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Effect of different curing systems on the mechanical and physico-chemical properties of acrylonitrile butadiene rubber vulcanizates

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ABSTRACT

In the present study, the effect of different curing systems including sulfur, dicumyl peroxide, dicumyl peroxide/coagent and radiation/coagent on the mechanical and physico-chemical properties of acrylonitrile butadiene rubber (NBR) was studied. In order to correlate, the effect of curing systems on rubber, the comparison was carried out at comparable value of volume fraction of rubber in swollen gel (V_r) for NBR vulcanizates. Mechanical properties like tensile strength, elongation at break, modulus, Young's modulus, tearing strength and abrasion loss of vulcanizates have been followed up for comparison. In addition, physico-chemical properties like swelling ratio, soluble fraction, and cross-link density were investigated. On the other hand, the effects of fuel, thermogravimetric analysis, and thermal ageing have been studied.

1. Introduction

Acrylonitrile butadiene rubber (NBR) has excellent oil resistance. However, shows no self-reinforcing effect, as there is no crystallinity, but when used in combination with reinforcing fillers, vulcanizates with excellent mechanical properties can be obtained from NBR [1]. Vulcanization occurs by a chemical agent, such as sulfur or peroxide. Alternatively, high-energy radiation, such as electron beam or gamma radiation can be used to vulcanize rubbers [2].

The use of organic peroxide as a cross-linking agent through a free radical process is also largely developed. The vulcanization rate is controlled essentially by the decomposition of the peroxide at a given temperature [3]. Compared with sulfur vulcanization, crosslinking by peroxides is a relatively simple process, with physical properties such as high modulus, low compression set and heat ageing properties superior to sulfur cure systems. On the other hand, the peroxide crosslinking has many disadvantages, such as low tensile and tear strength, and flex resistance, which have restricted their use in diene rubbers. Many unsaturated rubbers, such as natural rubber (NR), styrene–butadiene rubber (SBR), butadiene rubber (BR), and acrylonitrile butadiene rubber (NBR), contain a varying degree of unsaturation in the polymer backbone or in pendant positions. Peroxide radical could potentially react by addition to a double bond or by abstraction of an allylic hydrogen, and both mechanisms occur concurrently in the vulcanization of unsaturated elastomers [4].

The use of coagents in conjunction with peroxides to cure elastomers has been common practice in the rubber industry for many years. Coagents are typically multifunctional vinyl monomers that are highly reactive toward free radicals and readily graft to elastomer chains to form a complex crosslinked network. These coagents with peroxide are used to improve the physical properties and processability of peroxide-cured elastomers. Also, they increase not only the crosslinking efficiency of the vulcanization process but the cross-link density as well [5].

During this last decade, the crosslinking of rubbers by means of electron beams has strongly developed in place of the use of crosslinking agents, such as sulfur or peroxides. NBR belongs to the crosslinking type rubbers when exposed to high-energy radiation [6]. Compared with the conventional chemical processes such as peroxide [7] or sulfur [8] induced vulcanization used for crosslinking rubber, radiation crosslinking has the advantages of being faster and being more versatile, leads to more uniform crosslinking, consumes less energy, and occupies less floor space for processing.

Inherently waste free nature of the technology makes it less polluting than the conventional technologies. The disadvantage is that the physical properties of radiation vulcanized rubber were adversely affected by the high crosslinking dose required. To overcome this problem, several authors [9] have reported that polyfunctional monomers PFMs (coagents) such as multifunctional acrylates and methacrylates are useful to obtain optimum mechanical properties at lower dose levels. These PFMs form a network structure with polymeric materials at a lower dose because of its higher reactivity [10] and the resulting structure is useful for the improvement of mechanical properties as well as thermal stability [11] .

This article is a comparative study between the different techniques to vulcanize NBR rubber.

