POLYMERIC NANOSTRUCTURES BASED ON POLYOLEFINS AND RUBBER FOR THE FOOTWEAR INDUSTRY

MIHAELA NITUICA[1], MARIA SONMEZ[1], MIHAI GEORGESCU[1], LAURENTIA ALEXANDRESCU[1], DANA GURAU[1], AURELIA MEGHEA[2], MARIA DANIELA STELESCU[1], ION OVIDIU VASILESCU[3]

[1] *National Research and Development Institute for Textile and Leather - Division Leather and Footwear Research Institute, 93 Ion Minulescu St., district 3, Bucharest, icpi@icpi.ro, mihaela.nituica@icpi.ro*

[2] *"Politehnica" University of Bucharest, 011061, 1 Polizu, Bucharest, Romania, a.meghea@gmail.com*

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

Designing and constructing materials of technical and engineering interest with preset physical-chemical and mechanical properties have commanded the attention of researchers and engineers since the beginning of the technological era. Polymeric nanostructures based on rubber and plastics were identified as the best method to produce new polymeric materials able to satisfy complex performance requirements. Over the last few years, the global tendency to develop new advanced hybrid polymeric materials from a mixture of polymers (elastomers and plastomers: EPDM with thermoplastic polyolefins) and reinforcement agents with nano-sized particle has given new possibilities of extending their area of application. Nanostructures based on thermoplastic polymeric compounds – EPDM/polyolefins/nanoparticles – were selected because one polymer alone cannot meet all requirements regarding mechanical, physical and chemical properties. Thus, we combined characteristics of the two polymers, such as chemical resistance; low water permeability; resistance to high temperatures, ozone and radiation; flexibility at low temperatures; colour stability; processability properties adapted to the injection technology; green and waste-free technology; reduced working time; low energy consumption for processing into finished products; recirculation of material in approximately five cycles without changing its properties etc. Performance of polymeric nanostructures depends on the concentration and morphology of the elastomer and plastomer used, processing parameters, type and concentration of auxiliary materials used in compounding, the equipment and working parameters used in compounding, etc.

Keywords: polymeric nanostructures, EPDM, polyolefins, nanoparticles.

INTRODUCTION

Footwear manufacturers require advanced materials to process and usage, which resulted in the development of new polymeric structures with nanostructured reinforcing agents with optimized properties to conventional used materials in this area (Vilsan *et al.*, 2009). In this context, it has developed this theme of making a nanostructured material that combines the specific properties of each elastomer to obtain products with predetermined features, depending on the application. These polymeric structures obtained by combining in, different rubber proportions, polyolefin and nanoparticles, will be process to fit for use in the footwear industry and consumer goods (Sonmez *et al.*, 2014; Kurahatti *et al.*, 2010) .

In recent years, the worldwide trend of obtaining new advanced hybrid polymer consisting of a mixture of polymers (elastomers: EPDM thermoplastic polyolefin) and reinforcing agents, offers new possibilities to extend the aim of application (Stelescu *et al.*, 2013; Ionescu *et al.*, 2008; Manaila *et al.*, 2007). Polymeric structures based on thermoplastic polymers / EPDM ware selected as a single polymer cannot satisfy all the requirements required for assembly of mechanical, physical and thermal features, needed in a number of specific applications. In this way, it will combine the characteristics of the materials used, such as chemical resistance, low water permeability of thermoplastic polymer with excellent resistance to heat, ozone and sunlight, very good flexibility at low temperatures, resistance to alkalis and acids, steam and water low permeability, excellent color stability of EPDM, etc. (Volintiru *et al.*, 1974; Anandhan *et al.*, 2011; Koo *et al.*, 2005; Manaila, 2013).

