

HYBRID PE/PA/NANOPARTICLE COMPOSITES RESISTANT TO HIGH TEMPERATURES

MIHAI GEORGESCU¹, MIHAELA NITUICA¹, MARIA SONMEZ¹, LAURENTIA ALEXANDRESCU¹, DANA GURAU¹, ION OVIDIU VASILESCU²

¹ *National Research and Development Institute for Textile and Leather - Division Leather and Footwear Research Institute, 93 Ion Minulescu St., sector 3, Bucharest, mihai.georgescu@icpi.ro; mihai.georgescu@yahoo.com*

² *S.C. Protect Chemical S.R.L., 6 Cercetatorilor St, district 4, Bucharest, Romania, o_vasilescu89@yahoo.com*

In the field of polymeric materials, leading companies turned to the development of modified polymers with superior physical and mechanical properties compared to those of the basic constituents, individually considered, which offers a degree of versatility that was not obtained with any other material. Composite materials are produced with anisotropic properties both at the nano, micro- and macroscopic scale, formed by the assembly of several components whose organization and design allow use of the maximum specific properties of each component in order to obtain higher overall final properties of each component. The most common composites are polymeric, in which the combination of elastomers with fillers, nanoparticles and other ingredients lead to a significant variety of materials with much improved properties compared to the original and even directed towards predetermined properties according to the market requirements. This paper shows resistant polymeric nanocomposites (TEO) based on compatibilized polyethylene (PE) and polyamide (PA), with advanced characteristics based on reinforcement materials in the form of powders with nano structure and chemically activated surface, that provides qualitative performance and meeting the current requirements of quality and aesthetics for consumer goods.

Keywords: polymers, hybrid composites, thermal resistance

INTRODUCTION

In the field of polymeric materials, leading companies have been oriented towards the development of modified polymer structure elastomer/plastomer/ nanoparticles and superior physical and mechanical properties compared to those of the base constituents taken individually. These properties offers high use value in fields which require materials with performance characteristics: dimensional stability, resistance to weathering, UV radiation, ozone, microorganisms, solvents, aggressive chemical agents, waterproof and disperse systems, solid-gas, gas-liquid, electric resistance, lack of toxicity. In addition to the above, other important property is thermal resistance at a wide range of temperatures, etc. Properties are the result of a complex of original characteristics which arise from physical, mechanical and chemical interactions that occur during manufacturing processes that result in a polymer nanostructure.

Polymer nanocomposites (PNCs) are the class of composite materials comprising at least one of their components so called fillers bearing nanometer size scale (< 1000 nm) dispersed into a polymer matrix.

The physical, chemical and biological properties of the PNCs are largely related to physical characteristics of polymer matrix, their composition, dimensions of fillers, compatibility of fillers with polymer matrix, interfacial interactions between polymer matrix and nanofiller phase (Hussain *et al.*, 2006; Bitinis *et al.*, 2011; Faghihi *et al.*, 2013). Over past decades, significant progress is made on development of clay containing PNCs using various thermosetting and thermoplastic polymer

matrix. The development of PNCs for particular class of application is best exercised through appropriate combination of filler and polymer substrates (Das *et al.*, 2011; Zuzana *et al.*, 2012).

Polymer nanotechnology (Schaefer and Justice, 2007; Yoo and Paul, 2008) is a new domain in the nanosciences. Recently, polymer nanocomposites draw attention mainly due to their spectacular hybrids properties, which are synergistically derived from the two or more components of the composite. Due to the large contact area created by nanofillers is possible to obtain polymer nanocomposites with new properties. The advantages of nanoparticles (Alexandrescu, 2014) include reinforcing efficiency with minimal loss of ductility and impact strength, thermal stability, flame retardant, improved abrasion resistance, vapor and gas permeability, low shrinkage, minimum waste. In the last two decades has been developed a large variety of new multicomponent polymeric materials. Multiphase polymer nanocomposites have been identified as the most versatile economical method to produce new resistant polymers that are able to meet the complex requirements of performance.

