Influence of the Curing System on the Properties of Thermoplastic Vulcanized EPDM / Plasticized PVC

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In this paper were investigated influences of various types and concentrations of crosslinking agents on the properties of thermoplastic vulcanizates based on ethylene-propylene terpolymer rubber (EPDM) and plasticized poly (vinyl chloride) (PVC). Three different crosslinking systems were used: (a) common method with sulphur and vulcanization accelerators (tetramethylthiuram disulfide and mercaptobenzothiazole); (b) crosslinking with di(tert-buthyl peroxi-isopropyl) benzene Perkadox 14-40B-GR and co-agent trimethylol-propane trimethacrylate TMPT DL 75 (c) vulcanization with phenol resin Ribetak 75-30^{E} *and tin chloride dehydrate. The influence of each crosslinking systems on cross-link density, mechanical properties and DSC analysis of samples were investigated. The hardness shows a slight decrease as a result of dynamic vulcanization, because this is a way to disperse large amounts of elastomer in the thermoplastic matrix, resulting in a refined morphology. It was observed that the highest values of crosslinking density and 100% modulus were obtained by using the classic cross-linking with sulphur and accelerators, and that for a reduced amount of crosslinking agents used, there was a decrease in crosslinking density. Elastomer crosslinking led to an increased* T_g *and decreased* T_m*. These blends can be used in the manufacture of hoses, gaskets, footwear constituents etc.*

Keywords: TPV, EPDM, PVC, cross-link density, differential scanning calorimetry

Thermoplastic vulcanizates (TPVs) have become a very useful class of thermoplastic elastomers since their introduction in 1981. These materials have the processing characteristics of a thermoplastic and the functional performance of a conventional thermoset rubber. TPVs are blends consisting of cross-linked elastomer particles dispersed in a thermoplastic matrix, which leads to an unique combination of elastic properties and melt processability [1-3]. TPVs are produced by a process known as dynamic vulcanization, where the elastomer phase is selectively cross-linked during melt mixing with the thermoplastic. The increasing viscosity of the elastomer phase during dynamic vulcanization affects the phase continuity by promoting phase inversion, which enables the cross-linked elastomer to become the dispersed phase, even when it is the major phase. The dispersion of a large amount of cross-linked rubber into the thermoplastic matrix results in soft and highly elastic products, while the continuous thermoplastic phase enables melt processability [1-3]. The properties of TPVs depend strongly on the blend composition, the cross-link density of the rubber phase, the rubber dispersion and domain size [1]. The dynamic vulcanization process was first described by [4] in 1962 and later developed by [5-7]. The process was further advancedin [8, 9] by the use of preferred curing agents to achieve improvement in elastomeric properties and flow characteristics, which led to successful commercialization of dynamic vulcanization technology.

The first commercial product was Santoprene® based on a blend (or alloy) of EPDM and polypropylene introduced in 1981. A similar product based on a blend of butadiene-acrylonitrile rubber (ASTM designation NBR) and polypropylene, Geolast® was introduced in 1985 [10].

TPV followed quick development between 2005 and 2010 (increases of 10%/year - according to a study developed by The Freedonia Group) due to their high-performance properties which render them usable in many areas such as: automotive area (over 50% of annual production), electric applications, buildings, production of rubber goods for medical use, lighting industry etc. [11].

The aim of the present work is to study the effect of different types and concentrations of crosslinking agents on the properties of a 20/80 ethylene propylene terpolymer rubber (EPDM)/plasticized poly (vinyl chloride) (PVC) TPVs. The influence of each crosslinking systems on cross-link density, mechanical properties and DSC analysis of samples were investigated too.

Experimental part

Materials and methods

The following raw materials were used: (1) EPDM rubber Nordel 47130; (2) plasticized PVC prepared from: PVC with a 64 K-wert value, dioctyl phthalate (DOP), PVC stabilizer (LGP 8008) and antioxidant (Uvinul 5050H); (3) crosslinking systems: (3.a) sulphur and vulcanization accelerators - tetramethylthiuram disulfide (TMTD) and mercaptobenzothiazole (MBT); (3.b) di(tert-buthyl peroxi-isopropyl)benzene Perkadox 14-40B-GR and co-agent trimethylol-propane trimethacrylate TMPT DL 75 (3.c) phenol resin Ribetak 75-30^{E} (8,8% methyl) and tin chloride dihydrate (98,6% purity). The table 1 presents the materials used in the mixtures and their main characteristics. To determine the crosslinking density toluene was used as a solvent (ρ_{toluen} = 0,866 g/cm^3).

