

**POLYMER NANOCOMPOSITES PE / PE-G-MA / EPDM / NANO ZnO
DYNAMICALLY VULCANIZED WITH PEROXIDE**

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Nanocrosslinked elastic-plastic nanocomposites are blends that economically combine, in a highly advanced way, the properties of at least two polymers (elastomer and plastomer) and nanoparticles in a single product. In these mixtures the elastomeric phase is cross-linked in the thermoplastic melt under conditions of thermodynamic technology. This paper presents the development of multiphase elastic-plastic polymeric nanocomposites, dynamically vulcanized, reinforced with nanoparticles for products used in food and pharmaceutical domain, a new variety of composite material based on elastomer (ethylenepropylene-ter-polymer rubber EPDM) and nanofiller (ZnO) dispersed in the plastomer matrix (high density polyethylene-HDPE). By nanometric dispersion in plastomer matrix, elastomers and nanofiller have led to obtaining a high-performance polymer material with multifunctional characteristics (rubber and thermoplastic) and processing properties specific to plastics. Also, the elastomer was dynamically cross-linked in the plastomer matrix, during processing, by classic vulcanization system with peroxide. The crosslinking method is ecological, without release of aromatic nitrosamines, which are carcinogenic in the crosslinking process. Experimented composites were physico-mechanically characterized by standard methods specific to plastics.

Keywords: nanocomposite, dynamical cross-link, peroxide.

INTRODUCTION

Thermoplastic elastomers (TPEs) are a class of copolymers or polymer blends that have the thermoplastic processing and functional characteristics of a conventional crosslinked elastomer. TPEs typically have a structure of two phases, a thermoplastic phase and the elastomeric phase. The thermoplastic phase melts at high temperatures at which the elastomeric phase disperses and thus the TPE becomes processable (Borcea, 2008). The advantages of TPEs compared to plastomers are: possibility of adapting the properties from rigid to low hardness, by varying the amount of plasticizer and/or reinforcing agents, processing by injection with low consumption of time and energy, waste recycling capacity etc. The disadvantages include: high temperature processing, physical and mechanical properties that not suitable for all applications and the material loses its properties after recycling (Lebel, 1994). The thermoplastic compounds - TPE based on rubber/polyolefin - are classified in two distinct classes: one class consists of simple mixing and is referred to as olefin thermoplastic elastomers (TEO) (ASTM D 5593 – 99) and the other class, the rubber phase is dynamically crosslinked obtaining a dynamically crosslinked thermoplastic (TPV) in compliance with (ASTM D 5046 – 98). Dynamically crosslinked thermoplastic materials (TPV) have taken a large marketshare in use as substitutes for polymers, plastics, wood and even metal, due to thermoplastic processability combined with elastomer behavior. TPVs contain elastomeric crosslinked particles into a thermoplastic matrix. The rubber particle size dispersed in thermoplastic

and interfacial adhesion with plastomer is the key of these materials, because they have a major influence on the quality and processability of this new material. Dynamic crosslinking process was tested by Gessler (Gessler and Haslett, 1962). The first dynamically crosslinked thermoplastic composite was introduced in 1972 (Fisher, 1972), which partially crosslinked elastomeric phase - EPDM of PP / EPDM compound with peroxide. Significant improvements of these compound properties were made (Coran *et al.*, 1978) by completely crosslinking the elastomer phase dynamically, while maintaining the compound thermoplasticity. TPVs represent the second group of elastic thermoplastic elastomers, the first being styrene block copolymers. These systems have properties similar to crosslinked rubber hardness in the range of 40-90 °Shore A (Harrats *et al.*, 2006; Rane and Abitha, 2015; Ito *et al.*, 2003). TPVs are obtained by melt compounding techniques in extrusion granulators with co-rotating twin screws and a high L (length) / D (diameter) ratio, continuous flow processing technology (Ellul *et al.*, 2004; Harrats *et al.*, 2006). The properties of the composites depend on the polymer, reinforcing agents, the type and amount of compatibilizer and their proportion in compounding and processing conditions. Therefore, the reinforcing agents properties must be known, they influence compound properties, and therefore the domain of interest (Thostenson and Chou, 2005; Koo, 2006). There are different types of nanoparticles that can be embedded into the polymer matrix which are selected depending on their properties and applications. ZnO nanoparticles show antimicrobial activity including for temperature and high pressure resistant spores (Emamifar, 2010). Besides the role of active filler or curing initiator, treating elastomers and plastomers (polyester, polyamide) with ZnO nanoparticles leads to an important reduction of bacterial cells by 78 and 62% respectively, and for fungus by 80.7 and 32% respectively (Kim, 2013).

