

INFLUENCE OF CROSSLINKING METHOD ON THE PROPERTIES OF NATURAL RUBBER MIXTURES

MARIA DANIELA STELESCU¹, ELENA M N IL², GABRIELA CR CIUN², MARIA SÓNMEZ¹, MIHAI GEORGESCU¹, MIHAELA (VÎLSAN) NI UIC¹

¹INCOTP - Division Leather and Footwear Research Institute, 93 Ion Minulescu St., Bucharest, Romania, dmstelescu@yahoo.com

²National Institute for Lasers, Plasma and Radiation Physics, Electron Accelerators Laboratory, 409 Atomistilor St, Magurele, Bucharest, Romania

The most important stage in the rubber processing technology is vulcanization / crosslinking, which confers mechanical and thermal stability to rubbers. During crosslinking, rubber molecules with chain configuration are linked by chemical bridges / bonds, and the rubber mass turns from its plastic mass into an elastic one. This is normally done by sulphur and accelerator for general purpose rubbers. The chemistry of vulcanization is complex and the resulting crosslinks may be mono-, di-, tri- or higher poly-sulphides, with a proportion which is among others largely determined by the vulcanization system, the cure time and the temperature. These compounds and their reaction products could be responsible for cytotoxicity and allergy-causing compounds, such as nitrosamines and nitrosatable materials. For these reasons, the aim was to eliminate or reduce toxic ingredients in elaborating and developing crosslinking technologies for natural rubber mixtures, so that the resulting materials may be used in the pharmaceutical or food industry, as well as in manufacturing other rubber goods (toys, various components for footwear, rubber plates, seals and hoses for various purposes, etc.). This paper presents a study on the influence of the vulcanization method on the characteristics of a natural rubber blend. The tested methods have been: (1) with sulphur and vulcanization accelerators, (2) with benzoyl peroxide in the presence of a polyfunctional monomer. Modification of characteristics was analysed depending on the crosslinking method.

Keywords: natural rubber, vulcanization, characteristics

INTRODUCTION

Natural rubber is the most frequently used elastomer worldwide due to its low cost, renewability, non-toxicity and excellent physical properties. This elastomer is obtained from a series of laticifers, such as *Hevea brasiliensi*, *Sf Ficus elastica*, etc. Natural rubber is a diene polymer with the structure of cis-poly(isoprene). Natural rubber is used in the carcass of passenger car cross-ply tires for its building tack, ply adhesion, and good tear resistance. It is also used in the sidewalls of radial ply tires for its fatigue resistance and low heat buildup. In tires for commercial and industrial vehicles, natural rubber content increases with tire size. Almost 100% natural rubber is used in the large truck and earthmover tires which require low heat buildup and maximum cut resistance. Natural rubber is also used in industrial goods, such as hoses, conveyor belts, and rubberized fabrics; engineering products, for resilient load bearing and shock or vibration absorption components; and latex products such as gloves, and adhesives. The macromolecular chains that make up the rubber structure harden at temperatures below 10°C, when a “frozen” structure with low elasticity is obtained. To prevent the slip of macromolecular chains and to improve elastic properties, natural rubber is vulcanized. Physical properties of vulcanized rubber systems are influenced by the curing process and chemical nature of the formed crosslinks. The bond strength of linkages can help predict the performance of a given vulcanizate in specific applications. Peroxide cured systems are often employed in static or compressive conditions where low set and heat resistance are required. A network derived from polysulfidic linkages is preferred for components subject to dynamic strain where improved flexural fatigue and tear properties are desired. Bond dissociation energies are often used to quantify the strength of the crosslinks and differentiate the systems (Henning and Shapot, 2005; Palys and Callais, 2003; Dluzneski, 2001). Carbon-

Influence of Crosslinking Method on the Properties of Natural Rubber Mixtures

carbon linkages possess high dissociation energies and resist failure to a limiting point, then fail catastrophically. Having lower dissociation energies, polysulfidic bonds break more readily under strain, but due to their chemical nature, also possess the ability to reform and alleviate stresses (Cooper, 1958; Bateman, 1963).

This paper presents a study on the influence of the vulcanization method on the characteristics of a natural rubber blend.