Blend preparation

Blends based on EPDM and plasticized PVC were obtained in two stages: (1) PVC plasticizing and (2) preparing 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, temperature of

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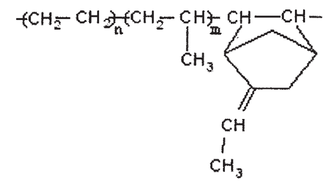
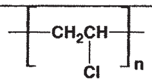
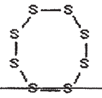
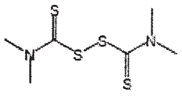
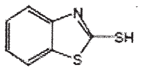
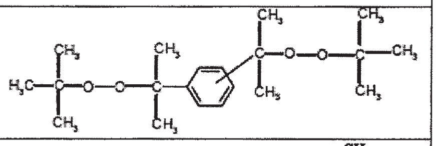
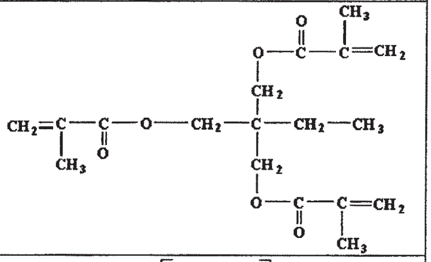
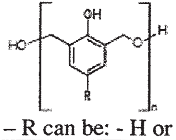
Table 1
CHARACTERISTICS OF MATERIALS USED

Materials used	**Characteristics**	**Chemical structure**
EPDM Nordel NDR 47130.	Ethylene content 67% Crystallinity degree 9 % 5-ethylidene-2-norbornene (ENB) content 4,9% Density 0,97 g/cm^3 Mooney viscosity ML (1+4) at 125 °C: 130 Carbon-black content 28%	
PVC	K-wert value 64 moisture and volatile 0,2% Absorbtion of plasticizer DOP 100%	
PVC stabilizer LFR 8008	Diatomic lead phosphite content 10-30% Tribasic lead sulphate content 30-60% Lead stearate diatomic content 10-30%	
Dioctyl phthalate (DOP)	Density 0.984 g/cm^3 pH 7 99.5% purity	$C_{24}H_{38}O_4$
Stearophanic acid	Titre fatty acids 59 Mineral acids absence	
Zinc stearate	Zn content 11% Melting point 127 °C	
Antioxidant Uvinul 5050H	Density 0.99 g/cm^3 Melting temperature range 95-125°C Heat stability than 300°C pH 7	HALS–amine secundare aromatice
Sulphur	Percentage of ash 0.1% Sulphur content 99.5% Melting point 117 °C	
Tetramethylthiuram disulfide (TMTD) - vulcanization accelerator	Density 1.3, g/cm^3 Melting point 140 °C	
Mercaptobenzothiazole (MBT) -vulcanization accelerator	Density 1.4 g/cm^3 Melting point 174 °C	
Zinc oxide - Vulcanization activator	Zinc oxide content 99.2 % Humidity 0.15 % Free zinc 0.14 %	ZnO
di(tert-butyl peroxy-isopropyl)benzene Perkadox 14-40B-GR	Density 1.6 g/cm^3 Active oxygen content 3.8% Peroxide content 40% Neutral pH	
Trimethylolpropane trimethacrylate Luvomaxx TMPT DL 75 C (***TMPT***)	Decomposition point than 250°C 74.2% active agent pH 9.2	
Phenolic resin Ribetak 75-30^E	Percentage of ash 0,040% 8,8% methyl Melting point 85 °C	 where – R can be: - H or –CH_3
Tin chloride dihydrate	Molecular weight 225,65 98,6% purity	$SnCl_2$ x $2H_2O$

40°C for 10 min. 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 being used in the next stage in the blend preparation. Table 2 presents the recipe of PVC plasticizing blend.

EPDM/plasticized PVC blends were prepared in a PLV 330 Brabender plasticorder of 70 cm^3 capacity, at 80 rpm and 175°C. The control blend was an EPDM/plasticized PVC blend containing 20 EPDM parts to 100 polymer parts. EPDM/plasticized PVC blends of 20 p/80 p, containing the vulcanization systems listed below, were prepared: (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 TMTD + 0,5 phr MBT + 5 phr ZnO and (S2) 1 phr S + 0,5 phr TMTD + 0,25 phr MBT + 5 phr ZnO.

Ingredients	Amounts (g)
PVC	1000
DOP	500
LFR 8008	40
Zinc stearate	5
Uvinul 5050	10

Table 2
RECIPE OF PVC PLASTICIZING BLEND

The adopted protocol was: first, the plasticized PVC was introduced into the cavity and sheared by itself for 3-4 min in order to ensure complete melting and thermal homogenization. Then, the rubber EPDM was mixed with plasticized PVC. After mixing them (4 min) the antioxidant was added. When it is embedded in a mixture the curing agents are introduced and continue to stir for 3 min. Then the mixture is unloaded from the mixer.

