Polymer Structures Based on Dynamically Cured Plastomer/Elastomer

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At global scale, the trend of developing new thermoresistant polymeric structures, obtained from a mixture of dynamically cured elastomer/plastomer, and compatibility and curing agents, broadens their area of application and leads to greening of their processing technology and qualitative performance. Through dynamic curing and compatibilization, the elastomeric particles disperse more readily in the mixture thus making it possible to develop new innovative materials and techniques. Polymer structures were obtained by extrusion granulation technology, tested physico-mechanically (hardness, elasticity, tensile strength) according to current standards and morphologically by electron microscopy (SEM).

Key words: polymeric structures, terpolymer rubber, polypropylene, dynamic vulcanization

Processing natural and synthetic elastomers involves the use of numerous auxiliaries with a clearly defined role and influence on the properties of finished products or on their cost. To obtain products with predetermined physical-mechanical properties, depending on their purpose, it is necessary to use fillers and structuring agents of different types and concentrations [1, 2].

Fisher first introduced the technique of dynamic curing of rubber dispersed in thermoplastic, while Coran and his collaborators have improved this process, and other researchers have shown that dynamic curing can optimize various properties such as tensile strength, high temperature resistance, etc. [3-5]. The new dynamically cured polymer structures based on plastomers/elastomers/ compatibilizer/curing agents ensure quality performance and greener development technology, meeting the current quality and aesthetics requirements for the footwear industry [6-8].

The practical value of such a material consists in the properties that it encompasses, that may be grouped into categories that are inextricably interdependent: fundamental properties; processing features or technology; operational or use characteristics [9].

In order to develop dynamically cured polymer structures experiments have been performed using elastomers with enhanced properties, ethylene-propylene-diene-terpolymer rubber (EPDM), and polypropylene (PP), made compatible with polypropylene-graft maleic anhydride (PP-g-MA), using an average curing agent specific to the type of elastomer, such as: sulfur (S), tetramethyl thiuram disulfide (TH), diphenylguanidine (D) [10-18]. The granules obtained by extrusion-granulation can be processed into finished products by injection molding. Depending on the properties, the granules can be used to make products for the footwear industry, consumer goods and other important areas of the economy [19-21].

The paper presents the technology for developing dynamically cured polymer structures using the extrusion-granulation technique, determining flow indices to establish operating parameters for finished products, making specimens by pressing and testing them physico-mechanically and morphologically by scanning electron microscopy.

Experimental part

Materials and methods

- polypropylene (PP - Hungary) - Tipplen K 948 (polypropylene impact copolymer, melt mass-flow rate (MFR) (230°C/2.16 kg) – 45 g/10 min; processing (melt) temperature – 190° to 240°C);

- ethylene-propylene-diene-terpolymer rubber (EPDM – DuPont,USA) - 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%);

- polypropylene-graft-maleic anhydride (PP-g-AM - Germany) – (average Mw~9.100 by GPC, average Mn~3,900 by GPC, maleic anhydride 8-10 Wt);

-sulfur (S - Romania) - Vulcanization agent (fine yellow powder, insoluble in water, melting point: 115°C, faint odor);

-tetramethylthiuram disulfide (TH - Bayer) – curing agent (density 1.40 g/cm, melting point <146°C, an ultrafast curing accelerator);

-diphenylguanidine (D - Bayer) – curing agent (slow curing accelerator, density 1.19 g/cm , Tt>145).

- Polymer structures (table 1) based on plastomer/ elastomer/compatibilizer/curing agents were made using a counter-rotating twin screw extruder granulator, TSE 35 – (Cheng Yieu Development Machinery Co., Ltd. China), resulting in a granular product with diameter and length of 3mm. Polypropylene is introduced at 150°C and 150-200 rotations/min and mixed until it becomes easy to process, then temperature is increased to 175°C, EPDM and PP-g-MA are added and mixed at 250-280 rotations/min, with the following temperatures in the 9 areas zone: 155-160-170-175-175-175-160-150-170°C and parameters kept constant until the mixture is homogenous, and then curing agents are introduced, maintaining the same parameters. The mixture is granulated through a die, as a string, cooled in a water bath fitted with a pull tape that directs the material entering the drying chamber with hot air and packed to be transported.

