

**Monika DOBRZYŃSKA-MIZERA, Monika KNITTER,
Mateusz BARCZEWSKI**

WALNUT SHELLS AS A FILLER FOR POLYMERIC MATERIALS

This work presents selected properties of polypropylene-based (PP) composites modified with an organic filler, namely walnut shells (NUT). Two series of composites were prepared via a twin-screw extrusion process, followed by injection molding. The first series, named PP/NUT, contained 10, 20 and 40 wt% of walnut shell powder, while the second, abbreviated PP/NUT/MAPP, apart from nut filler included polypropylene-graft-maleic anhydride (MAPP), which was intended to promote adhesion between the polymer and filler. The following measuring techniques were applied: differential scanning calorimetry, thermogravimetry, dynamic-mechanical thermal analysis, and scanning electron microscopy. The measurements showed the filler to have a significant influence on the properties of the PP/NUT composites in comparison with unmodified polypropylene. It was also shown that the addition of polypropylene-graft-maleic anhydride to the formulation enhanced interfacial bonding between the polymeric matrix and filler. Moreover, the introduction of organic filler to the polymeric matrix increased its stiffness without altering the crystallization kinetics of polypropylene.

Keywords: composite, walnut shells, polypropylene

Introduction

As environmental awareness increases, there is growing interest in developing materials with natural fillers as desirable reinforcements for composites [Wambua et al. 2003; Malkapuram et al. 2008; Paul et al. 2008; El Achaby et al. 2012; Essabir et al. 2013]. This interest is stimulated by a combination of several benefits of these fillers, including low cost, light weight, non-toxicity, longer life for tooling especially with high shearing stresses, limited abrasiveness during processing, and improved possibilities of recycling when compared with conventionally used inorganic fillers [Essabir et al. 2013; El-Sabbagh 2014; Bula and Knitter 2016; Salasinska et al. 2016]. Despite their many advantages, natural

Monika DOBRZYŃSKA-MIZERA (monika.dobrzynska-mizera@put.poznan.pl), Monika KNITTER✉ (monika.knitter@put.poznan.pl), Mateusz BARCZEWSKI (mateusz.barczewski@put.poznan.pl), Poznan University of Technology, Institute of Material Technology, Poznan, Poland

reinforced materials still suffer from numerous issues that slow down their implementation on the market. The most common of these are limited processing temperature range [Błędzki et al. 2002; Bogoeva-Gaceva et al. 2007], hydrophilicity of natural fillers [Saheb and Jog 1999; Van de Velde and Kiekens 2002; Panthapulakkal and Sain 2007], bacterial degradation [Dixita 2014], dimensional instabilities due to water absorption [Espert et al. 2004; Taha and Ziegmann 2006] and processing difficulties [Moran et al. 2007]. However, the greatest challenge is the different natures of the hydrophobic matrix and hydrophilic filler. To overcome this issue, various methods of compatibilization are applied. In the case of PP-based composites, the most frequently used method is the addition of maleic anhydride grafted polypropylene (MAPP) [Lu et al. 2000; Beckermann and Pickering 2008]. MAPP consists of long polymer chains with maleic anhydride functional groups attached. It links the non-polar polypropylene matrix and the polar lignocellulosic filler through interaction with the organic hydrogen groups available on the surface, which then adhere to the matrix by linking molecular chains.

Solid lignocellulosic residues of plants, such as walnut shells (*Juglans regia* L.), fulfil the conditions to serve as sustainable reinforcements for polymeric composites [Pirayesh et al. 2012; Dobrzyńska-Mizera and Barczewski 2014]. Their chemical composition includes hemicellulose (holocellulose), α cellulose and lignin. As evidenced in the literature [Nemli et al. 2009; Pirayesh et al. 2012] each ingredient plays an important role in the properties of the final polymeric product. High lignin content increases the brittleness of the material, while cellulose causes a lowering of that parameter. Moreover, cellulose and hemicellulose contain a large number of polar hydroxyl groups, which are able to initiate interaction between the filler and polymeric matrix [Ayrilmis et al. 2009; Pirayesh, and Khazaeian 2012]. These functional groups are also responsible for water uptake, as they bond water molecules, and determine surface wettability and absorption of the resin on the lignocellulosic surface [Gwon et al. 2010; Nourbakhsh et al. 2011]. Besides these main components, walnut shells also contain extractives such as tannins, pectins, fats, waxes, gums, essential oils, volatile materials and ash [Pirayesh et al. 2012]. The high content of extractives, combined with the poor wettability of walnut shells, may result in the weakening of bonding between particles and low internal bonding strength in the final product [Li et al. 2010]. Therefore, the introduction of a compatibilizer is often necessary to improve interfacial adhesion between the components.

The aim of this study is to investigate the influence of a walnut shell filler and MAPP coupling agent on the crystallization behavior, thermal stability and thermomechanical properties of polypropylene-based composites.

Materials and methods

Materials

A commercial isotactic polypropylene (PP), Moplen HP500N (BasellOrlen Polyolefin, Poland), with a density of 0.90 g/cm^3 and melt flow rate of 12 g/10 min ($230^\circ\text{C}/2.16 \text{ kg}$) was used as the polymeric matrix. The filler was ground walnut shells (NUT), illustrated in figure 1, obtained from crops grown in 2013 in the Wielkopolska region of Poland. Their particle size was less than 1 mm , and the fraction below $630 \mu\text{m}$ was 82%. The chemical coupling agent was Polybond PB3200, with $\text{MFR} = 115 \text{ g/10 min}$ ($230^\circ\text{C}/2.16 \text{ kg}$), and 1 wt% of maleic anhydride (MAPP) from Chemtura (UK) was used as a compatibilizer.

