0.5	8
0.5-1	14
1-2	53
2-3	12
3-5	4
5-7	3

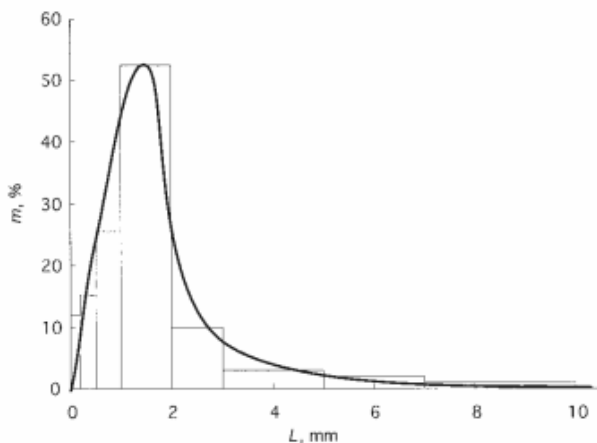


Fig. 1 – Differential curve of the weight distribution of the wood particles.

The packing factor F of the wood filler was calculated for a statistic mixture of particles, according to Fig. 1, and its value was 0.71. For particles with determined length, $L=1.0$ and

0.20 mm, F was 0.57 and 0.58, respectively. In our case, a higher value for F indicated that the distance between particles increased, which is favourable for composites processing because it allows an increased amount of polymer to penetrate between wood chips and inside their tracheids, yielding in composites with improved elastic properties. The calculated value of ρ_f is 0.496 g/cm^3 for wood particles of each fraction.

The granulometric study was completed by the direct observation of wood particles and their images obtained by microscopy are shown in Fig. 2.

Images illustrate in detail the irregularities on the wood chips surface (torn and/or broken fibres, asperities of different size) due to the harsh conditions of wood processing, as well as the tracheids in their structure.

Thermal behavior evaluation

TGA curves registered for samples without wood (C0, C1, C5 and C9) indicated that upon addition of clay (1 to 5 phr), the decomposition temperature increased with 67°C at the 50% weight loss compared to neat PP, phenomenon attributed to the hindered diffusion (*i.e.*, barrier effect) of volatile decomposition products caused by the dispersed clay particles.²³ TGA thermographs of samples C0-C4 are presented as example in Fig. 3.

The addition of MAPP (3 phr) to the composites formulation increased the decomposition temperature by about 20°C , probably due to the physico-chemical adsorption of the volatile products on the clay,²⁴ which indicates an improved clay dispersion inside the matrix due to the compatibilizer.

The further addition of wood (10-30 phr) entailed changes in the decomposition temperature: at 50% weight loss level, the decomposition temperature was higher by 40°C for samples C2 and C3, whereas it slightly decreased for sample C4.

The DSC data are summarized in Table 3.

All composite samples displayed a higher melting temperature (T_m) compared to neat PP. The highest value was recorded for C11, sample containing the highest amounts of clay and compatibilizer, whilst C12, the sample with the highest amount of wood, had a lower T_m . This trend was observed for all series (10, 20, 30% wood).

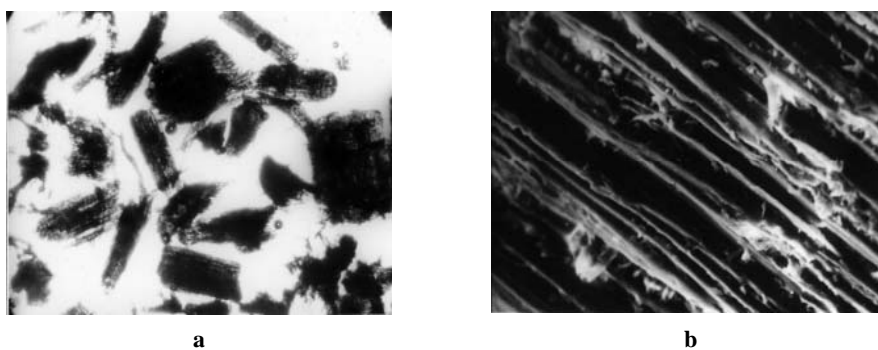


Fig. 2 – Microscopy images of wood chips: a) x15; b) detail (x300).

