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Advanced Materials Based on Ethylene-Propylene-Diene Terpolymers and Organically Modified Montmorillonite

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***Abstract*—**This paper presents studies on the development and characterization of nanocomposites based on ethylene-propylene terpolymer rubber (EPDM), chlorobutyl rubber (IIR-Cl) and organically modified montmorillonite (OMMT). Mixtures were made containing 0, 3 and 6 phr (parts per 100 parts rubber) OMMT, respectively. They were obtained by melt intercalation in an internal mixer - Plasti-Corder Brabender, in suitable blending parameters, at high temperature for 11 minutes. Curing agents were embedded on a laboratory roller at 70-100 ºC, friction 1:1.1, processing time 5 minutes. Rubber specimens were obtained by compression, using a hydraulic press at 165 ºC and a pressing force of 300 kN. Curing time, determined using the Monsanto rheometer, decreases with the increased amount of OMMT in the mixtures. At the same time, it was noticed that mixtures containing OMMT show improvement in physical-mechanical properties. These types of nanocomposites may be used to obtain rubber seals for the space application or for other areas of application.

***Keywords*—**Chlorobutyl rubber, ethylene-propylene-diene terpolymers, montmorillonite, rubber seals, space application.

I. Introduction

POLYMER nanocomposites based on layered clay have attracted interest in both fundamental research and industrial applications by presenting a combination of properties that their components alone or classical composites do not have. Compared to the initial polymer blend, these nanocomposites show improvements in mechanical and rheological properties, chemical stability, etc. [1]. All these advantages are obtained by introducing a small amount of layered clay nanofiller (less than 7% by weight). The most commonly used clay for the production of nanocomposites is montmorillonite. In order to achieve a nanometric dispersion of clay in the polymer matrix, the clay is modified with alkyl ammonium or phosphonium salts, which allow the surface polarity to be changed and the distance between the clay layers to be increased. In this way, the clay can be easily dispersed in the polymer matrix forming nanocomposites with interlaced structure (where the polymeric chains penetrate the clay layers aggregated into particles) or exfoliated structure (in which nanometer-sized clay layers are dispersed in the polymer matrix). Interlacing and exfoliation of clay is the most important phenomenon, influencing the improvement of the rheological and physico-mechanical properties of rubber-clay nanocomposites.

Obtaining clay-based elastomeric nanomaterials is similar to traditional rubber materials and is a very complex process that can be influenced by several factors such as: number of rotations during mixing, working temperature, mixing time, the order of adding ingredients to the mixture, etc. [2]-[4].

This paper presents our studies on the influence of introducing an OMMT into a compound based on EPDM and IIR-Cl. The first is a non-polar, saturated rubber (very low C = C content) and has several properties, including very good resistance to aging and chemical agents, mechanical properties, low cost etc. [5], [6]. The second, IIR-Cl, is a polar elastomer due to the existence of chlorine, with good compression strength, good mechanical properties, and can be combined with other elastomers [7]. In order to obtain elastomeric materials with good characteristics, it is necessary to have a good interaction among elastomers, fillers/nanofillers and other ingredients, suitable proportions of the components, the correct order of adding ingredients, suitable equipment for making the composites, and optimal work parameters to ensure high quality elastomeric (nano)materials. This paper will analyze the changes in the processing, rheological and physico-mechanical characteristics of an EPDM/II-Cl mixture by introducing OMMT.