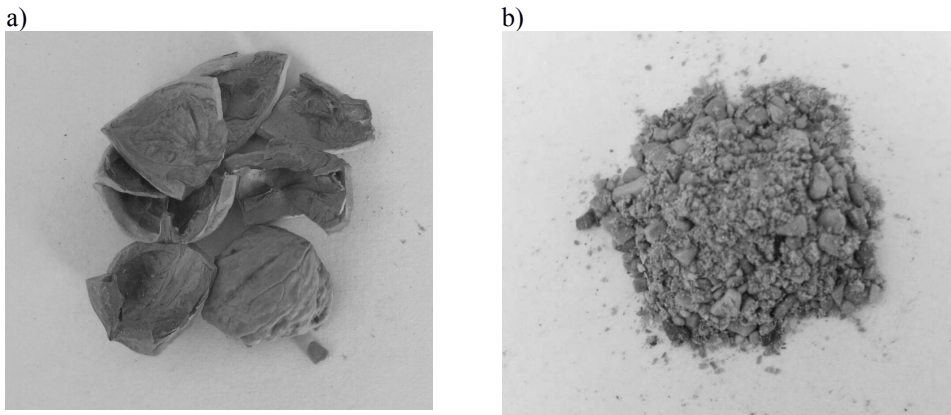


Fig. 1. The walnut shells before (a) and after fragmentation (b)

Sample preparation

The polymer was mixed with ground walnut shells for the reference samples, and additionally with MAPP in the case of compatibilized series, in a Retsch GM 200 rotary mixer for 3 min at a rotation speed of 3000 rpm. Fragmentation of walnut shells was performed using a Retsch ZM200 knife grinder. Then the filler was sieved in a Fritsch Analysette 3 PRO vibratory sieve shaker, with a 1 mm mesh sieve, to obtain an appropriate particle size. The compositions containing organic filler were dried at $80 \pm 2^\circ\text{C}$ for 24 hours prior to melt processing. The homogenization of the premixed blends with different filler contents (10-40 wt%) and a fixed MAPP concentration of 3 wt% was achieved by molten state extrusion with a Zamak co-rotating twin screw extruder operating at 190°C and 70 rpm. The extrudates were ground using a Shini SG-1411 low-speed granulator. Tensile test specimens were produced according to the ISO 527-2:2012 standard using an Engel ES 80/20HLS injection molding machine at 200°C and an injection speed of 90 mm/s , as shown in figure 2.

PP/NUT and PP/NUT/MAPP blends with various compositions were prepared, as summarized in table 1.



Fig. 2. Selected tensile test specimens of pure PP (a), PP/10NUT (b), PP/10NUT/MAPP (c)

Table 1. PP/NUT and PP/NUT/MAPP blends with various compositions

Reference series	NUT		Compatibilized series	MAPP		
	content [wt%]	PP		content [wt%]	PP	content [wt%]
PP	–	100				
PP/10NUT	10	90	PP/10NUT/MAPP	10	87	3
PP/20NUT	20	80	PP/20NUT/MAPP	20	77	3
PP/40NUT	40	60	PP/40NUT/MAPP	40	57	3

Methodology

Scanning Electron Microscopy (SEM). Morphological analysis of cryogenically fractured PP-based composites was performed using a Jeol 7001TTLS scanning

electron microscope (SEM) (Boston, USA) in low vacuum mode, with an accelerating voltage of 10-20 kV. Before analysis, the samples were sputter-coated with Au alloy and mounted on aluminum stubs.

Differential Scanning Calorimetry (DSC). The thermal properties of PP and its composites were investigated using a Netzsch DSC 214 Polyma calorimeter, equipped with an intracooler for fast cooling. The calorimeter was calibrated for temperature and energy using indium. Dry nitrogen was used as a purge gas at a rate of 30 ml/min. To set the structure for the analysis of crystallization kinetics, each sample was heated from 30°C to 250°C at a rate of 10°C min⁻¹, melted at 250°C for 5 min to erase previous thermal history, and then cooled at a rate of 10°C min⁻¹.

Crystallization is an exothermic process, and the heat evolved during the phase transition may cause some thermal gradients within the sample. As a consequence, transitions can occur at temperatures that do not correspond to those detected by the instrumentation [Di Lorenzo et al. 2001; Vyazovkin et al. 2014]. The thicker the sample, the more critical this problem becomes. To minimize this issue, the sample mass was limited to 4.0 ±0.5 mg.

Thermogravimetric analysis (TGA). The progress of thermal degradation of PP/NUT composites was determined by thermogravimetric analyses at temperatures between 30°C and 600°C, at a heating rate of 10°C min⁻¹ under nitrogen atmosphere using a Netzsch TG 209 F1 apparatus. Samples weighing approximately 10 mg were placed in ceramic pans. The decomposition onset temperature T₀ was determined at the point of intersection of tangents to two branches of the thermogravimetric curve. The first derivatives of the TG curves (DTG), indicating the maximum intensity of thermal degradation, were also calculated.

Moisture content (M). The moisture content of the materials was determined using an AXIS ATS 60 moisture analyzer. The measurement was carried out at 105°C for a time of 10 min. Each measurement was repeated three times to verify its reproducibility. Moisture content was calculated using equation (1):

$$M = \frac{m_1 - m}{m} \cdot 100 [\%] \quad (1)$$

where: m_1 is the initial mass [g];

m is the final mass [g].

