OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 5, May 2010, p. 722 - 725

Correlation of chemical composition and microstructure with technical properties of an elasto-plastic composite material

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The behaviour of some microstructured polymers obtained under dynamic vulcanization conditions in a pilot reactor containing a mixture of EPDM rubber and high density polyethylene (HDPE) at various elastomer/plastic polymer weight ratios in the presence of sulphur (system I) and peroxides (system II) as cross-linking agents was studied. We correlated the swelling in the solvent and the thermal properties with the chemical composition and microstructure of the polymer. The results are very useful in choosing the appropriate utilisation of these polymer mixtures in various industrial domains.

(Received May 04, 2010; accepted May 20, 2010)

Keywords: EPDM (ethylene-propylene-dien monomer) rubber, Polyethylene, Microstructure, Swelling, Thermal analysis

1. Introduction

The obtaining of micro and nanostructured polymer materials with particular characteristics is one of the scientific and technological development priorities. The required properties depend on the elastomer type and micro-structuring level of elastomer inside the thermoplastic material, as well as on the particle size, nature of thermoplastic material, elastomer/plastomer ratio etc. the existing polymeric materials (requiring no existing investment for their synthesis) and applied procedures can be combined to obtain new composite products corresponding to the quality standards imposed by the economic manufacturers and customers. These new technologies require no high cost investment and can be rapidly integrated.

The elastomer microstructure is simultaneously achieved by choosing thermoplastic and elastic polymer with adequate macromolecular chain type and unsaturaton level during the dynamic vulcanization process. Elasto-plastic structure and elastomer micro-structuring of the resulting composites impart high performance characteristics, such as: processing behaviour similar to thermoplastic materials, low density, high tensile strength, high elasticity as pure rubber, very low abrasive wear, high resistance to atmospheric and thermo-oxidative ageing, high strength to breaking, tear and impact, chemical resistance, etc. [1-3]. Taking into account the above characteristics, such composite materials are recommended for practical applications of medium and long life in the footwear domain (manufacture of soles, heels, protective boots) as well as in other industrial domains (conveyer belts, air-tighten fittings for windows, pipe coatings, hoses etc.) [4-8].

In this paper we correlated the behaviour of some micro-structured polymers (EPDM-HDPE) obtained in dynamic vulcanization conditions with their microstructure and chemical composition.

2. Materials and methods

2.1 Materials

The elastomer in the mixtures was *Nordel IP 3745P* type (DuPont) with chemical composition: 70% ethylene, 29.5% propylene, and 0.5% ethylene-norborene and the polyethylene *HDPE B 084* type (Hostalen). We used 5 phr paraffin to achieve compatibility between EPDM and HDPE and 1 phr Irganox as stabilizer. Two different systems were used to crosslink the blend: mixture I consisting in sulphur (S, 2phr), tetramethylthiuram (Th, 1 phr), 2-mercaptobenzthiazole (M, 0.5 phr), ZnO (0,5 phr) and a peroxide system II (benzoyl peroxide, BP, 3 phr). The elastomer was crosslinked in a pilot reactor within the plastic polymer melt (HDPE) at various elastomer/plastic polymer ratios: 75/25 50/50 and 25/75 (w/w).

2.2 Methods

2.2.1 Characterization of the crosslinked polymer mixtures

The chemical resistance to oil products was assessed by measuring the weight change during immersion in three solvents. Rectangular test coupons with 20x20x2 m dimensions were immersed separately in organic solvents (Merck): benzene, p-xylene and carbon tetrachloride.

Measurements were carried out for immersion time of 1, 2, 3, 24, 48 and 72 h at 20°C temperature. Mass changes have been expressed as swelling degree:

$$G_M = \frac{G_f - G_0}{G_0} \tag{1}$$

where G_f is the weight after immersion in solvent and G_0 the initial weight.

The thermo-oxidative behaviour ot he polymer mixtures was investigated by a MOM/TGA V5 1[a] (DuPont) derivatograph, working in atmosphere within 20-750° temperature range at a heating rate of 10°/min.

Scanning Electronic Microscopy (SEM) was perfoemed on a Philips XL-30 E-SEM Turbo Molecular Pump (TMP) at 20 keV equipped with an EDX detector UTV-Saphire. The analyzed surface was a section of the fractured test coupons.

3. Results and discussion

3.1 The behaviour of microstructured composite polymers during the immersion in organic solvents

We have previously shown [6] that EPDM elastomer increases its mass about two times after one hour immersion either in benzene or in carbon tetrachloride; thereafter it was completely dissolved in both solvents. In contrast, the high-density polyethylene (HDPE) has shown a low swelling kinetics in all three solvents. Thus, the mass increase has values of maximum 2% after 3 hours in benzene and 14.05% after 72 hours in carbon tetrachloride, respectively. The results of present investigation about swelling behaviour of composite polymers obtained with three weigth ratios of EPDM and HDPE (75/25, 50/50 and 25/75) using two crosslinking systems (I with sulphur and II with peroxide) are presented comparatively in Figs. 1-3.