- The resulting granules are introduced in molds, according to samples used for physical-mechanical characterization, using an electrically heated press, TP 600 (Fortijme Grotness, Netherlands), by compression method,

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at pressure of 150KN and the temperature of 165°C, preheating time 2, 10 min pressing and 10 minutes cooling with water, figure 2.

- Polymer structures have been tested physico-mechanically: hardness ^{0}Sh D - SR ISO 7619-1:2011; elasticity, %, ISO 4662:2003; tensile strength, N/mm^2, ISO 37:2012.

- SEM analysis was performed using the QUANTA INSPECT F scanning electron microscope (Netherlands), equipped with a field emission gun - FEG with 1.2 nm resolution and energy dispersive X-ray spectrometer (EDS) with MnK resolution of 133 eV.

-The Melt flow index (MFI) was determined on a THERMO- HAAKE 2000 MeltFlow (Thermo electron Corporation, Germany), can operate in a wide temperature range (max. 300°C), and pressing forces 1.8 at 21 kg. To determine melt flow indices using HAAKE MELTFIX 2000, working parameters are set using the device's software. Characteristics and parameters of tested materials are: type of material, colour, required amount, work temperature, pressing weight, preheating time, value reading interval, cutting time. After all parameters have been set, the work temperature is 175°C, a 5 kg load, for samples considered, the material to be tested is introduced in a vertical steel cylinder and thus, the material is extruded (capillary rheometer) through a die using a piston loaded with weights. The maximum amount of input material is 6 g. All the samples were prepared according to ISO 1133/2003.

The technology of developing dynamically cured polymer structures based on plastomer/elastomer/compatibilizer/curing agents (PP/EPDM/PP-g-MA/curing agents), specific for soles and footwear components is schematically illustrated in figure 1.

Results and discussions

Physical-Mechanical Tests

Figures 3-5 show results of physical-mechanical results in normal state and after accelerated ageing at 70°C for 168h of dynamically cured polymer structures based on plastomer/elastomer, after conditioning for 24 h at the temperature 20±2^{0}C.

The hardness of polymeric structures based on PP/EPDM decreases compared to the reference sample, PP. The addition of elastomer in variable proportions leads to its decrease (3-6°Sh D) proportionally with the increase in the amount of elastomer (EPDM) and PP-g-MA compatibilizer, and after accelerated aging at 70°C for 168 hours, there are small increases in hardness, of a few °Sh D, of samples, because as a result of this process the plasticizing degree is reduced.

As a result of crosslinking polymer structures with curing agents a slightly higher elasticity is observed compared to the control sample, which demonstrates a homogeneous crosslinking with stable sulfur bridges. After accelerated

Sample code							
Material	UM	M_{1A}	M_{2A}	M_{3A}	M_{11A}	M_{21A}	M_{31A}
PP	%	90	70	50	90	70	50
EPDM	%	10	30	50	10	30	50
PP-g-MA	%				5	5	5
S	%	1.5	1.5	1.5	1.5	1.5	1.5
TH	%	1	1	1	1	1	1
D	%	0.5	0.5	0.5	0.5	0.5	0.5