Ash content determination. Ash content was analyzed according to PN-EN ISO 3451-1:2010 (direct calcination method). Samples of 30 ±5 mg were prepared and burnt in air at 850°C for 3.5 h until complete calcination. Ash content after burning, expressed as a percentage, was calculated using equation (2):

$$A = \frac{m_a}{m_s} \cdot 100 [\%] \quad (2)$$

where: m_a is the ash content [g];

m_s is the initial sample mass [g].

Dynamic mechanical thermal analysis (DMTA). These tests were performed using an Anton Paar MCR 301 rheometer equipped with a torsion measuring tool. Non-isothermal investigations were carried out at a constant frequency of 1 Hz and a strain of 0.01%. All samples were cooled to -50°C followed by heating up to 110°C , with a temperature ramp of $2^\circ\text{C}/\text{min}$.

Results and discussion

To gain information about the phase structure and morphology of the PP composites containing organic filler and compatibilizer, SEM analyses were performed. The results are presented in figure 3. Figure 3(a) illustrates the cryogenically fractured surface of injection-molded plain PP, which appears quite smooth as expected. The structure of the PP composite containing 40 wt% of organic filler is shown in figure 3(b). The fractured surface morphology reflects a polymeric matrix with particles adhering to the PP, revealing the presence of walnut shells in the structure. The pure surface of the filler particle, without traces of polymer, proves the poor bonding between the matrix and filler. The structure changes significantly upon the addition of compatibilizer to the composition, as illustrated in figure 3(c), which shows the scanning electron micrograph of the PP/40NUT/MAPP sample. The filler particle, visible in the middle part of the micrograph, differs significantly from that shown in figure 3(b), as polymeric matrix residue may be observed on its surface. This is probably because the presence of the compatibilizer improves interfacial adhesion between the matrix and filler.

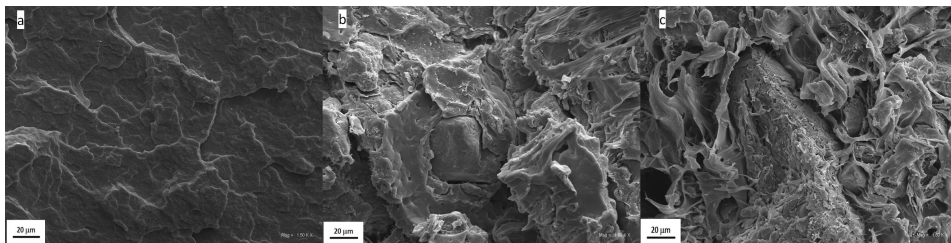


Fig. 3. SEM micrographs for PP (a), PP/40NUT (b), PP/40NUT/MAPP (c)

Non-isothermal crystallization was investigated by differential scanning calorimetry to provide information on the crystallization process of PP-based composites. The crystallization and melting curves and selected numerical data,

obtained from DSC measurements, are presented in figure 4-5 and table 2. The pure PP sample melts at 161°C and crystallizes at 117°C, as determined by the melting and crystallization peaks in figure 4. Upon the addition of the organic filler, irrespective of the amount added to the polymeric matrix, negligible changes were observed in the crystallization and melting temperatures of PP. Addition of the binder to the system caused a slight increase in crystallization temperature and did not affect the melting process, as shown in figure 5 and table 2. Hence, the addition of natural particles did not cause significant changes in the crystallization process of PP blends. However, upon the addition of compatibilizer, a slight nucleating effect was observed.

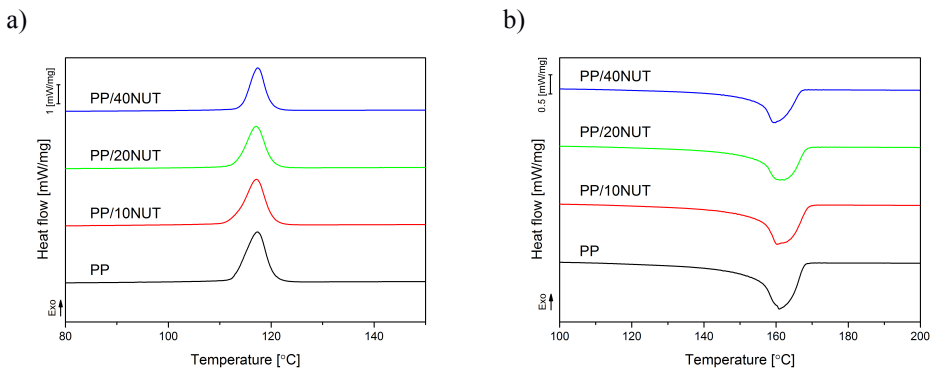


Fig. 4. DSC crystallization (a) and melting (b) curves for reference series of PP-based composites