II. Experimental Part

A. Materials

Materials used in the study:

- EPDM: Keltan 3960Q (Mooney viscosity 25 ML_{1+4} at 125 °C, ethylene content of 53% and 5-ethylidenenorbornene (ENB) content of 6 wt %, density 0.86 g/cm^3) and Keltan 2650 (Mooney viscosity 54 ML_{1+8} at 100 °C, ethylene content of 56% and ENB content of 11 wt %, density 0.86 g/cm^3) in a ratio of 2:1
- *II-Cl*: Lanxess X Butyl Cb 1240 Disp. (Mooney viscosity 38 ML (1 '+ 8') 125 °C, chlorine content 1.25%, ash content of 0. 5%, density 0.92 g/cm^3
- *Layered clay* - OMMT produced by Nanocor: Nanomer I44P - clay is organically modified using dimethyl dialkyl (C_{14}-C_{18}) (34-45%), particle size 14-18 microns, density

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1,9 g/cm^3

- *Compatibilizer*: polyethylene graft maleic anhydride (PE-g-AM) Bonyram TL 4109-E from Polyram, Israel (density 0,905 g/cm^3, MFI 2g/10' at 190°C with a 2.16 kg force)
- Precipitated silica: Egesil BM30, Turkey, with specific surface 155-195m^2/g, SiO_2 content over 98%, to which plasticizer was added di(butyl diglycol) adipate Alcanplast 188 (1.0236 g/cm^3 density)
- Polyethylene glycol PEG 4000 – produced by Advance Petrochemicals Ltd. (density 1.128 g/cm^3, melting point 4-8 °C).
- Antioxidant 2,2,4 trimethyl 1,1, dihydroquinone (TMQ) in the form of dark coloured granules (density 1,1 g/cm^3, melting point 85 °C) (produced by Interquimica Comercio e Industria de Produtos Quimicos Ltd)
- For crosslinking blends, the following were used: 1,3 1,4-Bis(tert-butylperoxyisopropyl) benzene Luperox F40P (3.45% active oxygen content, 40% peroxide content) and polyfunctional monomer trimethylolpropane trimethacrylate Alcanpoudre TMPTMA 70 (TMPT) (70 % active ingredient);
- Other ingredients: premium quality zinc oxide, stearin

B. Developing (Nano)Composites

TABLE I
FORMULATIONS

Ingredients	Mixture symbol		
	P10 (phr)	O3P10 (phr)	O6P10 (phr)
Internal mixer			
EPDM Keltan 3960Q	60	60	60
EPDM Keltan 2650	30	30	30
IIR-Cl Butyl CB 1240 DISP	10	10	10
Filler - Egesil BM30	50	50	50
Plasticizer - Alcanplast 188	10	10	10
ZnO	5	5	5
Stearin	2	2	2
PEG 4000	3	3	3
Antioxidant TMQ	2	2	2
OMMT Nanomer IP44	-	3	6
PE-g-AM Bonyram TL 4109-E	-	3	3
Laboratory two-roll mill machine			
Peroxide -Luperox F40P	8.0	8.0	8.0
TMPT-Alcanpoudre TMPTMA 70	3	3	3

(Nano)composites were developed using the melt intercalation method using a Brabender internal mixer to obtain semi-products in the form of rubber mixtures. Formulations are presented in Table I. The order of adding ingredients was the following: elastomers and compatibilizer are plasticised for 3' at 80 rotations/min, the nanofiller and the other ingredients are embedded for 4' at 30 rotations/min and then the mixture is homogenized for 4' at 120 rotations/min (see Fig. 1 and Table II). Curing agents were introduced by processing on an laboratory two-roll mill machine with heating-cooling system at: 70 – 100 ºC, 5 min and a friction of 1:1,1. The test specimen sheets of all compounds were obtained by compression, using a hydraulic press at 165 ºC and a pressing force of 300 kN. Optimum cure time is determined by means of the Monsanto rheometer (see Table III).