EXPERIMENTAL PROCEDURE

Materials

The following materials were used: (1) polypropylene (PP), impact copolymer Tipplen K 948, manufactured (by Tiszai Vegyi Kombinat RT (TVK), HUNGARY); (2) ethylene-propylene-diene (EPDM) terpolymer rubber, NORDEL IP 4760, specific gravity – 0.872, Mooney viscosity – 60 MU, ethylene content – 67.5 wt%, ethylidene norbornene (EBN) contents – 5.0 wt%, molecular weight distribution – medium, propylene content – 27.5 wt% (by – DuPont Dow elastomer, LLC, USA); (3) polypropylene-graft-maleic anhydride (PP-g-AM), average Mw~9.100 by GPC, average Mn~3,900 by GPC, maleic anhydride 8-10 Wt.%, manufactured (by Sigma - Aldrich Chemie USA); (4) montmorillonite (MMT), Nanoclay, surface modified I.31.PS, contains 0.5-5wt% aminopropyltriethoxysilan, 15-35wt% octadecylamine (Sigma-Aldrich Chemie, USA), (5) di(tert-butylperoxyisopropyl)benzen, powder 40% with calcium carbonate and silica (PD) - Perkadox 14-40B (1.65 g/cm^{3}density, 3.8% active oxygen content, pH 7, assay: 39.0-41.0%).

Procedure

The polymeric nanocomposites based on EPDM rubber and polyolefins, compatibilized with maleic anhydride grafted polypropylene – PP-g-MA, were carried out on a Counter-rotating twin screw extruder granulator, TSE 35 type (Tabel 1), then the obtained granules are prepared by means of blending technique, on a mixer-type Plastic-Corder Brabender Mixer (table 2 A and B, Table 3 A and B) and reinforced with chemically modified layered mineral clay of the montmorillonite type and crosslinking agent, and 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.

Table 1. Sample for comparison (test specimen) PP, PP/EPDM, PP/EPDM/PP-g-MA

Symbol	MU	M_0	M_1	M_2	M_3	M_{11}	M_{21}	M_{31}
Polypropylene	%	100	90	70	50	90	70	50
EPDM	%	-	10	30	50	10	30	50
PP- g-AM	%	-	-	-	-	5	5	5

The method for achieving polymer nanocomposites based on PP/EPDM and PP/EPDM/PP-g-MA on a Counter-rotating twin screw extruder granulator, is as follow: polypropylene is added at 150°C and a speed of twin screws 150-200 rpm, is mixed until it becomes easy to process then increase the temperature to 175°C, add EPDM 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.

The obtained polymer nanocomposite granules based on thermoplastic polymers/ compatibilizer/nanoparticles/ crosslinking agents are prepared by means of blending technique, on a Plastic-Corder Brabender Mixer 350 E at mixing speed of 280 rpm, the temperatures in the three zones are 165/175/175°C, air cooled, 3-5 minutes mixing according to the added ingredients.

Table 2. Polymer nanocomposites formulation based on PP/EPDM/PP-g-MA/MMT (A and B)

A

Symbol	MU	$M_{11}M_1$	$M_{11}M_2$	$M_{11}M_3$	$M_{21}M_1$	$M_{21}M_2$	$M_{21}M_3$
PP	%	90	70	50	90	70	50
EPDM	%	10	30	50	10	30	50
PP- g-MA	%	5	5	5	5	5	5
MMT	%	1	3	7	1	3	7

B

Symbol	MU	$M_{31}M_1$	$M_{31}M_2$	$M_{31}M_3$
PP	%	90	70	50
EPDM	%	10	30	50
PP- g-MA	%	5	5	5
MMT	%	1	3	7

Table 3. Polymer nanocomposites formulation based on PP/EPDM/PP-g-MA/MMT/ PD (A and B)

A

Symbol	MU	$M_{11}M_1$	$M_{11}M_2$	$M_{11}M_3$	$M_{21}M_1$	$M_{21}M_2$	$M_{21}M_3$
PP	%	90	70	50	90	70	50
EPDM	%	10	30	50	10	30	50
PP- g-MA	%	5	5	5	5	5	5
MMT	%	1	3	7	1	3	7
PD	%	3	3	3	3	3	3

B

Symbol	MU	$M_{31}M_1$	$M_{31}M_2$	$M_{31}M_3$
PP	%	90	70	50
EPDM	%	10	30	50
PP- g-MA	%	5	5	5
MMT	%	1	3	7
PD	%	3	3	3

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, shown in figure 1, by means of compression method, between its platters at temperature of 165°C and 150 KN pressure for 2 minutes preheating, 10 minutes actual forming in the press and 10 minutes cooling (with water).

Figure 1. Electrically heated press, TP 600

RESULTS AND DISCUSSIONS

The obtained polymeric nanostructures have been tested in compliance with the physical-mechanical standards in effect and the results are presented in the tables below (Table 4, Table 5 A and B, Table 6 A and B).