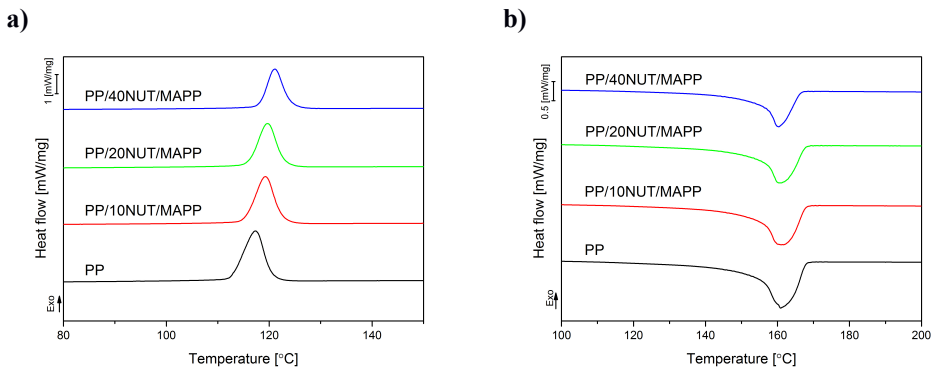


Fig. 5. DSC crystallization (a) and melting (b) curves for compatibilized series of PP-based composites

The crystal fraction developed upon cooling at 10°C/min, equal to $X_{cr} = 54 \pm 3\%$ independently of composite composition, is reported in table 2. The degree of crystallinity was calculated from the data obtained from the DSC plots using equation (3):

$$X_{cr} = \frac{\Delta H_M}{(1-\phi)\Delta H_0} \cdot 100[\%] \quad (3)$$

where ΔH_M is the experimental heat of fusion, ΔH_0 is the enthalpy of fusion of the fully crystalline polymer, equal to 207.1 Jg^{-1} [Monasse and Haudin 1985], and ϕ is the weight fraction of the modifiers. The addition of walnut shells alone or together with 3 wt% of compatibilizer does not influence the final crystalline content of polypropylene under the chosen experimental conditions. It affects only the crystallization efficiency of PP in case of the addition of MAPP, as the onset and peak points are shifted to higher temperatures due to the enhanced nucleation of PP spherulites.

Table 2. Crystallization and melting temperatures and degrees of crystallization for all samples

Material	T_m [°C]	T_{cr} [°C]	ΔH [J/g]	X_{cr} [%]
PP	161	117	110.2	53
PP/10NUT	160	117	100.2	54
PP/20NUT	162	117	84.0	51
PP/40NUT	159	117	72.2	58
PP/10NUT/MAPP	161	119	96.6	52
PP/20NUT/MAPP	161	120	89.9	54
PP/40NUT/MAPP	160	121	70.2	57

The influence of the organic filler and compatibilizer on the degradation process of PP-based composites was investigated by thermogravimetric analysis. The results are presented in figure 6 and table 3. Figure 6 shows TG and DTG curves for the reference composites. Pure PP undergoes a single-step degradation process with onset at 422°C . As shown by the first derivative thermogravimetric (DTG) curve, the fastest degradation occurs at 449°C , with a decay rate of $27\%/min$. Upon the addition of organic filler, the degradation process significantly changes in character, from single-step to two-step. According to the literature [Bodirlău et al. 2007; Jeskea et al. 2012] the degradation of walnut shells occurs in two steps: hemicellulose and cellulose degrade in the temperature range $200\text{--}350^\circ\text{C}$, while lignin breaks up between 250°C and 500°C . Hence, the first step shown in figure 6(a), between 250°C and 380°C , occurs due to the presence of cellulose in the filler. Lignin degradation overlaps with polypropylene decay, as is shown by the slight shift of the second degradation step towards higher temperatures in comparison with pure PP. Figure 6(b) shows the first derivative thermogravimetric (DTG) curves of PP-based composites, which exhibit double peaks (T_{P1} and T_{P2}) in the case of the composites containing the highest quantities (20 and 40 wt%) of the organic filler. The two

peaks reflect the two-step degradation process of cellulosics (hemicellulose and α cellulose) and of lignin and PP, occurring at about 330°C and 455°C respectively. In the case of the composite PP/10NUT, the first peak (T_{P1}) is not observed on the DTG curve due to the insufficient quantity of walnut shells in the polymeric matrix.

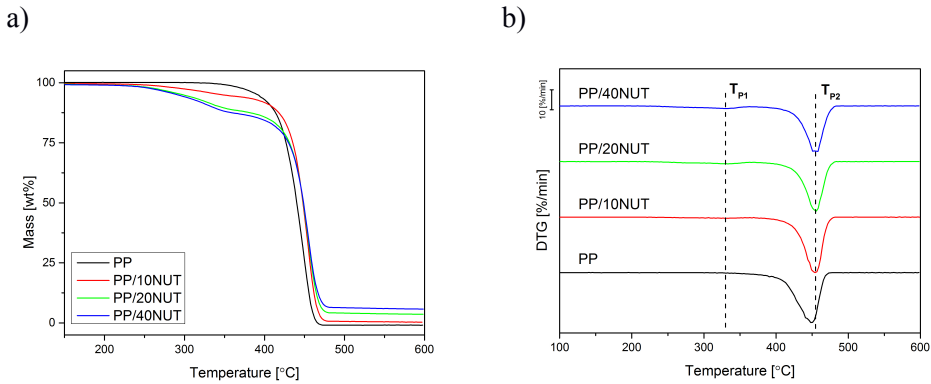


Fig. 6. TG (a) and DTG (b) curves for reference series of PP-based composites

TG and first derivative thermogravimetric (DTG) data for the compatibilized PP blends are given in table 3. The two-step decomposition proceeds by the loss of cellulosics (hemicellulose and α cellulose) followed by lignin and polypropylene [Jeskea et al. 2012; El-Sabbagh 2014]. This matches the degradation process of the non-compatibilized series described above; hence it was concluded that the addition of the coupling agent has a negligible effect on the thermal stability of the composites.

