DOI: 10.1002/masy.200850309

Physico-Mechanical Characteristics of Some EPDM/Plasticized PVC Blends

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Summary: In this study were prepared blends based on ethylene propylene terpolymer rubber (EPDM) and plasticized poly (vinyl chloride) (PVC). These blends are immiscible and need to be compatibilized. The following compatibilization methods were used: (1) *addition of a compatibilization agent*; there were used: maleinized EPDM, maleinized polyethylene (PE), chlorinated polyethylene (CPE) and maleinized polypropylene (PP); chlorinated polyethylene has proved to be the most efficient; the amount of the added CPE giving the best physico-mechanical characteristics was of 7,5 parts to 100 polymer parts; (2) *reactive compatibilization,* using crosslinked copolymer formation strategy; three different crosslinking systems were used: (a) common method with sulphur and accelerators, (b) crosslinking with benzoyl peroxide and trimethylpropane trimethacrylate (TMPT DL 75), (c) vulcanization with phenol resin and tin chloride. The best physico-mechanical characteristics were obtained with the EPDM/plasticized PVC blends crosslinked with 8 phr phenol resin. Such types of polymer blends can be processed by methods specific for plastics, removing thus vulcanization operation required in case of elastomers. These blends can be used in the manufacture of hoses, gaskets, footwear constituents etc.

Keywords: blends; compatibilization; ethylene propylene terpolymer rubber (EPDM); poly(vinyl chloride) (PVC); vulcanization

Introduction

Most polymer blends are immiscible and have to be compatibilized. The compatibilization must accomplish: (a) optimization of interfacial tension; (b) stabilize the morphology against high stress during forming; and (c) enhance adhesion between the phases in the solid state.[1] Compatibilization methods can be divided into two categories[2–6]:

Compatibilization by Addition

It is realized by the addition of a third component, usually a block or a graft copolymer. It is necessary for the copolymer only to have segment that have specific interactions with the main polymeric components (hydrogen bonding, dipole – dipole, dipole ionic etc.). There are a variety of parameters influencing the interface saturation such as: homopolymer molecular weight, copolymer molecular weights, polymer structure details, the compatibilization agent addition mode, processing conditions, copolymer affinity for the disperse phase, copolymer orientation at the interface etc.[7–8]

In the specialized literature,[8] experimental and theoretical studies have reported the interfacial saturation was reached by copolymer addition. Thus, the size of the disperse phase area decreases with the increase in the grafted copolymer percentage. The average area size decreases with the increase in the compatibilization agent level up to an equilibrium point which can be considered to be the so-called critical

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micelle concentration (CMC) when the micelles are formed. Further addition of copolymer above the CMC leads to micelle formation, often decreasing the overall performance of the blend system.

Reactive Compatibilization

The second and today the dominant method of compatibilization is based on specific chemical reaction between two polymeric components during mechanical blending. As a result of the process, the chemical reaction takes place within the interphase hence the interfacial agent is produces in situ, with segments from the two homopolymers.[1]

According to S.Bruce Brown's classification[9] of the reactive compatibilization strategies are: (1) redistribution or transreactions, (2) graft copolymer formation, (3) block copolymer formation, (4) crosslinked copolymer formation and (5) ionic bond formation.

In this study were prepared blends of ethylene-propylene terpolymer rubber (EPDM) and plasticized poly (vinyl chloride) (PVC). These two polymers are immiscible, leading to EPDM/PVC blends with poor characteristics; therefore, there are a few specialized studies[10–11] in this field.

Because of the significant application characteristics of such polymers, the purpose of this study is to improve physico-mechanical characteristics of such blends by using both compatibility methods as follows: (1) addition of a compatibilizer and (2) reactive compatibilization by establishing covalent links between the homopolymer phases by dynamical vulcanization employing three different crosslinking systems.