MATERIALS AND METHODS

Materials

All composites contain the same two polymers: the EPDM elastomer (Nordell IP 3745P-DuPont) and the high density polyethylene (HDPE-SIDPEC, Egyptene), in the ratio 60:40.

In addition to the polymers, other additives were used, as follows:

- compatibilizer: polyethylene graft maleic anhydride (PE-g-MA, Sigma Aldrich);
- crosslinking agent: di (tert-butylperoxyisopropil) benzene, powder 40% with calcium carbonate and silica – Perkadox 14-40B-PD, AkzoNobel, Germany;
- activators: zinc oxide and stearic acid – Bayer, Germany;
- antioxidants: di-lauril-orto-dipropionate (Irganox 1010) and N-isopropyl-N-phenyl-p-phenyldiamine (Irganox 4010), Bayer, Germany.

Preparation of Various Types of Thermoplastic Elastomers

HDPE and Irganox 1010 were mechanically mixed in Brabender Plasti-Corder PLE 360 at 160°C and 80 rot/min for 3 minutes, to melt the plastomer and mix it with the antioxidant. The temperature was decreased to 140°C and was added EPDM, PE-g-MA and Irganox 4010, continuing mixing at a speed of 100 rot/min for 4 minutes. Next, were added the crosslinking activators, ZnO (nano and micro) and stearic acid, at the same temperature and mixing speed, continuing mixing for 2 minutes. For the last

added constituent - peroxide, the rotation speed was increased (120 rot/min) and the temperature was decreased to 100°C. The total mixing time was 11-12 minutes. In the table 1 are shown the tested receipts. From the Brabender mixing diagrams, figures 1 and 2, it is seen that the temperature from mixing chamber does not change when adding compatibilizer and nanoZnO (starts from 90°C decrease to 72°C with a maximum of 233°C at the end), while for the mixing forces small changes are observed, the maximum force is when EPDM is added. The values are 144Nm for the control sample and 162Nm for N26 (nanocomposite with 75% ZnO nanopowder).

Table 1. Polymer nanocomposite recipes PE / PE-g-MA / EPDM / nanoZnO dynamically crosslinked with peroxide

| Materials/Symbol | N20 | N21 | N22 | N23 | N24 | N25 | N26 |
|------------------|-------|-------|-------|-------|-------|-------|-------|
| HDPE | 135 | 135 | 135 | 135 | 135 | 135 | 135 |
| Irganox 1010 | 2,7 | 2,7 | 2,7 | 2,7 | 2,7 | 2,7 | 2,7 |
| PE-g-MA | - | 1,35 | 4,05 | 6,75 | 4,05 | 4,05 | 4,05 |
| EPDM | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| Irganox 4010 | 1,8 | 1,8 | 1,8 | 1,8 | 1,8 | 1,8 | 1,8 |
| ZnO | 9 | 9 | 9 | 9 | 8,1 | 4,5 | 2,7 |
| ZnO nano | - | - | - | - | 0,9 | 4,5 | 6,3 |
| Stearic acid | 0,75 | 0,75 | 0,75 | 0,75 | 0,75 | 0,75 | 0,75 |
| Perkadox | 11,25 | 11,25 | 11,25 | 11,25 | 11,25 | 11,25 | 11,25 |

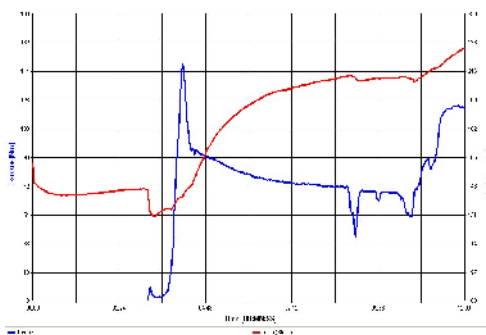


Figure 1. Brabender mixing diagram for the N20 composite control sample

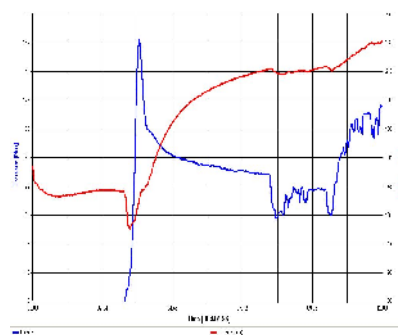


Figure 2. Brabender mixing diagram for nanocomposite with 75% ZnO nanopowders, N26

In order to establish the curing times, the samples were rheologically tested using Monsanto Rheometer with oscillating disc. From the data it is observed that ZnO nanoparticles do not influence the crosslinking time, diagrams are identical for the tests conducted, as demonstrated in figures 3 and 4.