EXPERIMENTAL

Materials

To obtain rubber mixtures the following materials were used:

- Natural rubber (NR) for pharmaceutical use, Crep from Sangtvon Rubber Ltd, in the form of white rubber sheets, Mooney viscosity 67.64 ML (1'+4') 100°C, volatile matter content of 0.5%, nitrogen content 0.45%, ash content of 0.25%, impurity content of 0.026%;
- Starch - produced by Lach-Ner - soluble potato starch (water insoluble substances 0.28%; loss on drying 16.9%, easily biodegradable: BOD₅ – 0.6 g/g – and COD – 1.2 mg/g) plasticized with glycerin: produced by SC CHIMREACTIV SRL (free acidity 0.02%, density 1.26 g/cm³, purity 99.5%); the starch was dried at 80°C for 24 h, then mixed with glycerine for 7 min at 2000 rpm and 70°C until obtaining a homogeneous mixture.
- Richon IPPD antioxidant (4010 NA) N-isopropyl - N-phenyl - phenylene diamine, 98% purity, molecular mass 493.6374;
- Curing activator: zinc oxide quality I in the presence of stearin;
- Polyethylene glycol coupling agent PEG 4000;
- For crosslinking blends, the following were used: (a) Perkadox 40 benzoyl peroxide (density 160 g/cm³, 3.8% active oxygen content, 40% peroxide content, pH 7) and two types of polyfunctional monomers with the characteristics presented in Table 1, (b) sulphur and 4 types of curing accelerators presented in Table 2.
- Maleated natural rubber (NR-g-AM) was obtained by roll mixing NR with 5 phr (parts per 100 parts of rubber) of maleic anhydride for synthesis, S6855208, produced by Merck KGaA, Germany (melting point 52°C) and 0.75 phr of Perkadox 40; the resulting mixture was kept at a temperature of 160°C for 30 minutes and then used as such.

Table 1. Chemical structure, molecular weight and boiling points of the polyfunctional monomers used in the experiments

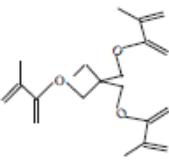
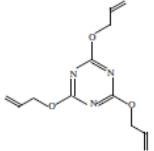
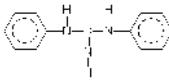
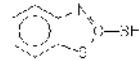
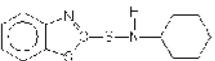
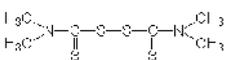
Polyfunctional monomer	Chemical structure	Chemical characteristics
Trimethylolpropane trimethacrylate Luvomaxx TMPT DL 75 (TMPT)		Molecular weight: 338.4 Boiling point: 200°C 75 ± 3 % active ingredient 22 % of ash pH 9.2 Density: 1.36 g/cm ³ Volatility: moderate
Triallylcyanurate Luvomaxx TAC DL 70 (TAC)		Molecular weight: 249.27 Boiling point: 119-120°C Density: 1.34 g/cm ³ 26 % of ash 30 % active synthetic silica Volatility: moderate

Table 2. Accelerators used in sulfur curing

Accelerator	Chemical Structure	Property
a) Diphenyl guanidine (DPG) Group: Guanidines. Speed: Scorchy & Slow cure rate.		Molecular weight: 211.27 Melting point: 148°C Density: 1.15 g/cm ³
b) 2- Mercaptobenzothiazole (MBT) Group: Thiazoles. Speed: Scorchy Ultra fast		Molecular weight: 167.2 Melting point: 177-182°C Boiling point: 302°C Density: 1.42 g/cm ³
c) N-Cyclohexyl-2-benzothiazole sulfenamide (CBS) Group: Sulfenamides Speed: Delayed Action. Ultra fast.		Molecular weight: 264.4 Melting point: 97-105°C Density: 1.31 g/cm ³
d) Tetramethylthiuram disulfide (TMTD) Group: Thiurams Speed: Ultra fast		Molecular weight: 240.4 Melting point: 155-158°C Boiling point: 129°C Density: 1.43 g/cm ³

Obtaining Mixtures

Mixtures have been made by means of blending technique, on a laboratory roll. Table 3 presents mixture formulations. The operating mode was: (1) natural rubber (NR) and maleated natural rubber (NR-g-AM) are bound on the roll and homogenized for 3', (2) zinc oxide, stearin, PEG 4000 and antioxidant are added and embedded in the blend, the time needed being 2', (3) glycerine-plasticized starch is added and embedded for 10' (4) curing agents are added for 2', (5) homogenization of the blend and taking it off the roll in the form of a sheet, time needed about 3'. Work parameters on the roll were: friction of 1:1.1 and roller temperature of 30-50°C.