Materials and Methods

Materials

The following raw materials were used: (1) *EPDM rubber* Nordel 47130 (with 54,7% ethylene content); (2) *plasticized PVC* prepared from: PVC with a 64 k value, dioctyl phthalate (DOP), PVC stabilizer (LGP 8008) and antioxidant (Uvinul 5050H); (3) *compatibilization agents:* chlorinated polyethylene CPE TX10 (with 35% chlorine content), polyethylene chemically modified by grafting with maleic anhydride Polybond 3009 (with 0.2% maleic anhydride content), polypropylene chemically modified by grafting with maleic anhydride Polybond 3002 (with 1% maleic anhydride content) and maleinized ethylene propylene terpolymer rubber Royaltuf 498 (with 1% maleic anhydride content); (4) v*ulcanization agents:* sulphur, M and Th vulcanization accelerators, di(tert-buthyl peroxi-isopropyl)benzene Perkadox 14-40B-GR (40% peroxide), trimethylol-propane trimethacrylate TMPT DL 75 (pH = 9,2, 74,2% active agent), phenol resin Ribetak 75-30^{E} (8,8% methyl) and tin chloride dihydrate (98,6% purity).

Blend Preparation

Blends based on EPDM and plasticized PVC were obtained in two stages: plasticizing the PVC and preparing the blends based on EPDM and plasticized PVC.

PVC plasticizing was accomplished by plasticizer (DOP) absorption into PVC when mixing in a 2 L vessel of Plasticorder PLV 330 Brabender at 70 rpm, at 40 °C temperature for 10 minutes. For a good thermal stability, temperature stabilizer and antioxidants have been introduced over time. The resulted plasticized PVC is processed into a sheet on a laboratory roll electrically heated up to 150 °C; the resulted sheet was used in the next stage in the blend preparation.

EPDM/plasticized PVC blends were prepared in a Plasticorder PLV 330 Brabender of 70 cm^3 capacity, at 80 rpm and 175 °C. Rubber sheets were obtained on a laboratory roll electrically heated. Samples for the physico-mechanical tests were obtained on electrically heated hydraulic press at a temperature of 160 °C and pressure of 150 MPa for 5 minutes. After molding, the mix was cooled under pressure to room temperature.

Blend Characterization

Physico-mechanical test were performed according to the following standards: SR ISO 7619:2001 (hardness), STAS 5570:1987 (elasticity), SR ISO 37: 1997 (modulus, tensile strength, elongation at break and elongation set), SR ISO 34-1:2000 (tear strength).

Melt flow index of the thermoplastic materials was measured by means of an extrusion plastometer (capillary rheometer) at 190 °C and a press force of 2,16 kg (according to SR ISO 1133/1991).

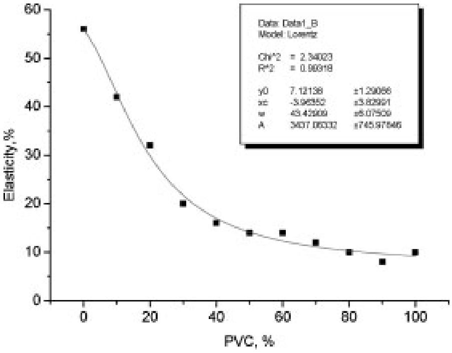

Figure 2.
Elasticity versus the PVC level.

Results and Discussions

Establishing the Composition Influence on the Physico-Mechanical Characteristics

In order to establish how the compositions acts on the characteristics were prepared blends based on EPDM (Nordel 47130)/ plasticized PVC and containing different percentages (100, 90, 80, 70, 60, 50, 40, 30, 20, 10 and 0%) by weight of elastomer (from the total polymer mass).

The results of physico–mechanical tests for the EPDM/plasticized PVC blends have revealed the following features:

- *Hardness* (Figure 1) has shown a linear increase (from 58°ShA up to 84°ShA) when PVC level was increased up to 70%, a further increase in PVC level has shown only insignificant changes (±2°ShA). This illustrates the fact that for a concentration of PVC higher than 70% of the whole polymer mass, plasticized PVC represents the continuous phase.
- *Elasticity* (Figure 2) has shown a 4 times decrease when the PVC level was increased from 0% up to 50%, a further increase in PVC level has shown only insignificant changes.
- *Tensile strength* (Figure 3) has shown an insignificant increase when the plasticized PVC level was increased from 0 up to 80%, and an increase of 92% at a further increase in PVC level from 80 up to 100%.
- *Elongation at break* (Figure 4) has shown a minimum for 50% plasticized PVC (it has decreased from 940% for 0% PVC down to 33% for 50% plasticized PVC), thereafter increasing up to 213% for 100% plasticized PVC.