The compound was then compression-molded (using an electrically heated hydraulic press at 170°C under 200 MPa pressure) into a sheet of about 2 mm thick. The sheet was then cooled down to room temperature under same pressure. The specimens were die-cut from the compression molded sheet and used for testing after 24 hours of storage at room temperature.

Polymer Nanocomposites PE / PE-g-MA / EPDM / Nano ZnO Dynamically
Vulcanized with Peroxide

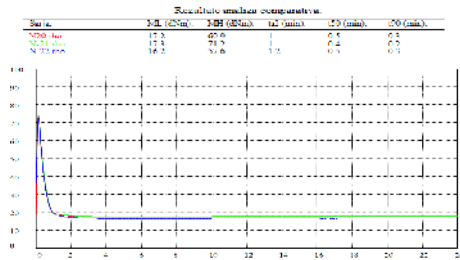


Figure 3. Overlapping rheogram for samples N20-N22

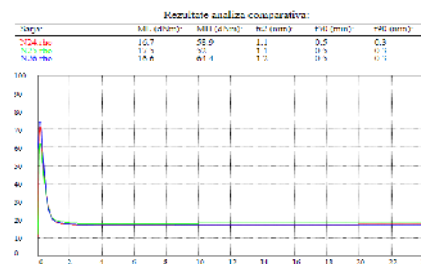


Figure 4. Overlapping rheogram for samples N24-N26

Apparatus for Physical-Mechanical Tests

Tensile tests of the samples were carried out in compliance to SR ISO 37:2012 using a Schopper Tensile Testing machine 1445, at a constant crosshead speed of 500 ± 5 mm/min.

Hardness of the samples was determined with Shore “A” Durometer, in compliance with SR ISO 7619-1:2011.

Attrition test is carried out with the *roll abrader*, in compliance with SR ISO 4649/2010, and the melt flow index with – Haake Meltflow MT.

RESULTS AND DISCUSSION

Physical-mechanical tests were carried out in the Investigation laboratory from INCDTP - Division ICPI, accredited by RENAR, and materialized in the determination of hardness, elasticity, tensile and tear strength, attrition, residual elongation and elongation at break for thermo-oxidative aging (168h x 100°C) and normal state, and melt flow index.

The hardness, for normal state, is 93°Sh A and increase to 94°Sh with the addition of ZnO nanoparticles. Thermo-oxidative aging increase the hardness value to 98°Sh A, which demonstrates that the curing process continues during processing. Peroxide crosslinking system creates more stable cross bridges between the polymer chains, which are harder to break under temperature action;

The tensile strength falls in the range from 9.6 to 10.5 N / mm², for normal state and 8.9 to 9.4 N/mm² after aging. The high values of this parameter are to be noted, values that are not found in classic rubber blends with the same hardness;

Nanostructuring of EPDM rubber in the polyolefin matrix and PE-g-MA compatibilization requires *elasticity* with increased values at high hardness, performance characteristic of these materials (Tables 2 and 3), maintaining its high values even after accelerated aging;

Tear strength is an index with performance values, maintaining the same values (102-105N/mm) due to tested elastic-plastic nanocomposites morphology (Tables 2, 3).

Table 2. Physical-mechanical characterization, normal state

| Symbol | N20 | N21 | N22 | N23 | N24 | N25 | N26 |
|---|------|------|-------|-------|------|------|------|
| Hardness °Sh A SR ISO 7619-1:2011 | 93 | 93 | 93 | 93 | 94 | 94 | 94 |
| Elasticity % ISO 4662:2009 | 22 | 21 | 22 | 22 | 22 | 21 | 20 |
| Tensile strength, N/mm ² SR ISO 37:2012 | 10.5 | 9.7 | 9.3 | 9.1 | 9.0 | 8.9 | 8.6 |
| Elongation at break, % SR ISO 37:2012 | 340 | 340 | 360 | 400 | 280 | 240 | 220 |
| Residual elongation, % SR ISO 37:2012 | 212 | 193 | 200 | 180 | 140 | 180 | 220 |
| Tear strength, N/mm SR EN 12771:2003 | 102 | 118 | 112.5 | 104.5 | 106 | 105 | 105 |
| Density, g/cm ³ , SR ISO 2781:2010 | 0.98 | 0.97 | 0.96 | 0.96 | 0.93 | 0.93 | 0.93 |
| Attrition, mm ³ , SR ISO 4649/2010 | 50 | 41 | 41 | 42 | 43 | 42 | 41 |