C. Laboratory Tests

Curing tests were performed according to ISO 3417/2008, with the following parameters: temperature 165 °C and time 12 min. In order to determine the optimum curing time, the delta torque is required. The determination method of this parameter is by subtracting of the minimum torque (ML) value from the maximum torque (MH) value. Optimum cure time (T_{90}) represents the necessary time to reach 90% of the delta torque. Scorch time (T_{s2}) represents the time needed to reach 2% of the delta torque. The cure rate index (CRI) is a measure of the rate of curring based on the difference between optimum vulcanization time, T90, and incipient scorch time, Ts2. The value of CRI was determined based on (1):

$$\text{CRI } (\text{min}^{-1}) = \frac{100}{T_{90} - T_{s2}} \quad (1)$$

Physical-Mechanical Characteristics: Tensile strength tests were carried out with a Schopper strength tester with testing speed of 460 mm/min, using dumb-bell shaped specimens according to ISO 37/2012 and angular test pieces (Type II) according to EN 12771/2003, respectively. Elongation set is the elongation of a specimen measured 1 minute after rupture in a tensile test. It was calculated using (2):

$$\text{Elongation set } (\%) = \frac{L - L0}{L0} 100 \quad (2)$$

where L_0 is the initial length between two marks and L is the length between the marks 1 minute after the sample broke in a tensile test.

The hardness was measured by using a hardener tester according to ISO 7619-1/2011 on 6 mm thick samples. The elasticity was evaluated with a Schob type test machine, according to ISO 4662/2009.

Permanent compressive deformation was performed for a 25% compression at 25 °C for 24 hours according to SR ISO 7791-67 method B. The specimens were obtained by punching rubber plates in the form of discs with a thickness of 6 mm.

III. RESULTS AND DISCUSSIONS

A. Brabender Mixer Processing Characteristics

Torque was widely used to study the rheological behavior of polymer melts under processing conditions. The total torque required for rotating the mixer rotors in the polymer melt at a given rotational speed that can be continuously changed is measured by a lever system. The temperature of the polymer mixture, which changes with time due to the dissipation of viscous energy, is determined by means of a thermocouple that exits into the sampling chamber. Therefore, the data include measured torque and temperature values at constant rotation over time [8]. Fig. 1 shows the variation of torque and temperature versus time, recorded during mixing on Brabender Plasticorder. Analyzing the diagrams in Fig. 1, it

can be seen that in the first portion, A-B, that lasts about 3' at 80 rpm the elastomers and the compatibilizer are introduced into the mixer and therefore the torque is initially increased in A point. The first loading peak, A, corresponds to the introduction of polymers. As torque increases, the temperature increases due to friction. The torque begins to decrease near A to B, mainly due to the homogenization and plasticization of the elastomers, as well as to the increase in temperature as a result of shearing. In B point, the nanofiller, filler, plasticizer, and other ingredients are introduced, and the rotation speed is reduced to 30 rpm for 4 minutes. Between point B and point X, the torque starts to increase due to the addition of (nano)filler and other ingredients, compaction, melting and reinforcement of the elastomers. Torque increases up to X, where we have the second loading peak that corresponds to the introduction of the ingredients. Once the second peak is reached, the rotation speed increases to 120 rpm and the temperature rises exponentially until it reaches a point of ML. The increase in temperature is attributed to the shearing of the loading area parallel to the plane perpendicular to the applied force. Then the temperature rises gradually, which leads to fusion when a MH is observed. Finally, the temperature reaches a steady state. The interval between the loading point and the fusion point is defined as the fusion time. Similarly, the temperature and torque in relation to this fusion point refer to the fusion temperature (FT) and the fusion torque (Fτ) respectively [8]. As can be seen from Fig. 1 and Table II, the fusion time is 6-7' and increases by increasing the amount of OMMT nanofiller; the fusion times and fusion temperatures for the analyzed mixtures increase in the same way.

Table II shows the final results of the mixing process, namely: fusion time and rate of gelation, calculated from the second loading peak and the fusion point. Table II also contains data on the energy required for mixtures. When adding the OMMT nanofiller into the blends, a variation of total energy consumption is observed.