After stabilization for 24 hours at room temperature, the plates are submitted to physico-mechanical determinations: density, g/cm^3; wear, mm^3; hardness, ^{0}Sh D; elasticity, %; tensile strength, N/mm^2.

Table 4. Physical-mechanical characterisation – Sample for comparison (test specimen) PP, PP/EPDM, PP/EPDM/PP-g-MA

Symbol	M_0	M_1	M_2	M_3	M_{11}	M_{21}	M_{31}
Wear, mm^3, SR ISO 4649/2010	192	310	147	171	219	181	243
Density g /cm^3 SR ISO 2781:2010	0.91	0.91	0.89	0.89	0.87	0.88	0.91
Hardness ^{0}Sh D SR ISO 7619-1:2011	70	65	54	42	62	53	43
Tensile strength, N /mm^2, SR ISO 37:2012	11.4	11.9	9.6	7.0	10.9	7.6	5.5
Elasticity, %, ISO 4662:2003	28	28	28	30	26	28	30

Density decreases with the amount of EPDM rubber and PP-g-AM compatibilizer added to the mixture; the presence of montmorillonite (MMT) should have a weak influence on density values. Wear increases, in the standard range, proportionally to the amount of copmatibilizing agent added to the mixture. The presence of montmorillonite should not influence the degree of wear. Tensile strength decreases proportionally with adding EPDM and compatibilizer – PP-g-MA, compared to the raw material – PP. It is noticed that by adding rubber and compatibilizer, elasticity is approximately constant.

Table 5. Physical-mechanical characterisation – Polymer nanostructure formulation based on PP/EPDM/PP-g-MA/MMT (A and B)

A

Symbol	$M_{11}M_1$	$M_{11}M_2$	$M_{11}M_3$	$M_{21}M_1$	$M_{21}M_2$	$M_{21}M_3$
Hardness ^{0}Sh D SR ISO 7619-1:2011	68	68	66	57	57	60
Tensile strength, N/mm^2, SR ISO 37:2012	15.5	12.2	10.8	19	16.4	11.7
Elasticity, %, ISO 4662:2003	32	30	28	30	30	30

B

Symbol	$M_{31}M_1$	$M_{31}M_2$	$M_{31}M_3$
Hardness ^{0}Sh D SR ISO 7619-1:2011	47	43	42
Tensile strength, N /mm^2, SR ISO 37:2012	8.5	7.8	5.6
Elasticity, %, ISO 4662:2003	32	30	28

Table 6. Physical-mechanical characterisation – Polymer nanostructure formulation based on PP/EPDM/PP-g-MA/MMT/PD (A and B)

A

Symbol	$M_{115}M_1$	$M_{115}M_2$	$M_{115}M_3$	$M_{215}M_1$	$M_{215}M_2$	$M_{215}M_3$
Hardness ^{0}Sh D SR ISO 7619-1:2011	63	63	64	57	58	58
Tensile strength, N/mm^2, SR ISO 37:2012	Could not be determined	5.6	10.2	8.2	9.8	10.7
Elasticity, %, ISO 4662:2003	26	26	26	26	26	24

B

Symbol	$M_{315}M_1$	$M_{315}M_2$	$M_{315}M_3$
Hardness ^{0}Sh D SR ISO 7619-1:2011	48	49	51
Tensile strength, N /mm^2, SR ISO 37:2012	8.1	8.5	10.6
Elasticity, %, ISO 4662:2003	24	24	28

- Hardness of polymeric structures by adding EPDM in varying proportions decreases below the raw material - PP, and by adding PP-g-AM compatibilizer, values are approximately similar to those mentioned above. In the case of polymeric nanostructures with 1% MMT hardness decreases compared to PP, and with 3% and 7% MMT it significantly decreases below polypropylene hardness, as well as by adding crosslinker (PD) hardness decreases compared to the value of raw material (PP).
- Due to the fact that by adding the crosslinker during the mixing process, EPDM rubber vulcanizes, tensile strength has values below those of polymeric nanostructures based on PP/EPDM/PP-g-AM, as well as below those of the control sample (PP).
- It can be seen that with the addition of MMT in different percentages, elasticity increases slightly versus polypropylene, with the addition of crosslinking agent - PD due process of EPDM rubber vulcanization, elasticity decreases.