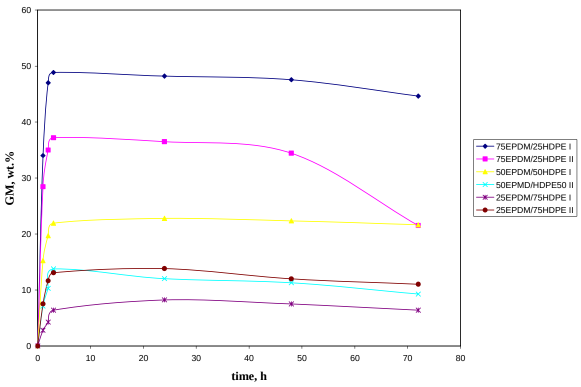

Fig. 1. Swelling degree versus time for EPDM/HDPE in benzene.

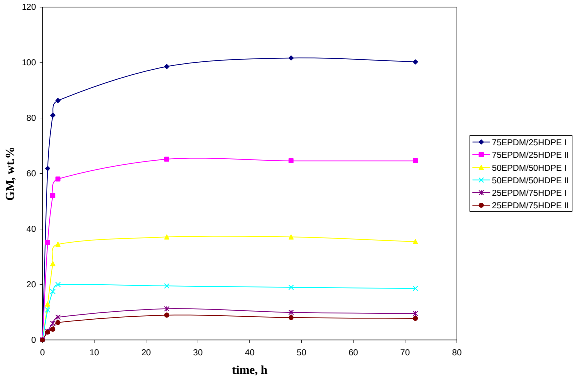

Fig. 2. Swelling degree versus time for EPDM/HDPE in p-xylene.

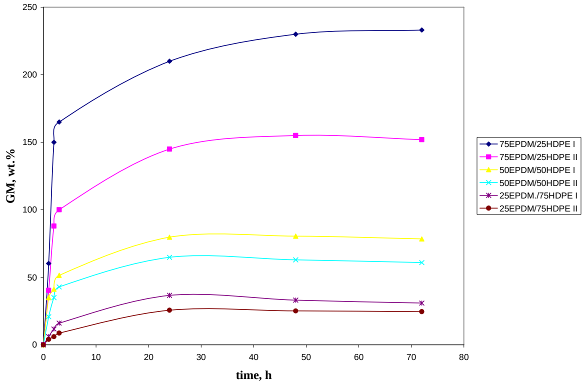

Fig. 3. Swelling degree versus time for EPDM/HDPE in carbon tetrachloride.

The swelling of the polymer crosslinked mixtures increases rapidly after 1-3 hours of contact with the solvents and than attains equilibrium value. This value depends on the nature of the solvent, on the ratio EPDM/HDPE and on the crosslinking system. The swelling limit decreases in the order CCl_4>p-xylene>benzene (for the same composition and the same crosslinking system) in accordance with the values of Hildebrand solubility parameter δ (Table 1) because it is known that the compatibility of the system solvent-polymer decreases with the increase of the difference $\delta_{solvent}-\delta_{polymer}$.

Table 1. Hildebrand solubility parameter [9]

Solvent	δ, $(cal/cm^3)^{1/2}$
Benzene	9.2
p-Xylene	8.85
Carbon tetrachloride	8.6
Ethylene	8.0
Propylene	9.3

For the same solvent the swelling limit drecreases with the increase of the ratio HDPE/EPDM according to the δ values for ethylene and propylene (Table 1).

Generally, the swelling values G_M for the composite polymers crosslinked with peroxides are lower than those crosslinked with sulphur and accelerators. The crosslinked polymer with peroxide has a higher density than the polymer vulcanized with sulphur and accelerator because the length of the bridges formed with peroxide is shorter than the bridges obtained with sulphur.

3.2 Thermogravimetric analysis of the microstructured composite polymers

Composite polymers consisting in EPDM/HDPE 50/50 ratio and microstructured by crosslinking either with sulphur and accelerators or with peroxides were investigated for their thermal stability by performing the thermogravimetric analysis; the results are shown in figure 4.

The composite polymer crosslinked with peroxide (II) has a better thermal stability than the polymer vulcanized with sulphur (I) up to 450°C but the temperature for total thermal degradation is about the same for both crosslinking systems: 595°C for I and 585° for II.

Generally, we can consider that both crosslinking systems I and II impart a high thermal stability (up to 300°C) for the composite polymer EPDM/HDPE 50/50.

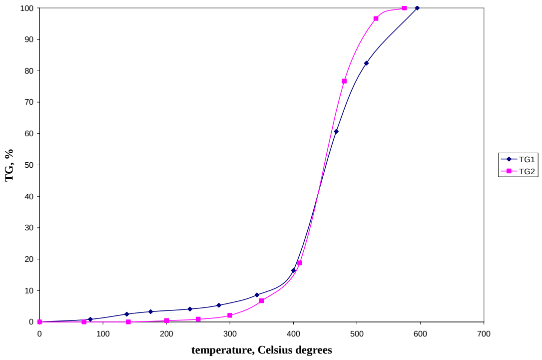

Fig. 4. TGA curves for EPDM/HDPE 50/50 crosslinked with sulphur (TG1) and peroxide (TG2).