MATERIAL AND METHODS

Materials

In order to achieve the thermal resistance hybrid composites, the following materials were used: (1) HDPE injection ERACLENE MP 64, HD 60-70 UA (Basplast), (2) polyethylene-*graft*-maleic anhydride viscosity 500 cP (140°C)(lit.); PE-g-MA (Sigma-Aldrich Chemie, USA), (3) Standard PA for injection - Sebamid 6 s3c (Basplast), (4) Montmorillonite – mmt, nanoclay, surface modified i.31.ps, contains 0.5-5wt% aminopropyltriethoxysilan, 15-35wt% octadecylamine (Sigma-Aldrich Chemie, USA).

Method

The PE/PA hybrid composites, compatibilized with maleic anhydride grafted polyethylene – PE-g-MA (Scaffaro *et al.*, 2008), and reinforced with chemically modified layered mineral clay of the montmorillonite type argile were carried out on a Counter-rotating twin screw extruder (Machado *et al.*, 1999) granulator, TSE 35 type. Finally being processed into finished products (boards) by molding method using a Electrically heated press, considering the optimal technological parameters of processing. After stabilization for 24 hours at room temperature, the plates are submitted to physico-mechanical determinations.

The method (Figure 1) for achieving multiphase polymer nanocomposites based on PE / PE-g-MA / PA / MMT on the extruder-granulator, is as follow: polyethylene is added at 150°C and a speed of twin screws 150-200 rpm, is mixed until it becomes easy to process (softening plastics) then increase the temperature to 215°C, add PA, MMT and PP-g-MA and continue mixing at speed of 250-280 rpm until ingredients are embedded and the mixture is uniform, obtaining cylindrical granules in the end.



Figure 1. Counter-rotating twin screw extruder granulator, TSE 35 type

The obtained polymer nanocomposite granules are added in the molds, to process them according to test specimens used for physical-mechanical characterization for finished products, using the electrically heated press, TP 600, by means of compression method, between its platters at temperature of 220°C and 300KN pressure for 2 minutes preheating, 5 minutes actual forming in the press and 10 minutes cooling.

Table 1. PE, PE/PA, PE/PE-g-MA/PA samples

Samples	MU	M0	M1	M2	M3	M4	M5
Polyethylene	%	100	90	70	89	85	65
Polyamide	%	-	10	30	10	10	30
PE-g-maleic anhydride	%	-	-	-	1	5	5
Total	%	100	100	100	100	100	100

Table 2. PE/PE-g-MA/PA/MMT polymeric nanocomposite samples

Samples	MU	M6	M7	M8	M9
Polyethylene	%	88	82	84	78
Polyamide	%	10	10	10	10
PE-g-maleic anhydride	%	1	1	5	5
Montmorillonite	%	1	7	1	7
Total	%	100	100	100	100

RESULTS AND DISCUSSIONS

The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm⁻¹, using a 4200 FT-IR equipped with ATR crystal diamond and sapphire head. Samples analyzed are divided into two categories:

- PE;
- Polymeric architectures (M1 – M9).

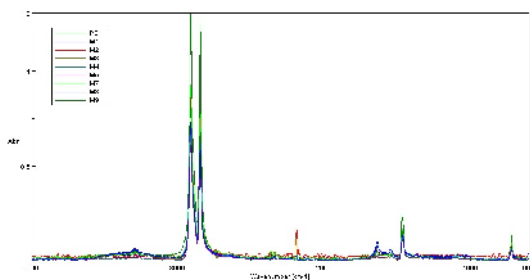


Figure 2. Overlapping IR spectra of PP / PP-g-MA / PA / MMT polymer architectures

From overlapping spectra is noted the presence of PE and PA in compounds. The presence of PA in variable percentages by the intensity of characteristic peaks is observed. Note that PE is in excess of the other components, being the main ingredient. PE-g-MA and MMT cannot distinguish so well, primarily due to the small amount (PE-g-MA max.5% and 4% -MMT).