Rubber sheets were obtained on a laboratory roll electrically heated. Plates for the physico-mechanical tests were obtained by compression molding into 2 mm thick sheets on a laboratory electrical press at a temperature of 160°C and pressure of 150 MPa for 5 min. The molded samples were stored away from light, at room temperature.

Blend characterization

*Tear st*rength were performed according to SR EN 12771/2003 using angular test pieces (type II). 100% Modulus was measured using dumb-bell shaped specimens according to ISO 37/2005. The testing speed of 460 mm/min at room temperature in case of a Schoppler strength tester machine was used. Hardness of samples in terms of Shore A was measured according to ISO 7619-1/2004 using 6 mm thick samples. The densities of elastomer samples were measured according to ISO 2781/2008.

The cross-link density of the EPDM/PVC plasticized TPVs samples was determined on the basis of equilibrium solvent-swelling measurements (in toluene at 23-25°C) by application of the well-known modified Flory-Rehner equation for tetra functional networks. The samples (2 mm thick) were initially weighed (m_i) and immersed in toluene for 24 h. The swollen samples were removed and cautiously dried to remove excess solvent before being weighed (m_g) and, during this operation, the samples being covered to avoid toluene evaporation during weighing. Traces of solvent and other small molecules were then eliminated by drying in air for 6 days. Finally, the samples were weighed for the last time (m_s), and volume fractions of polymer in the samples at equilibrium swelling ν_{2m} were determined from swelling ratio G, and calculated as follows:

$$\nu_{2m} = \frac{1}{1+G} \qquad (1)$$

where:

$$G = \frac{m_g - m_s}{m_s} \times \frac{\rho_e}{\rho_s}\ ; \qquad (2)$$

ρ_e and ρ_s are the densities of elastomer samples and solvent, respectively.

The samples cross-link densities, ν, were determined from measurements in a solvent, using the Flory–Rehner relationship, given by

$$\nu = -\frac{Ln(1-\nu_{2m}) + \nu_{2m} + \chi_{12}\nu_{2m}^2}{V_1\left(\nu_{2m}^{1/3} - \frac{2}{\Phi}\nu_{2m}\right)} \qquad (3)$$

where V_1 = 106.5 cm^3/mol is the molar volume of solvent (toluene), ν_{2m} is the volume fraction of polymer in the sample at equilibrium swelling, $\Phi = 4$ is the cross-link functionality and $\chi_{12} = 0.49$ is the EPDM-toluene interaction parameter [12].

DSC measurements were carried out with DSC 204 F1 Phoenix calorimeter. Thermograms were run at heating rates of 10°C/min, on the temperature range from -70 to +350°C, argon atmosphere in chamber measurement (flow rate - 20 ml/min). Samples weighing between 2.5 mg - 13.5 mg were placed in aluminum crucibles without the cover. The vitrification temperature (T_g), melting temperature (T_m) and fusion heat (ΔH_f) were determined from DSC data [13].

Results and discussions

Mechanical Properties

Figure 1 shows a slight decrease in *hardness* (1-3 °ShA) as a result of dynamic vulcanization, due to the dispersion of a large amount of elastomer in the thermoplastic matrix, resulting in a refined morphology [14].

100% Modulus (fig.2) significantly increases by dynamic crosslinking of EPDM, as this parameter indicates the crosslinking density. The highest 100% modulus values were obtained for sulfur and vulcanization accelerators curing system (increase of 29.51% and 27.87%), followed by peroxide and TMPT system (increase of 29.51% and 22.95%) and with phenolic resin (increase of 24.59% and 21.32%). The values of this quantity slightly decrease (by 1.27% to 5.07%) as the amount of introduced crosslinking agent decreases.