Table 3. TG and DTG data obtained for PP/NUT and PP/NUT/MAPP blends with various compositions

Material	TG	DTG	
	T_0 [°C]	T_{P1} [°C; %/min]	T_{P2} [°C; %/min]
PP	422	–	449; 27
PP/10NUT	436	–	455; 30
PP/20NUT	437	334; 1	455; 27
PP/40NUT	430	332; 1	457; 25
PP/10NUT/MAPP	441	–	455; 28
PP/20NUT/MAPP	435	335; 1	456; 25
PP/40NUT/MAPP	442	331; 2	455; 20

Moisture content is crucial from the point of view of applications and processing in the case of composites containing natural fibers, where water absorption on the product surface is most probable. A high water content may

increase the mass of the product, reduce its strength, cause swelling, warping or buckling, enhance microbial inhibition, and contribute to mechanical destruction due to continuous changes in the physical state of the water [Hassan et al. 2013; Salasinska et al. 2016].

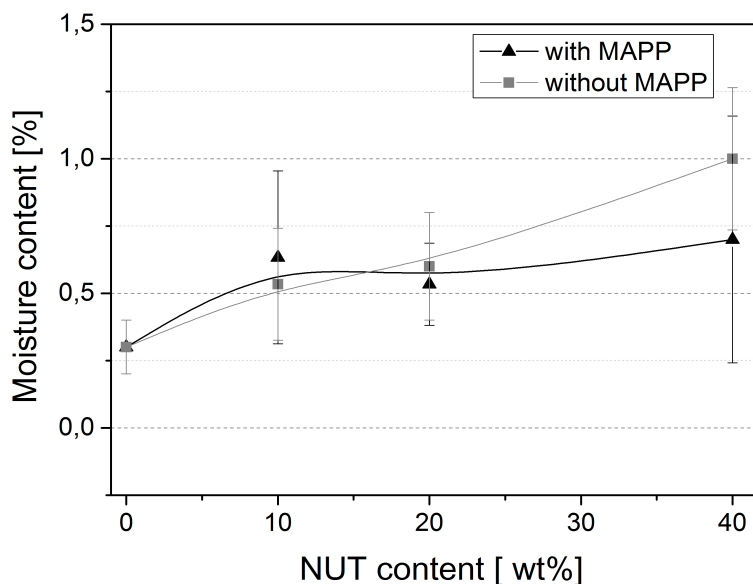


Fig. 7. Moisture content in pure PP and its composites

Figure 7 presents moisture content in pure polypropylene and its composites. The lowest value was recorded for the hydrophobic polypropylene matrix, as expected. Composites containing an organic filler only or coupled with compatibilizer have increased values of this parameter. The increased moisture content in all studied composites results from the introduction of a highly hydrophilic filler to the polymeric structure. Walnut shells are rich in cellulose, hemicellulose, lignin and pectin, which in turn are built from hydroxyl groups. The presence of these functionalities causes an increase in the hydrophilicity of the filler [Shalwan and Yousif 2013]. Therefore, it is important to ensure sufficient drying prior to formation of the final product. The use of adequate pre-process parameters results in a moisture content of 1%, which is satisfactory from the point of view of applications.

Ash content in polypropylene and its composites was determined after complete calcination. Results are presented in figure 8. No residue was recorded for the reference sample, as expected [Barczewski et al. 2014]. Ash content in PP-based composites varies between 0.5% and 2% depending on the composition. The residue is formed due to the presence of the filler, which does

not fully degrade even at 850°C. The addition of binder to the formulation caused a slight increase in ash content after calcination.

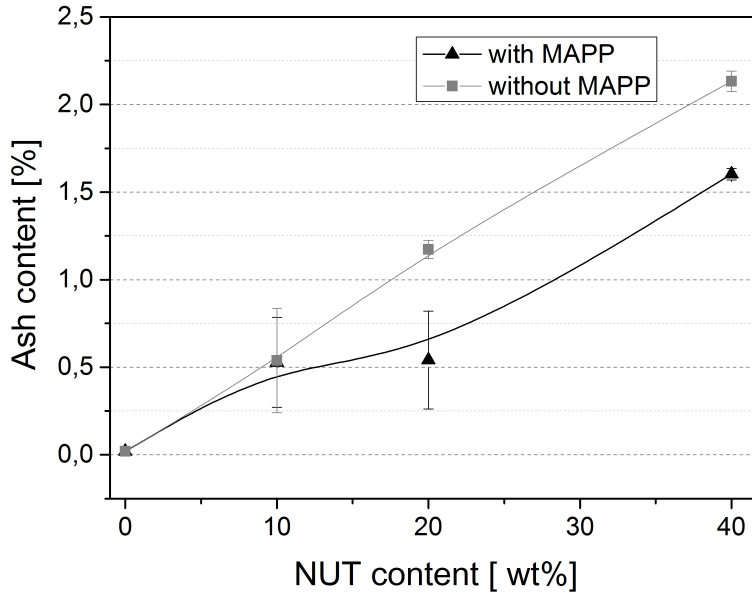


Fig. 8. Ash content after calcination in pure PP and its composites

In the design of new materials, consideration should be given to the issue of waste management after the completed product lifecycle. Currently the European Union recommends energy recycling. In this context, the proposed composites exhibit favorable properties, as they do not lead to the production of excessive amounts of residue upon burning.