Table 3. Formulations

Mixture symbol	P (phr)	PT1 (phr)	PT2 (phr)	S1 (phr)	S2 (phr)	S3 (phr)	S4 (phr)	S5 (phr)
NR	95	95	95	95	95	95	95	95
NR-g-AM	5	5	5	5	5	5	5	5
Glycerine-plasticized starch	30.8	30.8	30.8	30.8	30.8	30.8	30.8	30.8
Perkadox 40	8	8	8	-	-	-	-	-
TMPT	-	3	-	-	-	-	-	-
TAC	-	-	3	-	-	-	-	-
ZnO	1	1	1	5	5	5	5	5
Stearic acid	0.1	0.1	0.1	0.5	0.5	0.5	0.5	0.5
PEG 4000	3	3	3	3	3	3	3	3
Sulphur	-	-	-	2.5	2.5	2.5	2.5	2.5
DPG	-	-	-	-	0.5	0.5	-	-
MBT	-	-	-	0.5	0.5	0.5	0.5	0.5
TMTD	-	-	-	0.5	-	0.5	-	0.5
CBS	-	-	-	-	-	-	0.5	0.5
Antioxidant 4010 (g)	1	1	1	1	1	1	1	1

Preparation of Tensile Test Sample

For quality control of elastomer blends, plates have been made by compression, using a hydraulic press; work parameters were: work temperature 165°C, pressure of 150 MPa and vulcanization time was determined with Monsanto rheometer.

Testing

Tensile measuring and tearing strength test was carried out with a Schoppler strength tester with testing speed 460 mm/min, using dumb-bell shaped specimens according to ISO 37/2012, respectively angular test pieces (type II) in according to ISO 12771/2003. The hardness was determined using a hardness tester according to ISO 7619-1/2011 on samples with thickness of 6 mm. The unit of hardness was expressed in A Shore. Elasticity was estimated with a Schob test instrument on 6 mm thick samples, according to ISO 4662/2009. Curing characteristics were determined by an oscillating disk rheometer (Monsanto), according to ISO 3417/1997. Delta torque or extent of crosslinking is the maximum torque (MH) minus the minimum torque (ML). Optimum cure time (t_{90}) is the time to reach 90% of the delta torque above minimum.

RESULTS AND DISCUSSIONS

Rheological Characteristics

Rheological characteristics of blends crosslinked with peroxide and with sulphur respectively, obtained by means of Monsanto rheometer are presented in Table 4 and Figures 1 and 2. In the case of mixtures crosslinked with peroxide, when introducing polyfunctional monomers / curing co-agents, TAC and TMPT, respectively, there is an increase in the maximum torque, and in the variation of torque, and a decrease of the optimal curing time. The increase in torque level during vulcanization is proportional to the number of cross links formed per unit volume of rubber.

Table 4. Rheological characteristics of blends

Characteristic/Mixture symbol	P	PT1	PT2	S1	S2	S3	S4	S5
M min (dNm)	10.4	10.2	7.5	32.9	11.4	39.3	14.1	32.6
M max (dNm)	21.1	25.6	36.8	34.3	32.5	42.4	28.6	37.1
M (dNm)	10.7	15.4	29.3	1.4	21.1	3.1	14.5	4.5
T_{90} (minutes)	18.29	17.43	16.87	3.71	5.29	1.68	2.8	1.95