B. Rheometric Characteristics of Samples

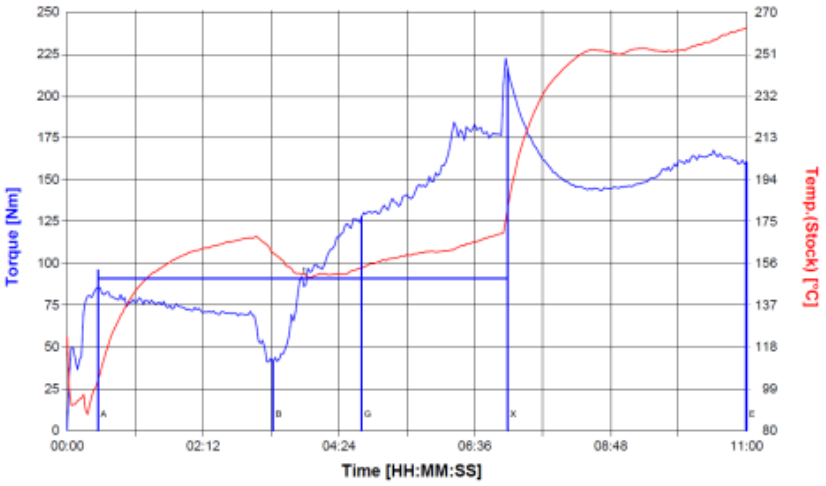
The rheometric characteristics of samples are reported in Table III. A ML is a measure of stiffness of the necured blends and a MH is a measure of the fully vulcanized samples [9]-[11]. It is noticed that mixtures containing the nanofiller have low ML values as a result of changing the morphology of the mixture, and MH is higher than that of the control sample, indicating an increase in crosslinking density by adding the filler. At the same time, it was noticed that introducing the nanofiller leads to an increase in CRI and a decrease in optimum vulcanization time, therefore a more rapid curing due to OMMT filler, which leads to increased crosslinking degree.

TABLE II
THE ENERGY REQUIRED TO OBTAIN MIXTURES AND FINAL RESULTS OF THE MIXING PROCESS, RECORDED BY THE BRABENDER PLASTI-CORDER

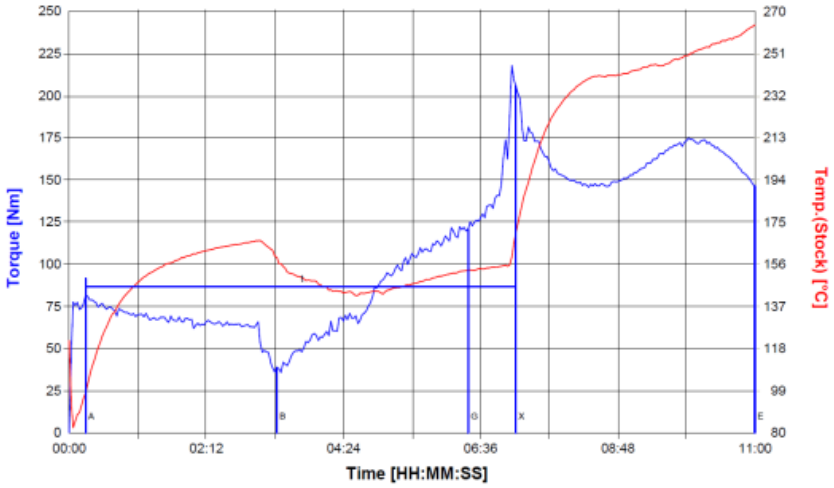
The characteristics	Mixture symbol		
	P10	O3P10	O6P10
Energy required to homogenize elastomers A-B [kNm]	97.3	97	97.5
Energy required to embed ingredients B-X [kNm]	107.8	111.6	84.7
Energy required to homogenize the mixture X-E [kNm]	460.4	470.0	464.8
Total energy required A-E [kNm]	665.5	678.7	646.9
Specific energy [kNm/g]	2.58	2.54	2.38
Fusion time (minutes)	6'38''	6'42''	6'54''
Rate of gelation (Nm/min)	26.5	28.7	27.6