To assess the effect of the addition of filler and binder on the mechanical properties of the polymeric matrix, dynamic mechanical-thermal analyses were performed. The results for samples with and without compatibilizer are presented in figure 9. Two DMTA parameters – storage modulus (G') and loss factor ($\tan\delta$) – were analyzed as functions of temperature (T). Selected additional data are summarized in table 4.

The incorporation of walnut shells into the polymeric matrix resulted in a significant decrease in storage modulus in comparison with pure polypropylene. The higher the content of the filler in the composite, the greater the decrease in value. Only for the sample containing 10 wt% of organic filler was a slight increase in the G' value range observed. Hence, the introduction of walnut shell particles into the polymer creates structural discontinuities (confirmed by the SEM microphotographs in figure 1), which are not able to transfer stresses under mechanical loads. The addition of MAPP to the system results in significant

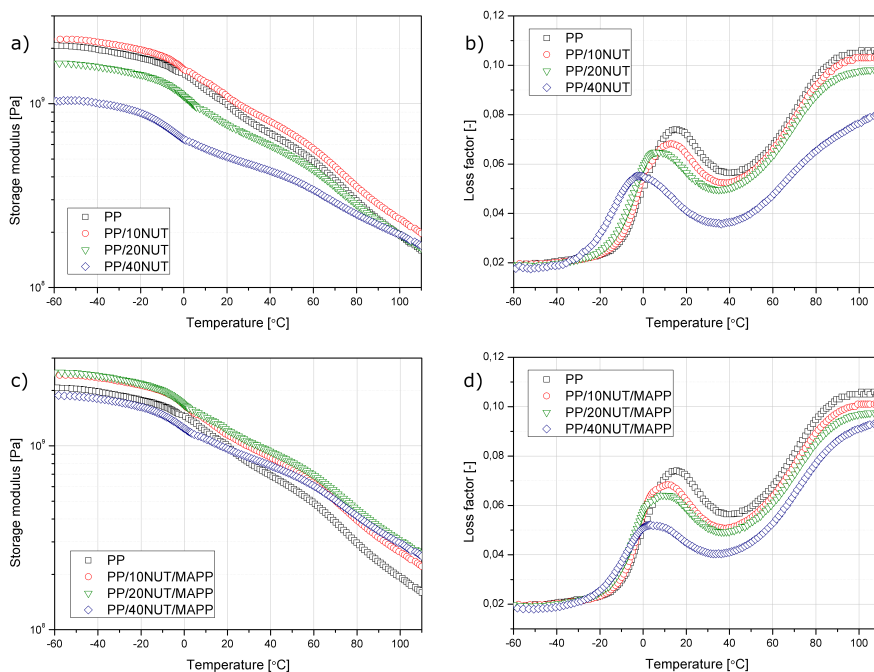


Fig. 9. Storage modulus and loss factor vs. temperature DMTA plots for reference (a, b) and compatibilized (c, d) series of polypropylene-based composites

Table 4. Selected DMTA data obtained for PP and PP composites

Material	G'_{-40}	G'_0	G'_{40}	G'_{80}	T_g [°C]	tan δ (at T_g) [-]
	[GPa]					
PP	1.97	1.45	0.69	0.29	15.5	0.0741
PP/10NUT	2.17	1.59	0.8	0.35	12.6	0.0682
PP/20NUT	1.59	1.1	0.59	0.28	5.58	0.0649
PP/40NUT	1.01	0.64	0.43	0.25	-2.72	0.0552
PP/10NUT/MAPP	2.34	1.67	0.87	0.39	11.6	0.0684
PP/20NUT/MAPP	2.41	1.67	0.93	0.45	10.7	0.0640
PP/40NUT/MAPP	1.80	1.25	0.78	0.41	3.94	0.0521

changes in thermomechanical behavior in comparison with the samples without binder. In the case of the compatibilized polypropylene samples, G' values are higher for the composites containing 10 and 20 wt% filler over the entire analyzed temperature range. The PP/40NUT/MAPP sample exhibits similar stiffness to PP at lower temperatures, but higher above 20°C, as seen in figure 9(c). Hence, at room temperature, the PP/40NUT/MAPP sample has similar thermodynamic behavior to the remaining composites with the coupling

agent. In general, the PP/NUT/MAPP samples demonstrate significant improvement upon the addition of compatibilizer, resulting in similar thermomechanical behavior to that of pure polypropylene. As previously described in the literature [Beckermann and Pickering 2008; Zahedi et al. 2013; Dobrzyńska-Mizera et al. 2015] the addition of MAPP influences adhesion between the matrix and filler through interaction with the organic –OH groups available on the surface, which adhere to the matrix by linking molecular chains, and enhances interfacial adhesion between the matrix and filler.

The loss factor ($\tan\delta$) determines the glass transition temperature (T_g) measured at a maximum near polypropylene β -relaxation, i.e. between -20°C and 20°C . It was found that an increasing amount of the filler caused a gradual decrease in T_g , along with the corresponding $\tan\delta$ value, for both the reference and compatibilized series. This may be attributed to the previously described poor adhesion between the polymer and filler [Liu et al. 2005]. However, it cannot be also excluded that decrease of T_g and composite samples stiffness, especially at lowered temperature range, is simultaneously connected to amount of incorporated to polypropylene matrix lignin, which is part of the filler and partial migration of crude oil residues from ground natural filler which may cause plasticizing effect. Higher glass transition temperatures were observed for the PP/NUT/MAPP series; this effect is attributed exclusively to enhanced interfacial adhesion.