Table 1
FORMULATIONS OF POLYMER STRUCTURES BASED ON PP/EPDM/CURING AGENTS, PP/EPDM/PP-g-MA/CURING AGENTS

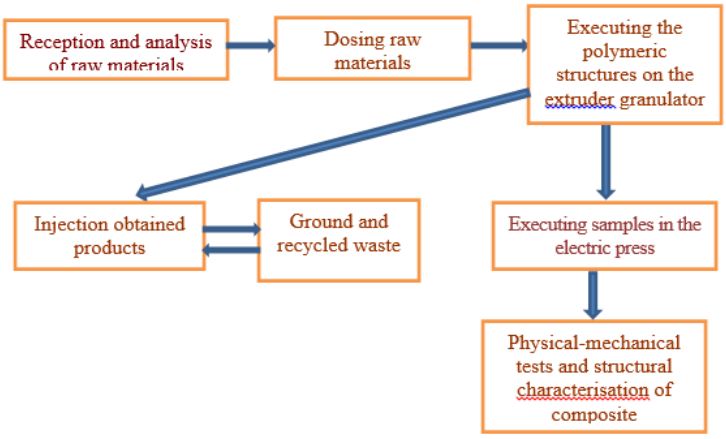


Fig. 1. Steps of the technologic process for developing polymer structures based on PP/EPDM/PP-g-MA/curing agents

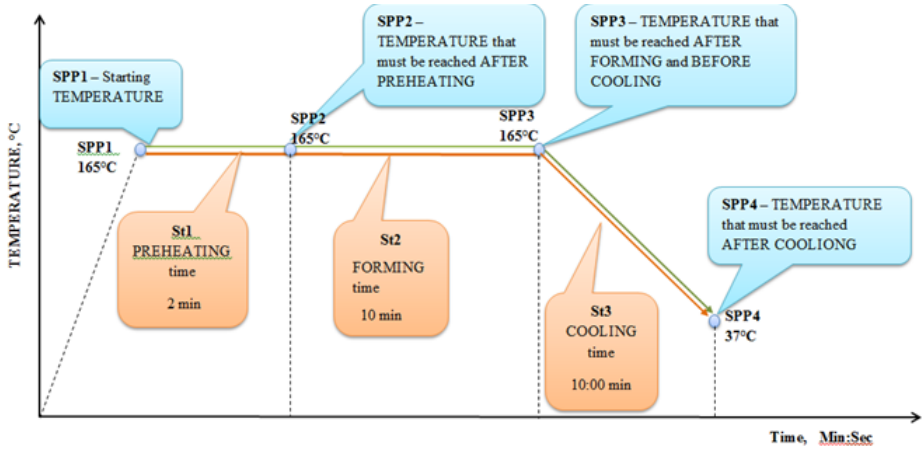


Fig. 2. Optimum temperature program for the electric press

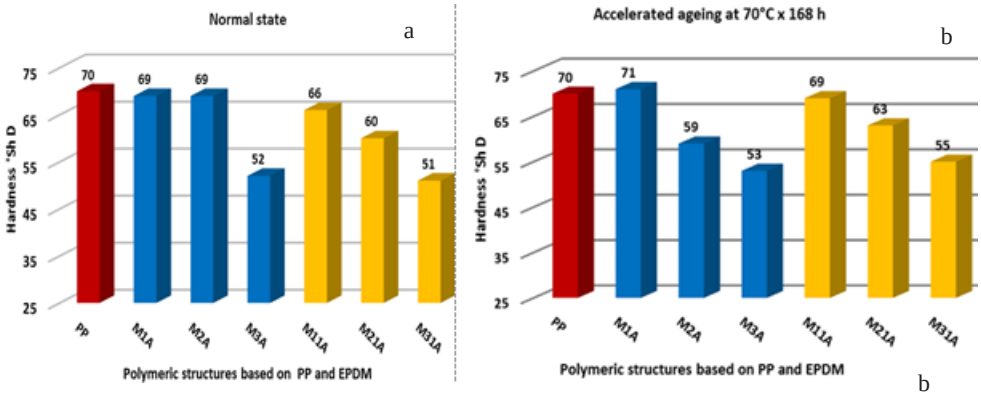


Fig. 3. Hardness of polymer structures based on PP/EPDM/ PP-g-MA/accelerators (a – normal state, b – accelerated ageing)