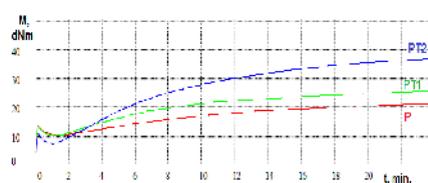


Figure 1. Rheograms of blends crosslinked with peroxide

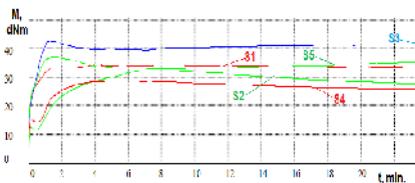


Figure 2. Rheograms of blends crosslinked with sulphur

NR compounds crosslinked with sulfur and curing accelerators show different cure behaviors, as Figure 2 shows. In these types of mixtures, the reversion phenomenon was noticed. Reversion is defined by a loss in physical properties associated with degradation of network integrity. The reversion process is thermally initiated and primarily associated with overcure or high temperature service conditions. Reversion involves reactions that lead to the desulfuration of polysulfidic linkages and main-chain modification (cis-to-trans isomerization) which results in weaker network structures (Mori, 2003; Chen *et al.*, 1981). As desulfuration progresses, the distribution shifts from polysulfidic to mono- and di-

sulfidic crosslinks and eventually crosslink density is also lost. The result is a degradation of physical properties and a decrease in the performance of the rubber article (Shankar, 1952). No such standard procedure exists for the quantification of reversion. To evaluate the value of reversion, the following equation was used in this paper:

$$\text{Degree of reversion (\%)} = (M_H - M_R) * 100 / M_H \quad (1)$$

where M_H is the rheometer maximum torque and M_R is rheometer cure torque at final (measurement) time.

It was noticed that the reversion of natural rubber blends cured with sulphur and curing accelerators varies as follows: S1 (0.01%) S3 (3.3%) S5 (5.66%) S4 (9.09%) S2 (16.92%). Therefore, there was a negligible reversion in mixtures with MBT and TMTD accelerators, and low reversion values for systems of three types of accelerators that also contain TMTD. The optimal curing time was lower than in the case of blends crosslinked with peroxide (Bristow, 1991; Sloan, 1992).

Physical-Mechanical Characteristics

Physical-mechanical characteristics of samples are presented in Table 5.

Table 5. Physical-mechanical characteristics

Characteristic/Mixture symbol	P	PT1	PT2	S1	S2	S3	S4	S5
Hardness, °Sh A	38	49	49	42	43	47	41	47
Elasticity, %	32	30	30	42	32	40	38	46
Tensile strength, N/mm ²	6.3	1.4	2.6	3.3	10.5	8.5	4.3	11.2
Elongation at break, %	620	200	440	660	780	660	780	740
Residual elongation, %	16	16	19	15	26	20	18	60
Tear strength, N/mm	16	9	10	20	20	22.5	21.5	2.3

The data shows that the crosslink type of a rubber vulcanizate determines the physical properties such as hardness, resilience, elongation at break etc.

The carbon-carbon bond is created by a free-radical mechanism, which can be initiated by a peroxide vulcanizing agent. The sulphur crosslinks are developed as previously outlined. The monosulfidic crosslinks are created by using sulphur donors (thiuram disulfide or morpholine disulfide). The di- and polysulfidic crosslinks are created by varying sulphur-accelerator. The results on crosslink type vs. crosslink mobility can be summarized as follows: (1) C-C crosslink limited rotation, (2) C-S-C bond increased rotation, (3) C-S-S-C bond increased rotation, limited linear motion. (4) C-Sx-C bond substantial rotation and linear motion. Crosslink mobility (ability to realign under strain) should further enhance tensile strength (Hertz, 1984; Choi and Choi, 2006; Stelescu *et al.*, 2010; Hofmann, 1967; Van Duin, 2002; Volintiru and Ivan, 1974). Thus, mixtures crosslinked with peroxide had lower values for elasticity, tensile and tear strength. Blends containing polyfunctional monomers have led to higher values of hardness. In the case of mixtures crosslinked with sulphur and curing accelerators, the best values of physical-mechanical characteristics were those for S5 and S3 blends that contain three types of curing accelerators. The best tear strength and hardness were obtained in the case of these mixtures, as well as very good elasticity, tensile strength and elongation at break. Residual elongation has good values for all types of blends, indicating a good return to the initial shape after applying a force, and therefore, good sample vulcanization.