In principle, the addition of a particle-shaped natural filler to a polymer matrix decreases the composite's capacity for mechanical energy dissipation. Therefore, less energy will be used to overcome frictional forces between molecular chains [Eng et al. 2014].

Conclusions

This study has provided detailed knowledge of the properties of PP composites filled with ground walnut shells. Introduction of the organic filler into the polymeric matrix increases the thermal stability of the composites. Moreover, higher moisture and ash contents were observed, depending on the composition. As evidenced by DMTA analysis, the glass transition temperature shifts towards lower values as the filler content increases. The presence of the filler does not influence the crystallization kinetics or melting behavior of the studied samples, irrespective of the amount added. Moreover, the incorporation of polypropylene-graft-maleic anhydride into the formulation enhances interfacial adhesion between the polymeric matrix and the filler, as evidenced by scanning electron microscope photographs. This in turn results in improved stiffness of the samples.

The research has confirmed that polypropylene-based composites filled with lignocellulosic modifiers may be used as an alternative to the traditional highly filled resins, and may be designed according to users' needs. Their main

applications include the production of low-demanding elements for civil engineering such as masking panels, fiberboards and plywood. Another important advantage, in comparison with inorganic materials, is their low density, which combined with sustainability is a reason for their more frequent use also in the automotive industry, especially for the production of interior elements such as parcel shelves, trunk covers and internal panels.

References

- Ayrilmis N., Buyuksari U., Avci E., Koc E. [2009]: Utilization of pine (*Pinus pinea* L.) cone in manufacture of wood based composite. *Forest Ecology and Management* 259: 65-70
- Barczewski M., Chmielewska D., Dobrzyńska-Mizera M., Dudziec B., Sterzyński T. [2014]: Thermal stability and flammability of polypropylene-silsesquioxane nanocomposites. *International Journal of Polymer Analysis and Characterization* 19: 500-509
- Beckermann G.W., Pickering K.L. [2008]: Engineering and evaluation of hemp fibre reinforced polypropylene composites: Fibre treatment and matrix modification. *Composites Part A: Applied Science and Manufacturing* 39: 979-988
- Błędzki A.K., Sperber V.E., Faruk O. [2002]: Natural and wood fibre reinforcement in polymers. *Rapra Review Reports* 13 [8]
- Bodîrlău R., Teaca C.A., Spiridon I. [2007]: Thermal investigation upon various composite materials. *Revue Roumaine De Chimie* 52: 153-158
- Bogoeva-Gaceva G., Avella M., Malinconico M., Buzarovska A., Grozdanov A., Gentile G., Errico M.E. [2007]: Natural fiber eco-composites. *Polymer Composites* 28: 98-107
- Bula K., Knitter M. [2016]: Properties of high-density polyethylene reinforced with pine-wood fillers. *Drewno* 59 [197]: 205-211. DOI: 10.12841/wood.1644-3985.C23.23
- Di Lorenzo M.L., Cimmino S., Silvestre C.J. [2001]: Nonisothermal crystallization of isotactic polypropylene blended with poly (α -pinene). I. Bulk crystallization. *Journal of Applied Polymer Science* 82 [2]: 358-367
- Dixita S. [2014]: Degradation analysis of lignocellulosic fillers infused coir epoxy composites in different environmental conditions. *International Journal of Lignocellulosic Products* 1 [2]: 160-179
- Dobrzyńska-Mizera M., Barczewski M. [2014]: Wpływ dodatku napełniacza organicznego na właściwości mechaniczne kompozytów na podstawie polipropylenu (Influence of organic filler on mechanical properties of polypropylene composites). *Przetwórstwo Tworzyw (Polymer Processing)* 5 [161]: 399-404
- Dobrzyńska-Mizera M., Dutkiewicz M., Sterzyński T., Di Lorenzo M.L. [2015]: Interfacial enhancement of polypropylene composites modified with sorbitol derivatives and siloxane-silsesquioxane resin. *AIP Conference Proceedings* 1695: 020049
- El Achaby M., Arrakhiz F.Z., Vaudreuil S., Essassi E.M., Qaiss A. [2012]: Piezoelectric β polymorph formation and properties enhancement in graphene oxide – PVDF nanocomposite films. *Applied Surface Science* 258: 7668-77
- El-Sabbagh A. [2014]: Effect of coupling agent on natural fibre in natural fibre/polypropylene composites on mechanical and thermal behavior. *Composites: Part B* 57: 126-135