CONCLUSIONS

Processing natural and synthetic elastomers involves the use of many auxiliaries with a well established role in influencing properties of finished products or cost price. To obtain products with preset physical-mechanical characteristics depending on their destination, it is necessary to use fillers and compatibilizers of various types and concentrations.

The polymeric nanocomposites based on EPDM rubber and polyolefins, compatibilized with maleic anhydride grafted polypropylene – PP-g-MA, were carried out on a Counter-rotating twin screw extruder granulator, TSE 35 type according to the added ingredients, and then the obtained polymer nanocomposite granules based on thermoplastic polymers/compatibilizers/nanoparticles/crosslinking agents were prepared by means of blending technique, on a Plastic-Corder Brabender Mixer 350 E at mixing speed of 280 rpm, the temperatures in the three zones are 165/175/175°C, air cooled, 3-5 minutes mixing according to the added ingredients.

Processing the obtained granules in boards form is possible by adding them in the molds, using the electrically heated press, TP 600, by means of compression method, between its platters at temperature of 165°C and 150 KN pressure for 2 minutes preheating, 10 minutes actual forming in the press and 10 minutes cooling, with water cooling.

Finally being processed into finished products by molding method using a Electrically heated press, considering the optimal technological parameters of processing and after stabilization for 24 hours at room temperature, the plates are submitted to physico-mechanical determinations.

Acknowledgements

This research was financed through PN 09-10 02 27/2014 project: “New polymeric alloys compounded with nanoparticles for footwear industry”; PN 09-10 02 20/2013 project: “Thermal resistance polymer nanocomposites for consumer goods” supported by Romanian Ministry of Education.

REFERENCES

Anandhan, S. and Bandyopadhya, S. (2011), “Polymer Nanocomposites: From Synthesis to Applications”, *Nanocomposites and Polymers with Analytical Method*, ISBN: 978-953-307-352-1.

Ionescu, F., Alexandrescu, L., Vilsan (Nituica), M., Georgescu, M., Ficai, M., Vilsan, S., Ciobotaru, V., Moldovan, Z., Teisanu, F., Grigorescu, V. (2008), “Ageing resistance under dynamic conditions – a quality performance of the structured elastoplastic materials”, Proceedings of The 2nd International Conference on Advanced Materials and Systems, CERTEX, ISBN 978-973-1716-39-8, 52.

Koo, J.H., Pilato, L.A., Wissler, G., Lee, A., Abusafieh, A. and Weispfenning, J. (2005), “Epoxy Nanocomposites for Carbon Fiber Reinforced Polymer Matrix Composites”, Proc. SAMPE ISSE, SAMPE, Covina, CA.

Kurahatti, R.V. and Surendranathan, A.O. (2010), *J. Defence Sci.*, 60(5), 551.

Manaila, E., Martin, D., Zuga, D., Craciun, G., Ighigeanu, D., Matei, C. (2007), “Ethylene-propylene terpolymer rubber processing by electron beam irradiation”, Sixth International Conference of the Balkan Physical Union, Book Series: AIP Conference proceedings, 899, 785.

Manaila, E. (2013), “The influence of TMPT coagent on the cross-link density of the EPDM rubber vulcanized by irradiation”, *Revista de Pielarie Incaltaminte* (*Leather and Footwear Journal*), 13(1), 13.

Stelescu, M.D., Manaila, E., Craciun, G. (2013), *Journal of Applied Polymer Science*, 128 (4), 2325-2336.

Sönmez, M., Alexandrescu, L., Georgescu, M., Nituica (Vilsan), M., Gurau, D., Ficai, A., Ficai, D. (2014), “Processing and morphological and structural characterization of polypropylene / silicon carbide nanocomposites”, 27th International Symposium on Polymer Analysis and Characterization, ISPAC, Les Diablerets, Switzerland, June 16-18, 111.

Volintiru, T., Ivan, Gh. (1974), *Technological fundamentals for elastomer processing* (in Romanian), Technical Press, Bucharest.

Vilsan (Nituica), M., Ficai, M., Georgescu, M., Panturu, L., Chelaru, C., Dragomir, T. (2009), “Application of advances polymers in the footwear industry”, *Revista de Pielarie Incaltaminte* (*Leather and Footwear Journal*), 9(1), 33.