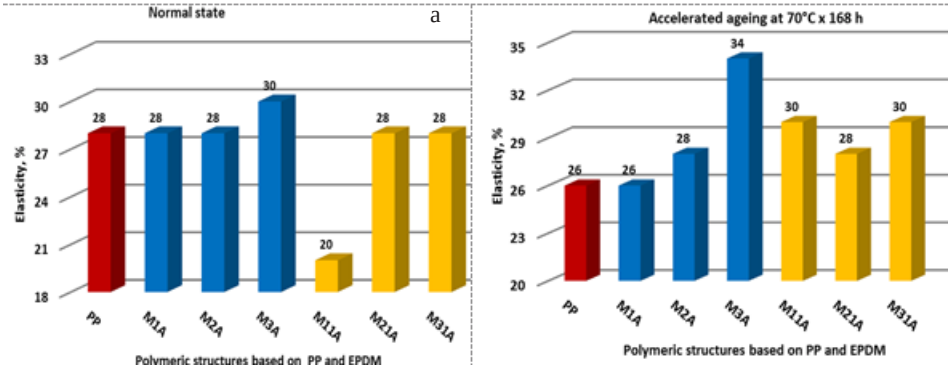


Fig. 4. Elasticity of polymer structures based on PP/EPDM/PP-g-MA/accelerators (a – normal state, b – accelerated ageing)

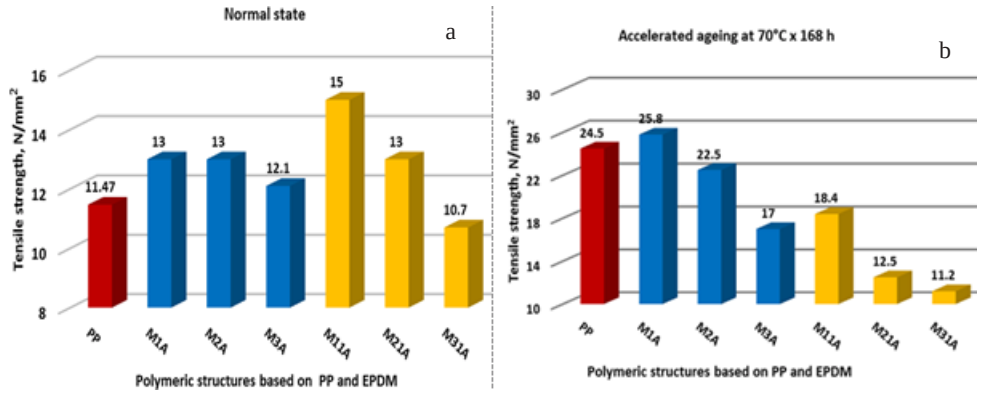
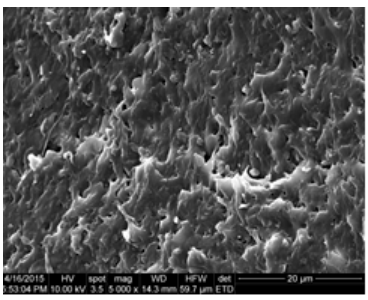
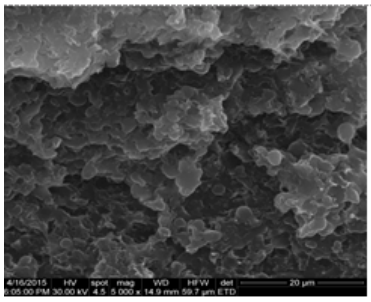


Fig. 5. Tensile strength of polymer structures based on PP/EPDM/PP-g-MA/accelerators (a – normal state, b – accelerated ageing)



x5000

Fig 6. SEM image of the sample M_{3A} – PP/EPDM/ accelerators (x5000)



x5000

Fig. 7. SEM image of sample M_{31A} – PP/EPDM/ PP-g-MA/accelerators (x5000)

aging at 70°C for 168 h, the elasticity increases by 2-4 percent.

The values of tensile strength of polymer structures in the normal state range between 10.7 N/mm^2 and 15 N/ mm^2, which shows a good compatibility with PP-g-MA. After the accelerated aging, because we have different percentages of elastomer and curing agents, tensile strength significantly decreases compared to PP.

Scanning Electron Microscopy:

The samples were tested morphologically by scanning electron microscopy, recording SEM images of samples M_{3A} and M_{31A}. Figures 6 and 7 present SEM images recorded for the fracture surface. Samples were coated with gold film and fracture surface images were recorded to highlight the uniformity of polymer structures after the dynamic curing process, and the degree of dispersion of the EPDM in PP.