- Eng C.C., Ibrahim N.A., Zainuddin N., Ariffin H., Yunus W.M.Z.W., Then Y.Y.** [2014]: Enhancement of mechanical and dynamic mechanical properties of hydrophilic nanoclay reinforced polylactic acid/polycaprolactone/oil palm mesocarp fiber hybrid composites. *International Journal of Polymer Science* 715801: 1-8
- Espert A., Vilaplana F., Karlsson S.** [2004]: Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties. *Composites: Part A* 35: 1267-76
- Essabir H., Nekhlaoui S., Malha M., Bensalah M.O., Arrakhiz F.Z., Qaiss A., Bouhfid R.** [2013]: Bio-composites based on polypropylene reinforced with Almond Shells particles: Mechanical and thermal properties. *Materials and Design* 51: 225-230
- Gwon J.G., Lee S.Y., Chun S.J., Doh G.H., Kim J.H.** [2010]: Effects of chemical treatments of hybrid fillers on the physical and thermal properties of wood plastic composites. *Composites: Part A* 41: 1491-7
- Hassan O., Ling T.P., Maskat M.Y., Ilias R., Badri K., Jahim J., Mahadi N.M.** [2013]: Optimization of pretreatments for the hydrolysis of oil palm empty fruit bunch fiber (EFBF) using enzyme mixtures. *Biomass and Bioenergy* 56: 137-146
- Jeskea H., Schirp A., Cornelius F.** [2012]: Development of a thermogravimetric analysis (TGA) method for quantitative analysis of wood flour and polypropylene in wood plastic composites (WPC). *Thermochimica Acta* 543: 165-171
- Li X., Cai Z., Winandy J.E., Basta A.H.** [2010]: Selected properties of particleboard panels manufactured from rice straws of different geometries. *Bioresource Technology* 101: 4662-4666
- Liu W., Misra M., Askeland P., Drzal L.T., Mohanty A.K.** [2005]: 'Green' composites from soy based plastic and pineapple leaf fiber: Fabrication and properties evaluation. *Polymer* 46: 2710-2721
- Lu J.Z., Wu Q., McNabb H.S.** [2000]: Chemical coupling in wood fiber and polymer composites: a review of coupling agents and treatments. *Wood Fiber Science* 32 [1]: 88-104
- Malkapuram R., Kumar V., Yuvraj S.N.** [2008]: Recent development in natural fiber reinforced polypropylene composites. *Journal of Reinforced Plastics and Composites* 28: 1169-1189
- Monasse B., Haudin J.M.** [1985]: Growth transition and morphology change in polypropylene. *Colloid and Polymer Science* 263: 822-831
- Moran J., Alvarez V., Petrucci R., Kenny J., Vazquez A.** [2007]: Mechanical properties of polypropylene composites based on natural fibres subjected to multiple extrusion cycles. *Journal of Applied Polymer Science* 103: 228-237
- Nemli G., Demirel S., Gümüokaya E., Aslan M., Acar C.** [2009]: Feasibility of incorporating waste grass clippings (*Lolium perenne* L.) in particleboard composites. *Waste Management* 29: 1129-1131
- Nourbakhsh A., Farhani Baghlani F., Ashori A.** [2011]: Nano-SiO₂ filled rice husk/polypropylene composites: physico-mechanical properties. *Industrial Crops and Products* 33: 183-187
- Panthapulakkal S., Sain M.** [2007]: Injection-molded short hemp fiber/glass reinforced polypropylene hybrid composites – mechanical, water absorption and thermal properties. *Journal of Applied Polymer Science* 103: 2432-2441
- Paul S.A., Boudenne A., Ibos L., Candau Y., Joseph K., Thomas S.** [2008]: Effect of fiber loading and chemical treatments on thermophysical properties of banana fiber/polypropylene commingled composite materials. *Composites Part A* 39: 1582-1588
- Pirayesh H., Khazaeian A.** [2012]: Using almond (*Prunus amygdalus* L.) shell as a biowaste resource in wood based composite. *Composites: Part B* 43 [3]: 1475-1479

- Pirayesh H., Khazaiean A., Tabarsa T.** [2012]: The potential for using walnut (*Juglans regia L.*) shell as a raw material for wood-based particleboard manufacturing. *Composites: Part B* 43: 3276-3280
- Saheb D.N., Jog J.P.** [1999]: Natural fiber polymer composites: a review. *Advances in Polymer Technology* 18: 351-363
- Salasinska K., Polka M., Gloc M., Ryszkowska J.** [2016]: Natural fiber composites: the effect of the kind and content of filler on the dimensional and fire stability of polyolefin-based composites. *Polimery* 61: 255-265
- Shalwan A., Yousif B.F.** [2013]: In state of art: mechanical and tribological behaviour of polymeric composites based on natural fibres. *Materials & Design* 48: 14-24
- Taha I., Ziegmann G.** [2006]: A comparison of mechanical properties of natural fiber filled biodegradable and polyolefin polymers. *Journal of Composite Materials* 40: 1933-1946
- Van de Velde K., Kiekens P.** [2002]: Development of a flax/polypropylene composite with optimal mechanical characteristics by fiber and matrix modification. *Journal of Thermoplastic Composite Material* 15: 281-300
- Vyazovkin S., Chrissafis K., Di Lorenzo M.L., Koga N., Pijolat M., Roduit B., Sbirrazzuoli N., Sunol J.J.** [2014]: ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations. *Thermochimica Acta* 590: 1-23
- Wambua P., Ivens J., Verpoest I.** [2003]: Natural fibres: can they replace glass in fiber reinforced plastics. *Composites Science and Technology* 63: 1259-1264
- Zahedi M., Pirayesh H., Khanjanzadeh H., Tabar M.M.** [2013]: Organo-modified montmorillonite reinforced walnut shell/polypropylene composites. *Materials & Design* 51: 803-809

List of standards

- PN-EN ISO 3451-1:2010** Tworzywa sztuczne – Oznaczenie popiołu – Część 1: Metody ogólne (Plastics – Determination of ash – Part 1: General methods)
- ISO 527-2:2012** Plastics – Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics

Acknowledgments

This work was supported by Poznan University of Technology research grant no. 02/25/DSPB/4400/2017. The authors wish to thank Celestyna Małecka M.Eng. for her help in laboratory work.

Submission date: 13.10.2017

Online publication date: 12.10.2018