3.3 SEM analysis of crosslinked polymer composites

SEM images of the surface for the fracture test coupons with composition EPDM/HDPE, 50/50 are presented in the Figs. 5-8. In the Fig. 5 (EPDM) and 6 (HDPE) the polymer is not structured. In the Fig. 7 EPDM vulcanized with sulphur (system I) forms microstructures (2-4 µm) in the mass of the mixtures. In the Fig. 8 the peroxide system can crosslink both EPDM and HDPE so the EPDM structures are more uniform dispersed in the mass of the mixture and that explains some differences in properties of vulcanized mixtures EPDM/HDPE even with the same chemical composition.

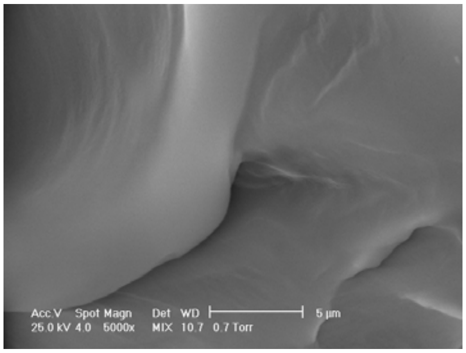

Fig. 5. SEM microphotographs for EPDM.

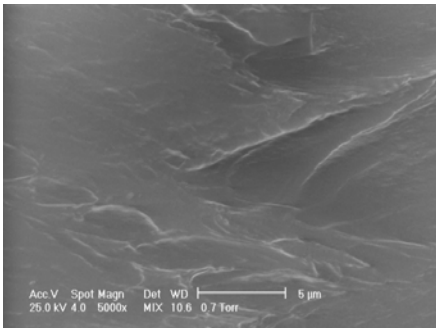

Fig. 6. SEM microphotographs for HDPE.

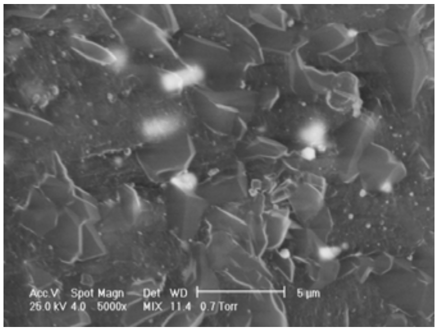

Fig. 7. SEM microphotographs for EPDM/HDPE 50/50 mixtures vulcanized with system I (sulphur and accelerators).

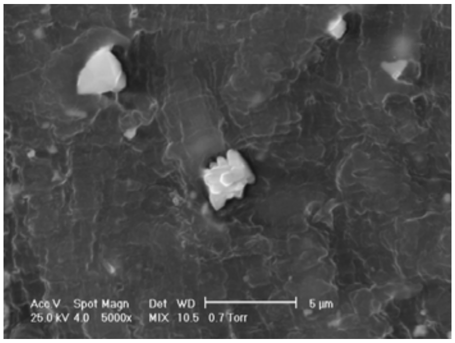

Fig. 8. SEM microphotographs for EPDM/HDPE 50/50 mixtures vulcanized with system II (peroxide).

4. Conclusions

The results show that it is possible to obtain en elasto-plastic material from EPDM and HDPE micro-structured by dynamic vulcanization. Polymer material crosslinked with peroxide has shown a lower swelling than the mixture vulcanized with sulphur and accelerators, so such a material can be used in aggressive media. The crosslinked EPDM/HDPE mixture with peroxide has a better thermal stability in the range 0-350°C than the same mixture vulcanized with sulphur and accelerators.

References

[1] S. C. Artego S. A., Romania, RO Patent No. 118018 B1/2001.
[2] Societé de vente de l'aluminium Pechiney, Paris, France, RO-BOPI Patent No. 91266/1998.
[3] S. C. Artego S. A., Romania, RO Patent No. 117022 B1/1999.
[4] S. Visan, V. Ciobotaru, F. Ionescu, P. Budrugeac, C. Ghica, Materiale Plastice **40**(3), 177 (2005).
[5] S. Visan, V. Ciobotaru, F. Ionescu, C. Ghica, Materiale Plastice **43**(2), 77 (2006).
[6] S. Visan, V. Ciobotaru, F. Ionescu, A. Anghelescu, Materiale Plastice **45**(1), 80 (2008).
[7] A. Y. Coran, L. Lee, Rubber Chem. Technolo. **65**, 231 (1992).
[8] R. C. Puydak, Elastomeric Alloys, Meeting of the Rubber Division, American Chemical Society, Nasjville-Tennessee, Nov. 3-5, 1992.
[9] J. Brandrup, E. H. Immergut, Polymer Hnadbook, Third Edition, John Wiley and Sons, 1989.

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