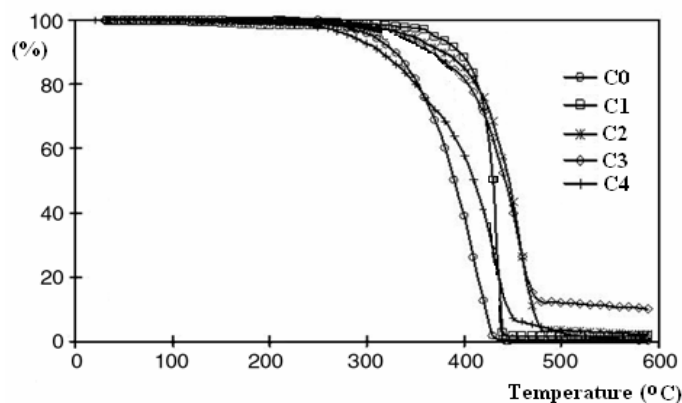


Fig. 3 – TGA curves of composite samples C0-C4.

Table 3

Thermal data of composites

Sample code	T_m (°C)	ΔH_m (J/g)	T_c (°C)	$-\Delta H_m$ (J/g)	X_c (%)
C0	163.1	81.5	108.9	91.0	39.01
C1	165.9	91.1	111.9	92.0	42.13
C2	164.8	88.5	113.6	87.1	43.22
C3	165.4	79.2	117.8	82.3	37.94
C4	165.2	78.9	118.3	78.0	37.75
C5	166.2	87.5	110.8	88.5	42.00
C6	164.7	76.0	117.8	81.3	41.88
C7	165.5	69.6	117.0	72.4	33.38
C8	164.6	67.8	118.6	70.8	32.33
C9	165.5	89.0	111.4	88.8	42.65
C10	165.4	79.9	115.6	82.6	38.09
C11	166.1	72.7	116.4	76.4	34.53
C12	164.9	65.4	118.1	68.7	31.20

T_m = melting point; ΔH_m = melting enthalpy; T_c = crystalline temperature; $-\Delta H_m$ = crystalline enthalpy; X_c = crystallinity

In samples without wood (C1, C5 and C9), this effect is due to the beneficial MAPP and clay influence. At low wood content, the matrix forms a continuous phase that covers wood particles, thus

slowing down diffusion phenomena and preventing thermal decomposition. Moreover, another possible explanation is the particle effect, given the cumulative contributions of clay and wood, the

diffusion depending on the path tortuosity introduced by impermeable particles. In addition, the cellulose, one of the wood components, is highly crystalline and makes wood thermally stable within certain limits and thus contributes to the composites thermal stability. But upon further addition of wood, this layer is modified so that T_m decreased (samples C2-C4, C6-C8 and C10-C12).

The melting enthalpy (ΔH_m) was determined at the heating rate of 10°C/min. Listed data showed an increasing thermal stability of composites along with the increasing content of clay and MAPP. Concurrently, the addition of wood flour decreased the ΔH_m to values much lower than that of pure PP and this may be an indication that wood absorbed more heat during the composites melting.¹²

The crystalline peak temperatures (T_c) increased upon addition of clay, MAPP, and wood, correspondingly, which led to the conclusion that clay acted as nucleating agent, as known, but wood filler enhanced its effect, in synergy with the increasing amounts of MAPP.

The crystalline enthalpy ($-\Delta H_m$), as presented in Table 3, decreased along with the addition of MAPP, clay and wood for all considered samples. An overall explanation might be the fact that clay and wood disturb PP crystallization, although composites crystallization is promoted by the same factors, clay particles and wood chips. But higher amounts of wood yielded in a reduced crystallization effect. Consequently, the crystallinity of samples without wood or with small amounts of wood (C1, C2, C5, C6, C9, C10) is higher than that of neat PP, while samples with high content of wood (C3, C4, C7, C8, C11, C12) displayed lower degrees of crystallinity. These data confirm that the X_c is generally affected by the

filler loading and dispersion, matrix-filler interface processes, rheology, etc.

Mechanical properties of composites

The tensile properties of composites, namely tensile strength and tensile modulus, are presented in Table 4. The effect of MAPP and clay addition on PP tensile properties is illustrated by the variation of the tensile strength and modulus. Samples C1, C5 and C9 showed slightly increased values for strength, although the modulus values increased more.