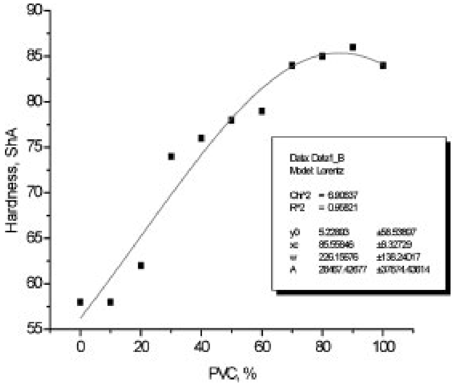

Figure 1.
Hardness versus the PVC level.

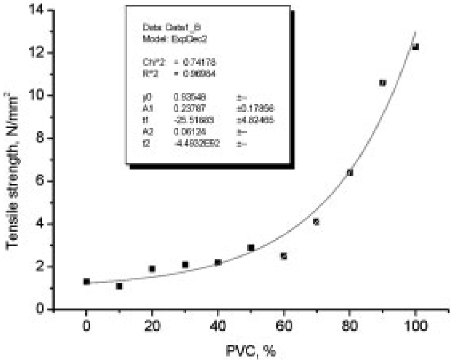

Figure 3.
Tensile strength versus the PVC level.

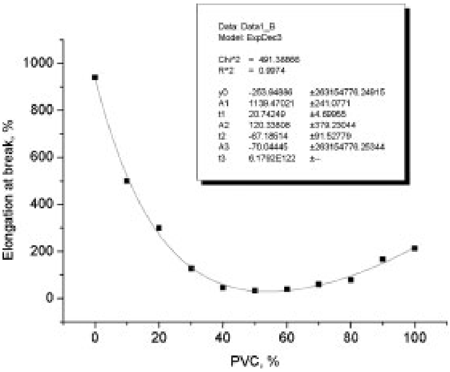

Figure 4.
Elongation at break versus the PVC level.

- *Elongation set* (Figure 5) has shown a minimum for 40–50% plasticized PVC, and thereafter a slight increase.
- Elongation at break and elongation set have shown a minimum in their changes according to the composition of the blend. In this minimum point the values for elongation at break and elongation set are lower than those for the constituents. This reveals a very slight interface adhesion between the constituents leading to phase separation under stress due to the immiscibility of the blends.[12–13]
- *Tear strength* (Figure 6) has shown a significant increase (from 14,5 N/mm up to 38,5 N/mm for 0–80% plasticized PVC), and thereafter an increase of 92% for 80–100% plasticized PVC.

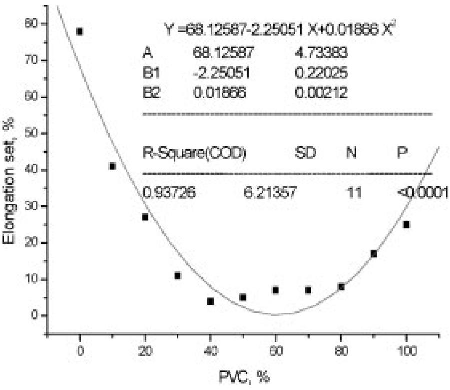

Figure 5.
Elongation set versus the PVC level.

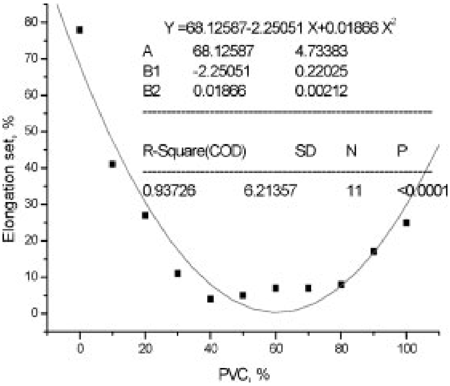

Figure 6.
Tear strength versus the PVC level.

- The *melt flow index* of the blends (Figure 7) varies with the increase of plasticized PVC level so: (a) polymer blends containing less than 40% PVC (by weight based on the total polymer amount in the blend) have shown no flow; (b) blends containing 40–60% PVC have shown a light increase in melt flow index; (c) blends containing more than 60% PVC have shown a significant increase in the melt flow index revealing thus a good processability of such blends by injection moulding (commonly used in thermoplastic material processing).

Analyzing the influence of the composition on the characteristics of EPDM/ plasticized PVC blends was selected the blend (NV80) with 20% EPDM from the whole polymer mass due to its good physico- mechanical characteristics am to its higher flow index leading to a better processability.