Table 3. Physical-mechanical characterization after thermo-oxidative aging for 168h at 70°C

| Symbol | N20 | N21 | N22 | N23 | N24 | N25 | N26 |
|---|-------|-----|-----|-----|-----|-----|-----|
| Hardness °Sh A SR ISO 7619-1:2011 | 98 | 98 | 98 | 98 | 98 | 98 | 98 |
| Elasticity % ISO 4662:2009 | 22 | 22 | 24 | 24 | 24 | 24 | 28 |
| Tensile strength, N/mm ² SR ISO 37:2012 | 9,4 | 9,1 | 8,3 | 9,6 | 9,1 | 8,9 | 9,0 |
| Elongation at break, % SR ISO 37:2012 | 453 | 345 | 380 | 460 | 420 | 460 | 540 |
| Residual elongation, % SR ISO 37:2012 | 227 | 210 | 220 | 240 | 140 | 214 | 340 |
| Tear strength, N/mm SR EN 12771:2003 | 127,5 | 127 | 118 | 111 | 107 | 105 | 116 |

CONCLUSIONS

The experiments pursued the obtaining and characterization of PE/PE-g-MA/EPDM/nanoZnO based polymeric nanocomposites, dynamically crosslinked with peroxide.

The technology for obtaining the elastic-plastic polymer nanocomposites with variable content of ZnO nanoparticles has the advantage of simultaneously crosslinking and processing the elastomer in the plastic melt, HDPE respectively. The nanostructured polymeric materials obtained are blends with the structure of plastic in which crosslinked EPDM elastomer and ZnO nanoparticles are dispersed, and can find the appropriate applications for their advanced properties, substituting existing products made from different rubbers and plastics, offering significant economic benefits to companies. In addition to high temperatures resistance, these materials are anti-microbial, characteristic to be tested biologically.

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REFERENCES

- ASTM D 5046 – 98: "Standard specification for Fully Crosslinked Elastomeric Alloys".
ASTM D 5593 – 99: "Standard Classification for Thermoplastic Elastomers-Olefinic (TEO)".
Borcea, V. (2008), "Radioactive ion implantation of thermoplastic elastomers", Presses univ. de Louvain.
Coran, Y., Das, B. and Patel, R.P. (to Monsanto Co.) (1978), U.S. Patent 3,130,535.
Ellul, M.D., Tsou, A.H. and Hu, W. (2004), "Crosslink densities and phase morphologies in thermoplastic vulcanizates", *Polymer*, 45(10), 3351-3358.
Emamifar, A., Kadivar, M., Shahedi, M. and Soleimani-Zad, S. (2010), "Evaluation of nanocomposite packaging containing Ag and ZnO on shelf life of fresh orange juice", *Innovative Food Science & Emerging Technologies*, 11(4),742-748;
Fisher, W.K. (to Uniroyal, Inc.) (1973) U.S. Patent 3,758,643.
Gessler, M. and Haslett, W.H. (to Esso Research and Engineering Co.) (1962), U.S. Patent 3,037,954.
Harrats, C., Thomas, S. and Groeninck, G. (2006), *Micro- and Nanostructured Multiohase Polymer Blend Systems*, Taylor and Francis Group, LLC;
Ito, E.N., Hage, E., Jr., Mantovani, G.L. *et al.* (2003), "Development of phase morphology for extruded and moulded PBT/ABS blends", *Proceedings of the 19th Annual Meeting of the Polymer Processing Society* PPs-19, Melbourne, CD, S2, 259, 1-5.
Kim, H.J., Pant, H.R., Park, C.H., Tijing, L.D., Hwang, B.S., Choi, N.J. *et al.* (2013), "Electrical Properties of ZnO/NYLON-6 Spider-Wave-Like Nanonets Prepared via Electrospinning". *Digest Journal of Nanomaterials and Biostructures*, 8(1), 385 – 393.
Koo, J. (2006), *Polymer Nanocomposites. Processing, characterization and applications*, McGraw-Hill Nanoscience and Technology Series, Companies, Inc.
Lebel, M.A. (1994), "Factors fueling the growth of thermoplastic elastomers", *Plastics Engineering*, 50(1), 23-26.
Rane, A.V. and Abitha, V.K. (2015), "Study of Mechanical, Thermal and Micro structural Properties of EPDM/Polypropylene/Nano clay Composites with Variable Compatibilizer Dosage", *Journal of Materials and Environmental Science*, 6(1), 60-69.
Thostenson, E., Li, C. and Chou, T. (2005), "Review Nanocomposites in Context", *Journal of Composites Science & Technology*, 65, 491–516. (Reproduced in part with permission from Elsevier, 2006).