These data seem to indicate that the high tensile strength is the result of the intercalation of clay layers and MAPP. On the other hand, the increased tensile modulus might be attributed to the increased strength of composites due to the clay addition.

Upon addition of wood, the tensile modulus of most composites increased even more. The maximum value was recorded for sample C12. This may indicate that the increased modulus is highly related to the increased stiffness of wood composites.

As for the tensile strength, it increased along with the content of clay and wood up to certain values, as illustrated in Fig. 4.

An interesting behavior was recorded for samples C6-C8: their strength values were the lowest of all wood composites, whilst having medium loading of clay and MAPP. Adding supplementary amounts of fillers and compatibilizer, the tensile strength significantly increased, but samples C11 and C12 displayed lower values than C10, the sample with maximum load of MAPP and clay, but the lowest amount of wood, 10%.

Table 4

Mechanical properties of composites

Sample code	Tensile strength (MPa)	Tensile modulus (MPa)
C0	32.79	441.5
C1	36.88	584.0
C2	37.80	751.1
C3	38.25	829.7
C4	39.97	905.1
C5	38.05	634.4
C6	36.67	781.8
C7	37.88	836.6
C8	36.50	958.5
C9	41.15	755.0
C10	47.55	871.6
C11	37.97	867.2
C12	39.68	963.3

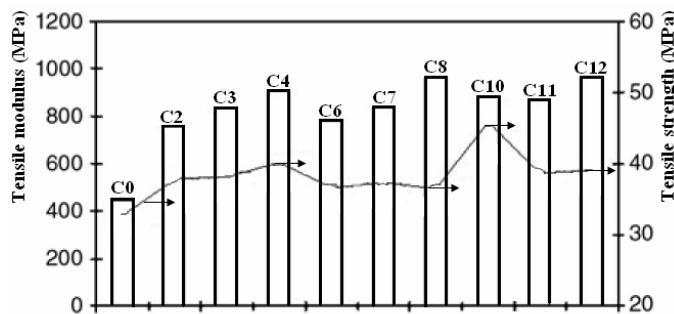


Fig. 4 – Tensile strength and modulus of wood composites.

These data led to the conclusion that high values of tensile strength are related to the improved bonding between wood and PP, mediated by clay and MAPP. Thus, organically modified clay platelets intertwined among the PP chains allowing wood particles to have easy access to the grafting sites. Small and medium size wood particles, that represent over 80% of the particles according to the granulometric study (Table 2), are privileged and will be able to interact with MAPP. Besides hydrogen bonds, if conditions are favorable, maleic anhydride moieties in MAPP may react with –OH groups from wood to create ester bridges and some polymer molecules will be grafted onto wood surface, leading to strengthened materials.²⁵ Consequently, the interfacial adhesion will be improved with beneficial effects on the load transfer upon mechanical testing, proven by the high values of the tensile strength.

Still, the decrease in tensile strength along with increasing content of wood (20 and 30%, respectively) at maximum loadings of clay and MAPP might be attributed to the increased stiffness and brittleness associated to the formation of a rigid wood scaffold inside the polymer matrix.

EXPERIMENTAL

Materials

The polymer used as matrix was polypropylene (PP, Malen P F401), obtained from Basell-Orlen, as pellets, with the following characteristics: melt flow index 3.2 g/10 min (230°C, 2160 g), density 0.9 g/cm³.

As compatibilizing agent, a maleated polypropylene (MAPP, Fusabond MZ 203D, courteously supplied by duPont Company), having the molecular weight 40000 g/mol, melt flow index 102 g/10 min (190°C, 2160 g) and MA content 0.74 wt%, was used as received.

The organoclay employed in the composite formulations was Cloisite® 20A (Cl20A) which is dimethyl bis(hydrogenated tallow) quaternary ammonium chloride montmorillonite (hydrogenated tallow is a blend of saturated alkyl chains and contains ~65% C18, ~30% C16 and ~5% C14), supplied by

Southern Clay Products, Inc., having the following characteristics: organic load 95 mequiv/100 g clay; organic content 39.6 wt%; density 2.83 g/cm³, $d_{001}=24.2\text{\AA}$ by XRS; particle size distribution: <15µm (90%); moisture <2%.

The wood filler, pine chips of *Pinus radiata*, was used as collected from a local furniture manufacture. The chip dimensions varied from 0.1 to 7 mm. Wood was dried to 1–2% moisture content prior to processing in an oven at 80°C.