Tear resistance shown in figure 3, increases significantly (by 29.87 to 46.76%) due to dynamic crosslinking of EPDM, the best value (56.5 N / mm) being obtained for the R2 blend containing 4 phr resin and 0.08 phr $SnCl_2 \times 2H_2O$. The obtained results reveal that the most efficient crosslinking system is the phenolic resin system closely followed by benzoyl peroxide and TMPT. These conclusions are

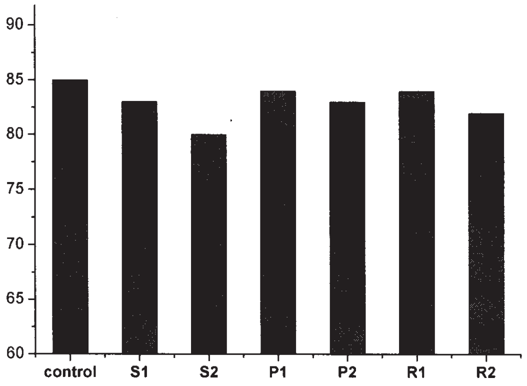


Fig. 1. Hardness versus the crosslinking system

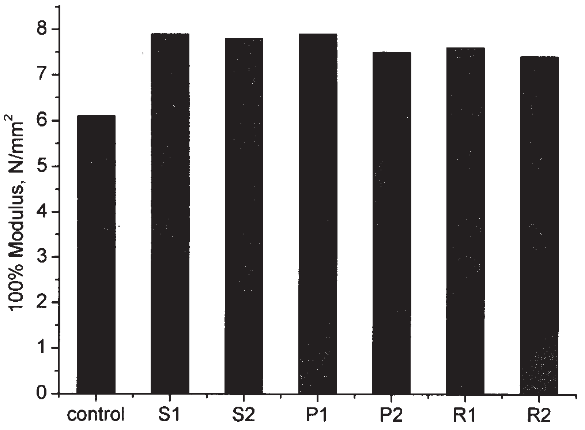


Fig. 2. 100% Modulus versus the crosslinking system

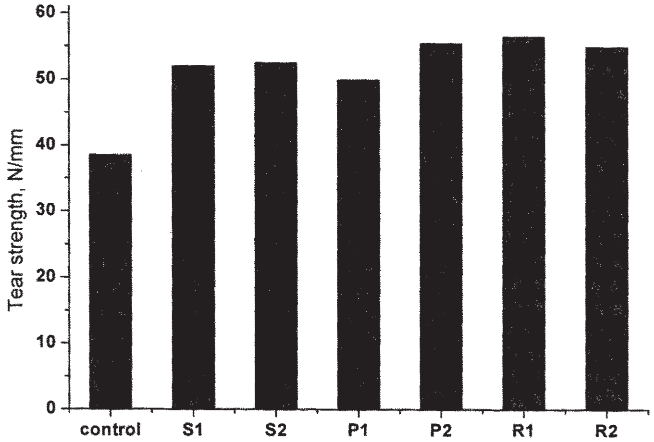


Fig. 3. Tear strength versus the crosslinking system

according to the studies performed on other polymer systems that revealed that these crosslinking systems are more efficient than the classical sulphur crosslinking but this has not been acknowledged for all polymer systems [6-9]. It was assumed that this effect is due to in situ formation of a graft copolymer which optimizes interfacial adhesion between rubber particles and the polyolefin matrix, which allows acquiring better properties. Morever, it has been reported that due to mechanism and structure of the sulphur curing system, the probability of coalescence is higher than in the case of the other two curing systems which lead to the formation of larger size dispersed rubber domains and implicitly obtaining of less desired properties [15].

Crosslinking density

Crosslinking densities (moles of crosslinked basic units per weight unit of the crosslinked polymer) were determined by measuring the level of inflation in the solvent, by applying the well-known Flory-Rehner equation to modified tetrafunctional networks. Table 3 presents cross-link density of samples. Note that the highest crosslinking density values were obtained by using the classic cross-linking with sulphur and accelerators, and peroxide curing system and TMPT, followed by phenolic resin curing system. Also, seemingly, with the decrease of the crosslinking agent amount, in all examined cases, there is a decrease of crosslinking density of the samples. These results are consistent with those obtained for 100% modulus. The highest values of 100% modulus and crosslinking density are related to sulphur curing system, because the efficiency of sulphur curing system appear to be better than those of other systems [16-17].

Differential scanning calorimetry

Differential scanning calorimetry was used to provide information on the vitrification temperature (T_g), melting temperature (T_m) and melting enthalpy. In figure 4 are given the DSC curves for: EPDM, PVC plasticized, reference mixture NV80 (containing 20% EPDM/80% PVC of the total amount of polymer mixture) and RV1 which have the same composition as the reference mixture but in which the elastomer was cross-linked with 8 PHR phenolic resin in the presence of tin chloride dihydrate. The obtained data are presented in table 4.

Note that by the plastification PVC using of DOF, a decrease in the T_g value takes place, compared to literature reported data, and that it is 81°C [18-19]. This drop in T_g in case of the plasticized PVC occurs as a result of improving segments mobility by plastification [20].

The T_g values of the control blend (NV80) and RV1 sample are placed between the T_g values of EPDM (-42°C) and plasticized PVC (58.3°C), indicating that polymers pairs are partially miscible [21-22].