TABLE III
THE CURING CHARACTERISTICS AT 165°C

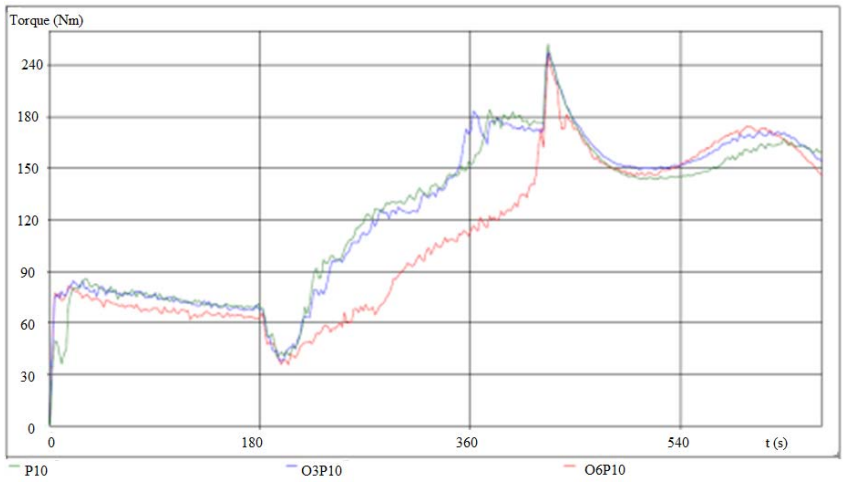
The curing characteristics	Mixture symbol		
	P10	O3P10	O6P10
The ML (dNm)	17.8	3	2.9
The MH (dNm)	65	75.2	75.2
Delta torque (dNm)	47.2	72.2	72.3
Scorch time,Ts2 (minutes)	1.17	0.13	0.13
Scorch time,Ts50 (minutes)	3.72	1.98	2.2
Optimal curing time,T_{90} (minutes)	7.62	3.84	4.35
Cure Rate Index (CRI), min-1	15.50	26.95	23.70



(a) P10 mixture



(b) O6P10 mixture



(c) Comparison: P10, O3P10 and O6P10

Fig. 1 Changes in the time-dependent torque recorded by the Brabender Plasti-Corder for the rubber mixtures, caused by adding the OMMT nanofiller: (a) P10 mixture, (b) O6P10 mixture, (c) comparison: P10, O3P10 and O6P10

C. Physical-Mechanical Characteristics of Samples

Physical–mechanical characteristics of samples are presented in Fig. 2. It can be seen that the nanoclay addition improves: hardness, elasticity, 100% elongation modulus, tear strength and elongation set. Density of mixtures containing nanofiller increases and may indicate a better packing of macromolecules as a result of changing the morphology of the mixtures. Also, permanent compressive deformation improves (decreases) by adding OMMT and the resulting mixtures meet the requirements for application in gasket production (O-rings not resistant to oil products) for various areas of application (automotive, food, spatial, constructions, agriculture etc.).

IV. Conclusion

The study on the influence of introducing an OMMT nanofiller on the behavior of a compound based on EPDM and *II-Cl* showed the following:

(1) adding the OMMT nanofiller in the mixture leads to a decrease in the specific energy required to obtain mixtures, fusion time is 6-7' and raises by increasing the amount of OMMT nanofiller and fusion and times and temperatures for analysed mixtures increase in the same way;
(2) in terms of rheological characteristics, it is observed that upon nanoclay addition, there is a decrease of ML (which indicates a change in raw morphology) and of the optimal time of vulcanization, and CRI increases (therefore a more rapid curing due to OMMT filler, which leads to increased crosslinking degree);
(3) the presence of OMMT in mixtures leads to the improvement of physico-mechanical properties: hardness, elasticity, 100% elongation modulus, tear strength and elongation set, permanent compressive deformation etc.