Establishing the Compatibilization Agent Influence on the Physico-Mechanical Characteristics

To improve the physico- mechanical characteristics of the EPDM/plasticized PVC blend by compatibilization by addition, in the blend containing 20 parts EPDM to 100 polymer parts, were introduced 5 parts of compatibilizing agents (maleinized PE, chlorinated PE, maleinized PP and mal-

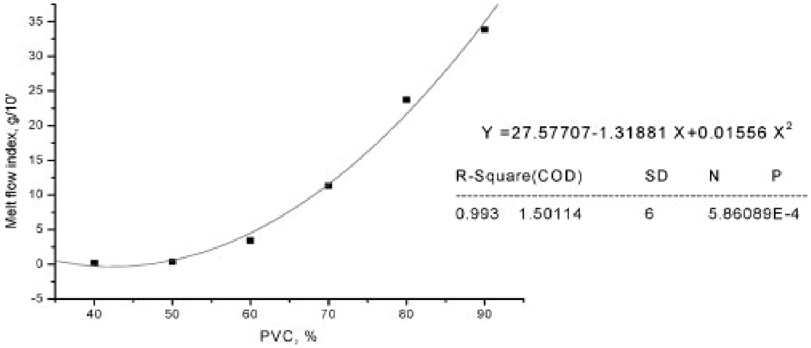

Figure 7.
Melt flow index versus the PVC level.

einized EPDM) for 100 parts polymer. Figure 8–10 show the changes in such physico-mechanical characteristics as tensile strength, elongation at break and tear strength according to the added compatibilization agent.

The results of physico-mechanical tests have revealed the following features:

- The best physico-mechanical characteristics were obtained by adding *chlorinated PE* to the blend. In this case an increasing in elongation at break, the highest increase in tensile strength and tear strength, and a slight decrease in elasticity were revealed.
- Addition of *maleinized polyethylene* has led to decreased elongation at break, tensile strength and tear strength.

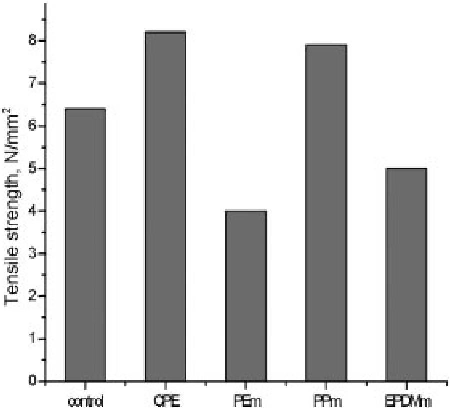

Figure 8.
Tensile strength versus the compatibilization agent type.

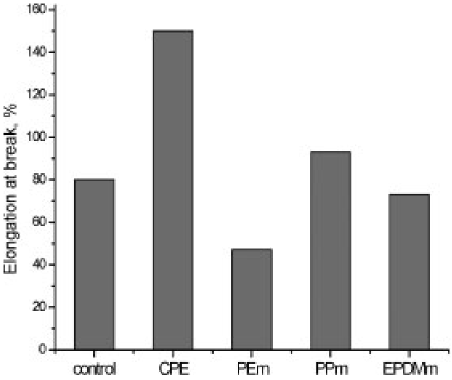

Figure 9.
Elongation at break versus the compatibilization agent type.

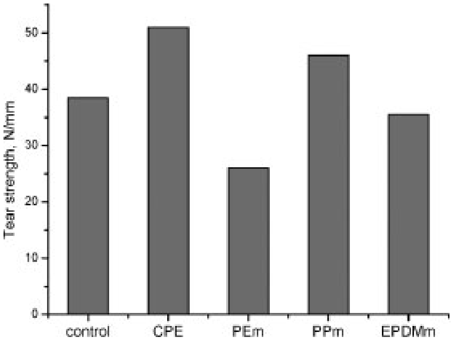

Figure 10.
Tear strength versus the compatibilization agent type.

- *Maleinized ethylene propylene terpolymer* (Royaltuf 498) has led to a slight decrease in hardness and tensile strength.
- *Maleinized polypropylene* has led to increased tensile strength, elongation at break and tear strength.

Following the performed tests the *CPE compatibilization agent* can be concluded to be *the most efficient compatibilization agent for the EPDM/plasticized PVC blends*.