CONCLUSIONS

The study leads to the following conclusions: the advantages of peroxide cure over sulphur cure include simple formulation, long term compound storage stability and possibility of using higher processing temperatures and yet no reversion. Another advantage of peroxide vs. sulphur cures is that the peroxide cures can more easily be made to impart better heat aging resistance. The reason is that the carbon–carbon bond strength is about 350 kJ/mol vs. sulphur–sulphur bond strength of only 115–270 kJ/mol and carbon–sulphur bond strength of only 285 kJ/mol (Palys, 2009). In contrast, in the case of curing with sulphur and curing accelerators, better physical-mechanical properties were obtained due to crosslink mobility, and the optimal curing time had lower values compared to peroxide crosslinking.

Acknowledgements

This research was financed through Nucleu Program 2016-2017 PN 16 34 01 01: “Development of biodegradable nanocomposites based on natural rubber, starch and OMMT with applications in the food and pharmaceutical industries” supported by Romanian Ministry of Education.

REFERENCES

- Bateman, L. (1963), *The Chemistry and Physics of Rubber-Like Substances*, MacLaren, London.
- Bristow, G.M. (1991), “Influence of Grade of Natural Rubber on Reversion Behavior”, *Journal of Natural Rubber Research*, 6(3), 137-151.
- Chen, C.H., Koenig, J.L., Shelton, J.R. and Collins E.A. (1981), “Characterization of the Reversion Process in Accelerated Sulfur Curing of Natural Rubber”, *Rubber Chemistry and Technology*, 54(4), 734-750.
- Choi, S.S., Choi, S.J. (2006), “Influence of Silane Coupling Agent Content on Crosslink Type and Density of Silica-Filled Natural Rubber Vulcanizates”, *Bulletin of the Korean Chemical Society*, 27(9), 1473-1476.
- Cooper, W. (1958), “Copolymers of butadiene and unsaturated acids: Crosslinking by metal oxides”, *Journal of Polymer Science Part A: Polymer Chemistry*, 28(116), 195-206.
- Dluzneski, P.R. (2001), “Peroxide Vulcanization of Elastomers”, *Rubber Chemistry and Technology*, 74(3), 451-492.
- Henning, S.K. and Shapot, S.A. (2005), *Multifunctional Acrylates as Anti-Reversion Agents in Sulfur Cured Systems*, The Fall 168th Technical Meeting of the Rubber Division, American Chemical Society, Pittsburgh.
- Hertz, D. (1984), “Vulcanization - In Theory and Practice”, *Elastomerics*, 116(11), 17-21.
- Hofmann, H. (1967), *Vulcanization and vulcanizing agents*, MacLaren and Sons Ltd, London, Palmerton Publishing Co. Inc., New York.
- Mori, M. (2003), “Study of Vulcanization and Degradation Chemistry in Natural Rubber by Solid-State C NMR and Physical Property Measurements”, *Rubber Chemistry and Technology*, 76(5), 1259-1275.
- Palys, L.H. (2009), “Peroxide Cure Systems”, in: J.S. Dick (ed.), *Rubber Technology, Compounding and Testing for Performance*, Hanser Publications, Munich, 434.
- Palys, L.H. and Callais, P.A. (2003), “Understanding organic peroxides to obtain optimal crosslinking performance”, *Rubber World*, 229(3), 35-41.
- Shankar, U. (1952), “Investigations of the Reversion of Vulcanized Rubber under Heat”, *Rubber Chemistry and Technology*, 25(2), 241-250.
- Sloan, J.M. (1992), “Reversion Studies of Natural and Guayule Rubbers”, Accession number ADA257501, U.S. Army Materials Technology Laboratory: Polymer Research Branch.
- Stelescu, M.D., Georgescu, M. and M n il , E. (2010), “Aspects regarding crosslinking of a natural rubber blend”, *Proceedings of the 3rd International Conference on Advanced Materials and Systems*, Bucharest, 313-318.
- Van Duin, M. (2002), “Chemistry of EPDM Cross-linking”, *Kautschuk Gummi Kunststoffe*, 55(4), 150-156.
- Volintiru, T. and Ivan, Gh. (1974), *Technological Bases for Processing Elastomers*, Technical Press, Bucharest.