For the RV1 blend, EPDM elastomer crosslinking led to an increase in the T_g compared with the control mixture. The increase in T_g of EPDM phase after the dynamic vulcanisation of blends in comparison to that of the EPDM (control) indicated compatibilisation [23]. In addition, it is well known that crosslinking of polymer chains increases the T_g [24-25]. Segmental motions are hindered by the crosslinking, which requires higher temperatures for the inception of rotation [26].

Table 3
CROSS-LINK DENSITY OF SAMPLES

Sample	m_i (g)	m_g (g)	m_s (g)	φ_e (g/cm^3)	G	v_{2m}	v (10^{-4} mol/cm^3)
RV1	0.4905	0.8255	0.3892	1.1171	1.4573	0.40695	6.0047
RV2	0.4704	0.8350	0.3765	1.0998	1.5466	0.39268	5.3370
SV1	0.4691	0.6912	0.3697	1.0912	1.0957	0.47716	10.3361
SV2	0.4846	0.7469	0.3997	1.0998	1.1032	0.47547	10.2080
PV1	0.4611	0.7955	0.3841	1.1085	1.3710	0.42177	6.7666
PV2	0.4776	0.8075	0.3822	1.1171	1.4355	0.41060	6.1857

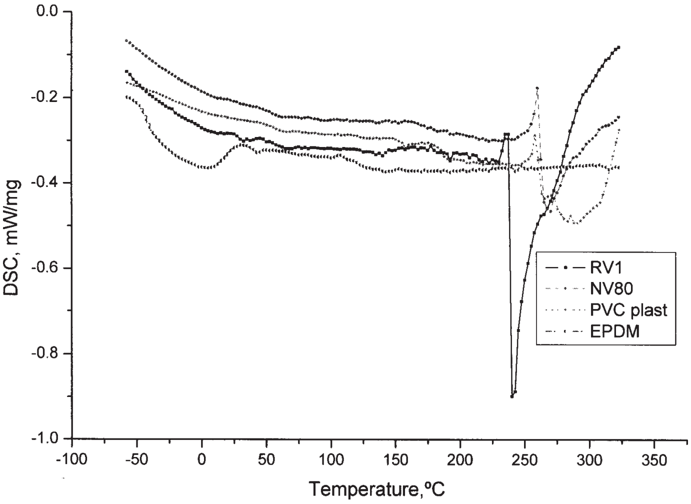


Fig. 4. DSC analysis for EPDM / plasticized PVC blends

Table 4

THERMAL CHARACTERISTICS OF POLYMER BLENDS EPDM/ PLASTICIZED PVC

Blend	T_g(°C)	ΔC_p (J/°C)	T_m(°C)	-ΔH (J/g)
NV80	22.5 51		269.6	103
RV1	27.8 53.3		240.7	86.12
EPDM	-42	0,422	5 42.5	15.27 0.4567
Plasticized PVC	58.3	0.124	288.9	112.1

The melting temperature (T_m) of plasticized PVC is 288.9°C (table 4), a result which is consistent with other data in the literature [27-28]. Melting temperatures of NV80 and RV1 blends are smaller than that of plasticized PVC, due to the decrease of the size and perfection of PVC crystals as well as to increase of the amorphous domains in elastomer which hinders the PVC crystallization [20]. In the case of vulcanized blend the reduction of T_m is noted as shown in figure 4, which means that the dynamic crosslinking influenced the crystallinity and the blend melts at lower temperature. According to the literature data [27, 29], the range 200-300°C also corresponds to PVC dehydrocholorination.

Conclusions

The influence of each crosslinking systems on crosslink density, mechanical properties and DSC analysis data of samples were investigated. The hardness shows a slight decrease as a result of dynamic vulcanization, because this is rather a way to disperse large amounts of elastomer in the thermoplastic matrix, resulting in a refined morphology. It was observed that the highest values of crosslinking density and 100% modulus were obtained by using the classic crosslinking way with sulphur and accelerators; whereas for the reduced amount of crosslinking agents entered there is a decrease in crosslinking density. Elastomer crosslinking led to an increased T_g and decreased T_m. The increase in T_g of EPDM phase after dynamic vulcanisation of the blend in comparison to that of the neat EPDM indicated compatibilisation. Melting temperatures of the NV80 and RV1 blends are smaller than that of plasticized PVC, due to the decrease of the size and perfection of PVC crystals as well as to increasing the amorphous domains in elastomer which hinders the PVC crystallization. These blends can be used in the manufacture of hoses, gaskets, footwear constituents etc.

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