Establishing the Compatibilization Agent Amount Action onto the Physico-Mechanical Characteristics

To establish the critical micelle concentration of the CPE compatibilization agent for the EPDM/plasticized PVC blends (with 20% EPDM from the total polymer mass), blends containing 2.5, 5, 7.5 and 10 parts CPE to 100 parts polymers were prepared. Test results have revealed that tensile strength (Figure 11), elongation at break (Figure 12) and tear strength (Figure 13) have increased fast when the CPE level was increased up to a level of 7,5 parts CPE to 100 parts polymers, thereafter showing a plateau for 7.5–10 parts CPE to 100 parts polymers or little decrease.

For such blends a level of *7,5 parts CPE to 100 parts polymers* may be concluded to be the best one to improve the EPDM/plasticized PVC blend characteristics. It can be the CPE critical micelle concentration (CMC) for such blends.

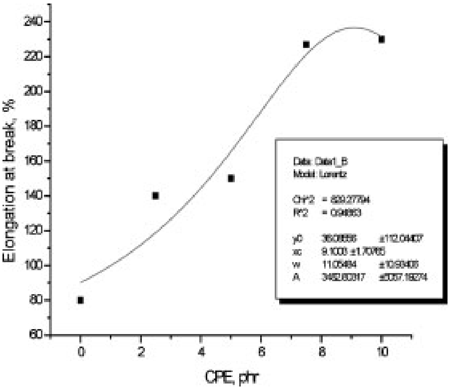

Figure 12.
Elongation at break versus the CPE amount.

Establishing the Influence of the Crosslinking System on the Physico-Mechanical Characteristics of EPDM/Plasticized PVC Blends

Reactive compatibilization between both phases in the EPDM/plasticized PVC blend used the crosslinked copolymer formation strategy

The control blend was an EPDM/plasticized PVC blend containing 20 EPDM parts to 100 polymer parts.

In EPDM/plasticized PVC blends having the control sample composition, the elastomer crosslinking was done employing

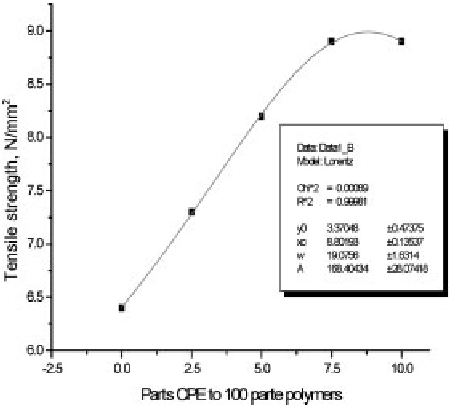

Figure 11.
Tensile strength versus CPE amount.

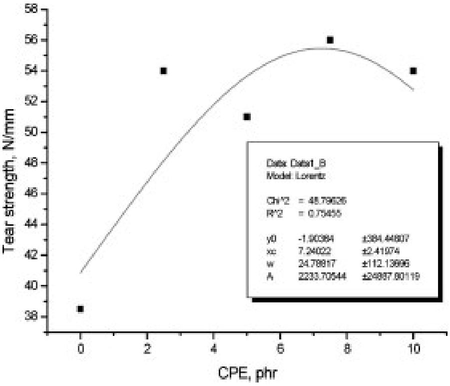

Figure 13.
Tear strength versus the CPE amount.

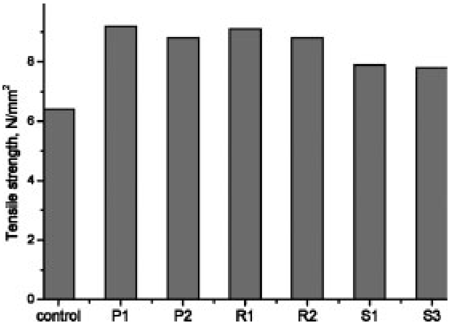

Figure 14.
Tensile strength versus the crosslinking system.

the following crosslinking systems: (1) *vulcanization system containing peroxide and TMPT*, in the following variants: (P1) 6 phr peroxide + 3 phr TMPT and (P2) 3 phr peroxide + 1,5 phr TMPT; (2) *vulcanization system containing phenol resin and tin chloride*, in the following variants: (R1) 8 phr resin + 1,6 phr $SnCl_2$ and (R2) 4 phr resin + 0,08 phr $SnCl_2$; (3) *vulcanization system containing sulphur and vulcanization accelerators,* in the following variants: (S1) 2 phr S + 1 phr Th + 0,5 phr M and (S2) 1 phr S + 0,5 phr Th + 0,25 phr M.