Melt blending processing

The polymer pellets, the compatibilizer and the clay were dried in a vacuum oven at 60°C over the night and then fed to a HAAKE RHEOCORD 9000 mixer (equipped with two internal roller mixers and a capacity of mixing chamber of 50 cm³). A compounding temperature of 190°C was used to prevent the thermal degradation of the wood. The screw speed for compounding was in the range of 100–150 rpm.

The compounding process included two stages: (1) PP, MAPP and Cl20A were compounded first in order to obtain hybrids, and (2) compounding hybrids with wood chips at 190°C. Finally, composites were cooled in air and then pelletized.

All blend components were calculated as parts per 100 parts resin (phr); composites formulations and sample codes are presented in Table 1.

Composites characterization

Geometrical dimensions of the wood particles were measured with an optical microscope (MBS-9; Moscow, Russia). Their weight was determined with a Sartorius 4431 microbalance (Gottingen, Germany). Ten particles of each fraction were selected for measurements. Optical observation of the wood chips and polymer granules morphology was performed with an optical microscope (IOR type MC1, Bucuresti, Romania).

Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (Paulik–Paulik–Erdey type Derivatograph, MOM – Budapest, Hungary) to characterize the thermal stability of composites. Each specimen was heated from room temperature to 600°C. All samples weight was 50 mg and the heating rate was set at 12°C/min. During testing, the heating unit was flushed under a continuous air flow of 30 mL/min.

Differential scanning calorimetric (DSC) thermograms were recorded using a Pyris Diamond DSC (Perkin Elmer, USA) at a heating rate of 10°C/min under dry N₂ atmosphere. The specimens were heated up to 200°C. The melting temperature (T_m), enthalpy (ΔH_m), crystallization temperature (T_c), crystalline enthalpy ($-\Delta H_m$) and crystallinity (X_c) were determined after the melt-crystallization process.

The mechanical properties of composites were assessed through tensile properties and modulus, and were determined according to ASTM D 638-01 and ASTM D790-00 specifications. A mechanical tensile machine (FU-1000; Rauenstein, Germany) with the crosshead speed was set at 20 mm/min was used. Dimensions of samples: 150x10x5 mm. All samples were conditioned at a temperature of 23±2°C and relative humidity (RH) of 50±5% for at least 40 h prior testing. At least five samples were tested for each type of measurement.

CONCLUSIONS

In this study, a series of composites based on PP and wood was prepared by melt blending, in a two-step procedure, using MAPP as compatibilizer and an organically modified clay, namely Cloisite 20A. The influence of clay particles on composites thermal behaviour and mechanical properties was evaluated.

TGA and DSC data registered for all samples indicated an improved thermal stability upon addition of clay and wood. All composite samples displayed higher melting temperatures (T_m) compared to neat PP, but at the highest amounts of clay, MAPP and wood T_m was lower, but still superior to pure PP. This is probably the result of the formation of a wood structure that absorbs more heat during composites melting.

The crystalline temperatures (T_c) increased upon addition of clay, MAPP, and wood, correspondingly, which proven that clay acted as nucleating agent and wood enhanced its effect, in synergy with the increasing amounts of MAPP. Despite this effect, composite samples with high content of wood displayed lower degrees of crystallinity, because clay and wood disturb PP crystallization. These data confirm that the crystallinity is generally affected by the filler loading and dispersion, matrix-filler interface adhesion, rheology, etc.

As for the mechanical properties, it was proven that upon addition of wood, the tensile modulus of most composites increased. The maximum value was recorded for the maximum load of clay, MAPP and wood, indicating that the increased modulus is highly related to the increased stiffness of wood composites.

Tensile strength measurements showed the highest value was reached for the sample containing the lowest amount of wood, at maximum load of clay and MAPP. This behavior

may be explained by the interpenetration of clay particles among PP chains, facilitating wood particles access to the MAPP bonding sites. In result, an increased interfacial adhesion occurred and it yielded in an enhanced load transfer between matrix and filler.

Given the importance of WPCs, such studies are of great interest, both theoretical and practical, as the final purpose is to provide new materials with appropriate characteristics for a wide variety of applications like packaging, decking, fencing, siding, garden furniture, exterior windows and doors, etc.

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