The SEM fracture image of the M3A sample shows that the new material has a heterogeneous appearance with different areas of rubber and plastic, chaotically distributed.

The image of figure 7, of the polymer material consisting of PP/EPDM/PP-g-MA/accelerators, shows the presence of compatibilizer, through the homogeneity of the mixture composed of two phases (rubber and plastic) and vulcanization agents in the form of small particles uniformly dispersed in the mixture. PP-g-MA leads to the uniform dispersion of EPDM in the plastomer matrix, demonstrated by the disappearance of the two distinct phases. Curing agents are dispersed in the mixture, their role being to cure EPDM in the stage of processing the mixture into finished products by injection at the specified temperatures of the curing process.

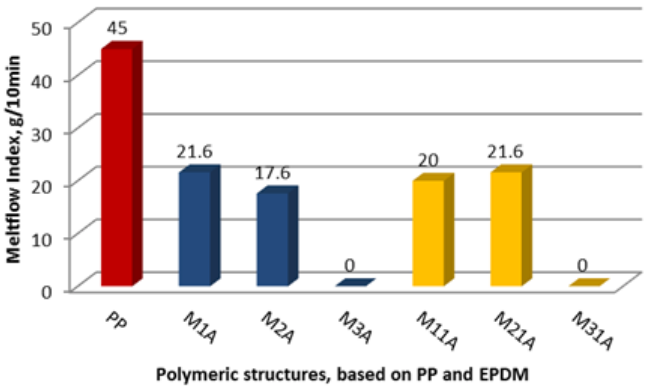


Fig. 8. Melt flow index values for polymer structures based on PP/EPDM/PP-g-MA/accelerators (M_{1A}, M_{2A}, M_{3A}, M_{11A}, M_{21A}, M_{31A})

Melt Flow Index

Melt flow index values resulting from testing the polymer structures are presented in figure 8.

Polymer structures have different characteristics and properties, such as density, hardness, etc. Determination of flow indices was performed at a temperature of 175°C and downforce 5 kg. The more viscous the materials, the greater force they require to be extruded through the MFI die. Flow index has a direct impact on the process used to manufacture the finished product, in that it specifies the work parameters: temperature, pressure and processing time.

According to the chart shown in figure 8, it is noticed that the flow index of tested polymer composites is strongly influenced by work temperature, the amount of elastomer introduced into the mixture and the compatibilizer. Flow index values decrease significantly (no flow - M_{3A} and M_{31A}) proportionally to the amount of EPDM added, due to increased melt viscosity. Thus, the process is controlled by the correlation that exists between basic properties of the new polymer structures and technological process parameters.

When the flow index decreases, flow properties and surface of materials change significantly. The polymer structures with high flow index are used for injection molding, and those with a lower flow index are processed by pressing.

Conclusions

Polymeric structures based on plastomer/elastomer, compatibilizer and curing agents (PP/EPDM/PP-G-MA/vulcanizing agents) were obtained using specific equipment for the rubber and plastics processing industry and the extrusion-granulation, mixing and compression/injection technologies. Physical and mechanical test results demonstrate a homogeneous crosslinking with curing agents and good compatibility with PP-g-MA. Scanning electron microscopy of polymeric structure without compatibilizer shows a heterogeneous dispersion with different areas of rubber and plastic, chaotically distributed. The image of the polymeric material made of PP/EPDM/PP-g-MA/accelerators shows the compatibilizer, through the homogeneity of the mixture consisting of two phases and the curing agents in the form of small particles uniformly dispersed in the mixture. By determining the indexes, parameters may be established, especially for finished products processed by injection. The polymer structures with high melt flow index are used for processing by injection, while those with lower melt index for extrusion processing. Polymer composites based on dynamically cured PP/EPDM/PP-g-MA/curing agent are suitable for applications in the footwear industry, for consumer goods and other important areas of the economy.

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