Figure 14–15 show the changes in tensile strength and elongation at break versus the employed crosslinking system. *Tensile strength* in dynamically vulcanized blends was 22–44% higher than the control blend; the most efficient systems were those crosslinked by peroxide (increases of 37% and 44%) and by phenol resin (increases of 37% and 42%), and the system crosslinked by sulphur has shown increases of 22%, respectively 23% of this characteristic. *Elongation at break* was increased significantly for the three crosslinking systems so that elongation at break was increased: by 75% and 83% with the system crosslinked by peroxide, by 75% and 109% with the system crosslinked by phenol resin, and two times for the both blends with the system crosslinked by sulphur as compared to the control blend.

Blends with higher crosslinking agent levels have shown better characteristics but the values of the physico-mechanical characteristics resulted by diminishing by half the crosslinking agent level have shown only little differences.

Melt flow index (MFI) (Figure 16) has decreased due to the dynamical crosslinking of EPDM elastomer within the molten plasticized PVC as a result of covalent linkages. By increasing two times the crosslinking agent level, MFI decreased significantly only for the crosslinking system containing peroxide and TMPT. The resulted MFI values have revealed that all the prepared blends can be processed by methods specific to the thermoplastics.

Results reveal that *the most efficient crosslinking system is the phenolic resin system* closely followed by benzoyl peroxide and TMPT. This results are conform to the studies[14–19] performed with other polymer systems that have revealed these crosslinking systems being more efficient than

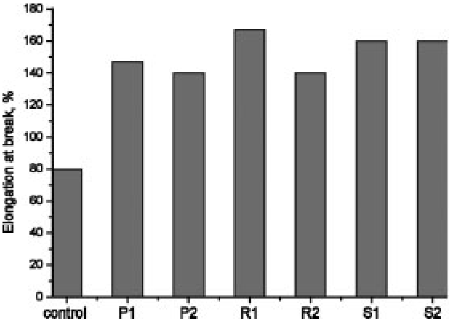

Figure 15.
Elongation at break versus the crosslinking system.

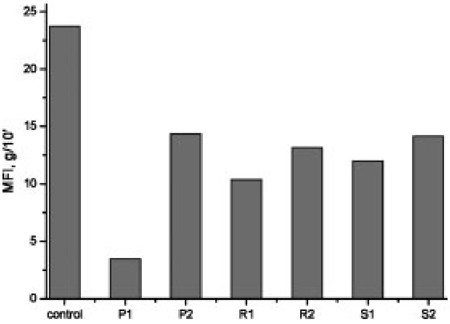

Figure 16.
Melt flow index versus the crosslinking system.

the classical sulphur crosslinking but his has not been acknowledged for all polymer systems.

Conclusions

- Analyzing the influence of the composition on the characteristics of EPDM/ plasticized PVC blends revealed that elongation at break and elongation set have shown a minimum. In this minimum point the values for elongation at break and elongation set are lower than those for the constituents. This reveals a very slight interface adhesion between the constituents leading to phase separation under stress due to the immiscibility of the blends.
- To improve the physico- mechanical characteristics of EPDM/ plasticized PVC blends both compatibilization methods were used: (1) addition of a compatibilizer and (2) reactive compatibilization.
- *Compatibilization by addition* used the following compatibilization agents: PE grafted with maleic anhydride (PEm (Polybond 3009)), PP grafted with maleic anhydride (PPm) (Polybond 3002), EPDM grafted with maleic anhydride (EPDMm) (Royalene 498) and chlorinated polyethylene (CPE). CPE was the most efficient compatibilization agent for the EPDM/PVC blend. The critical micelle concentration of CPE was of 7,5 parts of compatibilization agent to 100 polymer parts.
- *Reactive compatibilization* between both phases in the EPDM/plasticized PVC blend used the crosslinked copolymer formation strategy; this was accomplished by vulcanization, employing three different crosslinking systems: crosslinking system by peroxide, crosslinking system by phenol resin and crosslinking system by sulphur. Results reveal that *the most efficient crosslinking system is the phenolic resin system* closely succeeded by the benzoyl peroxide and TMPT crosslinking system.
- The selected products following the performed study have shown elastomer specific characteristics and could be processed by methods used currently in processing thermoplastic materials (injection, jet moulding etc.).
- These blends can be used in the manufacture of hoses, gaskets, footwear constituents etc.

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