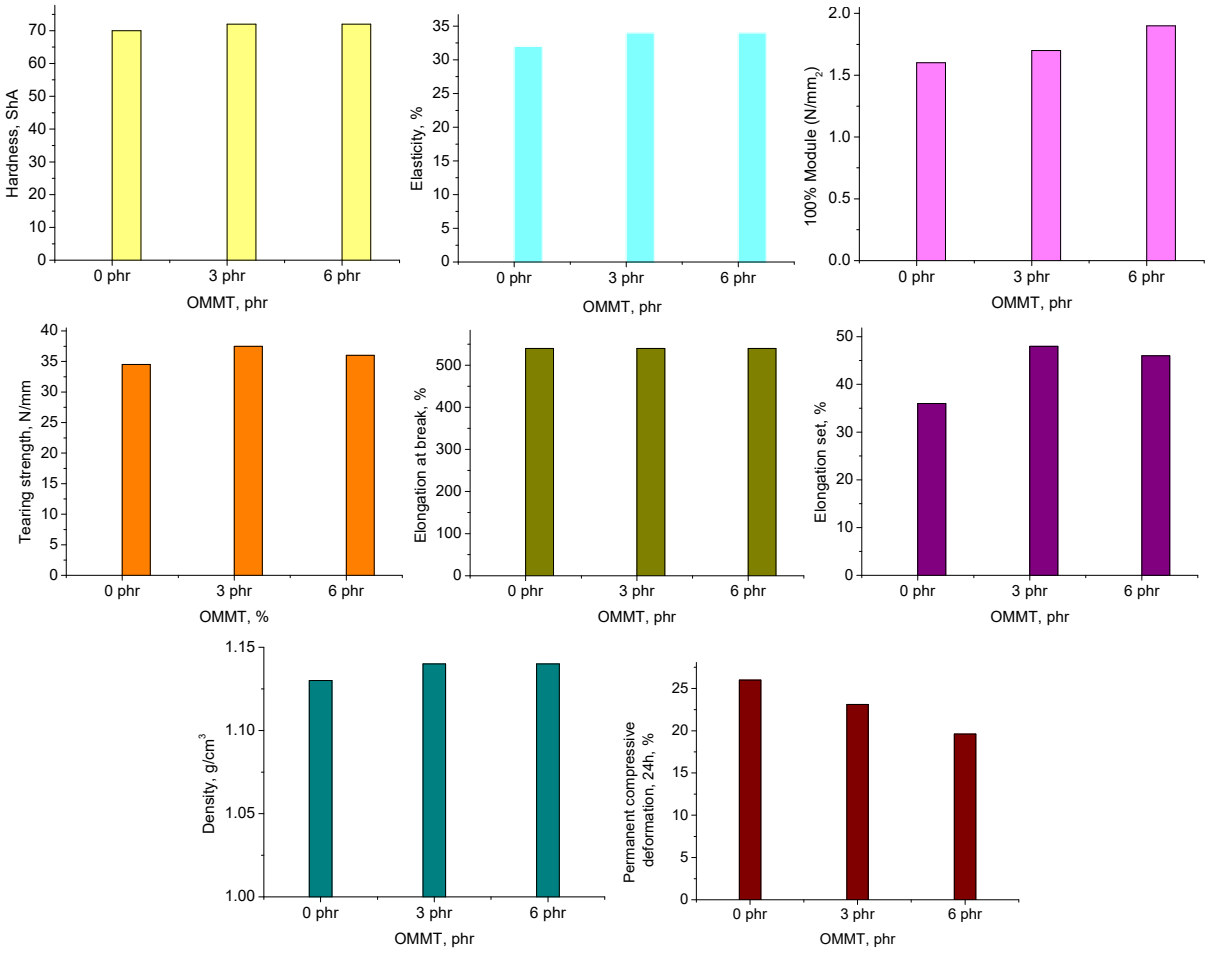


Fig. 2 Physical-mechanical characterisation

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