The results of the physico-mechanical properties of the samples obtained for the polymer mixture based on polyethylene and polyamide compatibilized with PE-g-MA and montmorillonite reinforced, compared with the reference samples M0 - M5 are shown in Figures 3, 4, 5.

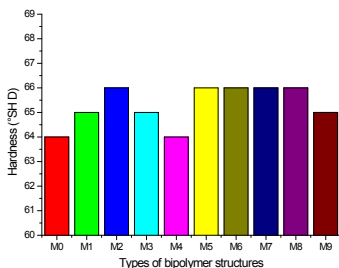


Figure 3. Variation of hardness of mixtures M0-M9

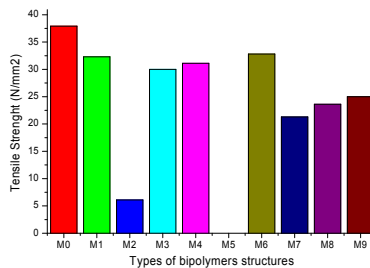


Figure 4. Variation of tensile strength of mixtures M0-M9

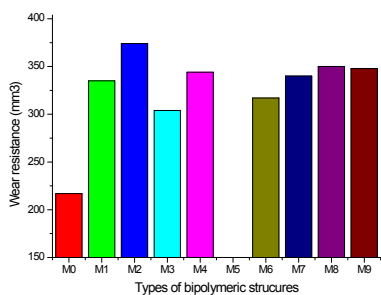


Figure 5. Variation of abrasion resistance of mixtures M0-M9

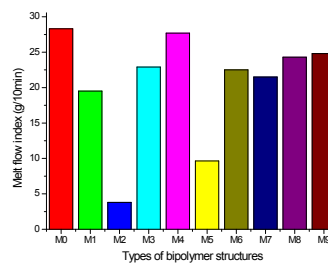


Figure 6. Variation of Melt flow index of mixtures M0-M9

Hardness (Figure 3) of polymer nanocomposites increases slightly compared to polyethylene as such – 64°Sh at 65°Sh and 66°Sh when increasing concentrations of polyamide (30%). MMT does not significantly affect the hardness values instead adding compatibilizer PE-g-MA decreases with 1°Sh hardness values, in composites this decrease is offset by increased percentage of polyamide and MMT.

Tensile strength (Figure 4) - decreases compared to the reference simple. Increase with the addition of compatibilizer PE-g-MA and MMT, but decreases with increasing the percentage of PA added in compositions. Neither the presence of MMT nor higher percentage (4%) affects the tensile strength values.

Wear resistance (Figure 5) - is within the standard, increasing with the amount of polyamide and compatibilizing agent. The presence of montmorillonite has no influence on the wear resistance.

Density - increases in proportion to the amount of polyamide added to the mixture, and the MMT has a weak influence over density values.

The more viscous materials are so requires a greater force to be extruded through MFI's die. According to the graph shown above, it is seen that the flow index polymer composites tested are highly influence by temperature, amount of reinforcing agent and the amount of coupling agent. Values of flow indexes significantly decrease proportional to the amount of PA due to increased melt viscosity, MMT compatibilizer positively influencing the flow.

CONCLUSIONS

Samples of PE / PA without compatibilizer are difficult to obtain due to high melting temperature difference of the two elastomers; PE-150°C and PA-210°C, which makes the dispersion of the matrix PA on PE matrix to be achieved at high speed (300 rpm) and to be non-uniform (PA grainules can be observed in the mixture), the mixture is rigid and becomes brittle after cooling.

Introducing compatibilizer (PE-g-MA) significantly improves the mixture processing, dispersion of discontinuous phase - PA is uniform, the mixture is homogeneous, flexible and non-brittle after cooling.

Increasing the percentage of compatibilizer does not visibly improve processability.

Montmorillonite increases hardness mixture, it disperses evenly, it is not necessary to increase the rate of mixing and the samples are not brittle after cooling.

Quantities of more than 4% MMT technical do not change mixing process, proven by physical and mechanical tests.

Hardness of thermo resistance polymer nanocomposites increases slightly compared to polyethylene as such – 64°Sh at 65°Sh and 66°Sh when increasing concentrations of polyamide (30%). MMT does not significantly affect the hardness values, instead adding compatibilizer PE-g-MA decreases with 1°Sh hardness values, in composites this decrease is offset by increased percentage of polyamide and MMT.

Similar to hardness, tensile strength decreases compared to the reference simple. Increase with the addition of compatibilizer PE-g-MA and MMT, but decreases with increasing the percentage of PA added in compositions. Neither the presence of MMT nor higher percentage (4%) affects the tensile strength values.

Wear resistance increase, is within the standard, with the amount of polyamide and compatibilizing agent. The presence of montmorillonite has no influence on the wear resistance.

Density increases proportional with the amount of polyamide added to the mixture,

and the MMT has a weak influence over density values.

Values of flow indexes significantly decrease proportional to the amount of PA, but MMT compatibilizer positively influencing the flow.

Acknowledgements

This research was financed through PN 09-10 02 20/2013 project: “*Thermal resistance polymer nanocomposites for consumer goods*” supported by Romanian Ministry of Education.

REFERENCES

- Alexandrescu, L., Sonmez, M., Ni uic , M., Gur u, D., Popa, N. (2014), “Hybrid bipolymeric structures based on butadiene-co-acrylonitrile and styrene-butadiene rubber reinforced with nanoparticles”, *Leather and Footwear Journal*, 14(1), 39-52.
- Bitinis, N., Hernandez, M., Verdejo, R., Kenny, J.M., Machado, M.A.L. (2011), „Recent Advances in Clay/Polymer Nanocomposites”, *Ad. Mat. Sp. Is. Mat. Sci. Mad.*, 23(44), 5229-5236.
- Das, A., Wang, D.Y., Stockelhuber, K.W., Jurk, R., Fritzsche, J., Kluppel, M., Heinrich, G. (2011), „Rubber-Clay Nanocomposites. Some Recent Results”, *Ad. Poly. Sci.*, 239, 85-166.
- Faghihi, K., Rahimi, A., Feyzi, A. (2013), „Synthesis and Properties of New Clay-Reinforced Aromatic Polyimide/ Nanocomposites Based 3, 3',4,4'-Benzophenonetetracarboxylic dianhydride and 1, 3-bis (4-Aminophenoxy) Propane”, *Sci.and Engi.of Com. Mat.*, 0(0) ,1-7.
- Hussain, F., Hojjati, M., Okamoto, M., Gorga, R.E. (2006), „Polymer-Matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview”, *J. Com. Mat.*, 40(17), 1511-1565.
- Machado, A.V., Covas, J.A. and van Duin, M. (1999), “Chemical and morphological evolution of PA-6/Epm/Epm-g-MA blends in a twin screw extruder”, *Journal of Polymer Science Part A: Polymer Chemistry*, 37 (9), 1311-1320.
- Scaffaro, R., Mistretta, M.C. and La Mantia, F.P. (2008), “Compatibilized polyamide 6/polyethylene blend/clay nanocomposites: Effect of the degradation and stabilization of the clay modifier”, *Polymer Degradation and Stability*, 93 (7), 1267-1274.
- Schaefer, D.W. and Justice, R.S. (2007), “How nano are nanocomposites?”, *Macromolecules*, 40 (24), 8501-8517.
- Yoo, Y. and Paul, D.R (2008), “Effect of organoclay structure on morphology and properties of nanocomposites based on an amorphous polyamide”, *Polymer*, 49 (17), 3795-3804.
- Zuzana, D., Dagmar, M., Miroslav, S. (2012), „Fire Retardation of Polystyrene/Clay Nanocomposites. Initial Study on Synergy Effect”, *J. of The. Com. Mat.*, doi: 10.1177/0892705712445301.