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2. Experimental

2.1. Materials

Acrylonitrile butadiene rubber (NBR) of Europrene N3345 from Enichem company Inc, Italy having (acrylonitrile content-34%, Mooney viscosity (ML (1 + 4) at 100 °C-46). Zinc oxide was supplied from Shijiazhuang Golden Color Chemical Co., Ltd., China, its concentration 99.7% in appearance of white powder. Stearic acid obtained from Hebei Liancheng Chemical Co., Ltd., China, it has small flakes shape and melting point 56 °C. Dioctyl phthalate (DOP) was supplied by Henan Tianfu Chemical Co., Ltd., China; it has acidity 0.01 maximum and ester value 99.5%. Sulfur was supplied by standard chemical company private Ltd., Madras. Mercapto benzothiazyl disulphide (MBTS) was obtained from Bayer India Ltd., Bombay. Tetra methyl thiuram disulphide (TMTD) was supplied by NOCIL, Bombay, India. 1,2-dihydro.2,2,4-trimethyl quinoline (TMQ) as antioxidant was obtained from Intatrade Chemicales (GmbH), Germany.Carbon black (N 375). The peroxide cross-linking agent was dicumyl peroxide [DCP] from Aldrich (Germany), its purity 99%. The polyfunctional monomer PFM (coagent) was penta erythritol triacrylate PETRA from Aldrich with a molecular weight of 298.29 g/mol and a density of 1.167 g/cm^3.

2.2. Compounding and curing

The compounding recipes of mixes are given in Table 1, the codes letters S, P, P-PFM and R-PFM represent the sulfur, dicumyl peroxide, dicumyl peroxide coupled with coagent and radiation vulcanized system respectively. The subscript indicates the weight in phr (part per hundred part of rubber) for sulfur, and dicumyl peroxide corresponding to each designation code; while subscript in case of radiation vulcanization indicate the radiation dose.

Mixing was carried out at room temperature using a two-roll mixing rubber mill having a friction ratio 1:1.4. The compounded mixes as follow

2.2.1. Sulfur and peroxide curing

The compounded mixes with different amounts of curing system were compression molded using an electrically heated hydraulic press at 160 °C under pressure 120 kg/cm^2 for their optimum curing times i.e. 5 min. for sulfur cured system and 20 min for peroxide and peroxide coupled with coagent cured systems.

2.2.2. Radiation curing

The compounded mixes were compression molded between aluminum foil at 160 °C under pressure 120 kg/cm^2. Irradiation was carried out in air at ambient temperature on the electron beam accelerator (1.5 MeV, 3 mA) facility installed at the National Center for Radiation Research and Technology, Cairo, Egypt. The irradiation was performed to give a total dose of 25 kilo gray (kGy) for each pass. Multiple passes obtained the total irradiation doses 25, 50, 75, 100 and 150 kGy for different measurements.

2.3. Measurements

2.3.1. Mechanical properties

The tensile strength was measured using dumbbell shaped test pieces at a crosshead speed of 500 mm/min at 25 ± 2 °C using tensile testing machine HOUNS FILD, England. The tearing strength (load at failure/thickness) of the samples was determined using unnicked 90 °C angle test pieces according to ASTM D 624-81. The experimental conditions for the tear measurements were the same as that of the tensile testing. The hardness of the samples was measured according to ASTM D 2240-2000 using durometer type A, and the units of hardness was expressed in shore A.

2.3.2. Physico-chemical measurements

2.3.2.1. Soluble fraction. Measurements of soluble fraction were carried out as follow, the cured samples, about 0.2 g were accurately weighed (W_o) and placed in a special stainless grids. The grids containing samples are transferred to special round flask 2/3 filled with acetone. The heating was carried out under reflux for 24 h. After extraction, the samples were dried to constant weight (W_1) in dry oven at 50 °C. The soluble fraction was calculated as follow:

$$\text{Soluble fraction} = W_o - W_1/W_o \tag{1}$$

2.3.2.2. Determination of cross-link density (v). The volume fraction of rubber in swollen network of the vulcanizates V_r, was determined by means of equilibrium swelling in acetone laboratory grade at 25 °C. The equilibrium swelling was used to calculate the cross-link density, which is the number of network chain density by applying the Flory–Rehner equation [12] as follow:

$$v = -1/V_s\left[\frac{\ln(1-V_r)+V_r+\chi_1 V_r^2}{V_r^{1/3}-V_r/2}\right] \tag{2}$$

where, v = cross-link density; χ_1 = polymer–solvent interaction parameter; V_s = molar volume of solvent; V_r = volume fraction of rubber in the swollen gel; V_r was calculated using the relation

$$V_r = \frac{(D_s - F_f A_w)\rho r^{-1}}{(D_s - F_f A_w)\rho r^{-1} + A_s \rho s^{-1}} \tag{3}$$

where V_r, D_s, F_f, A_w, A_s, ρ_r and ρ_s are volume fraction of rubber, deswollen weight of the sample, fraction of insoluble, sample

Table 1
Formulation of the mixes.

Code formulation (phr)*	S_1	$S_{1.5}$	S_2	P_1	$P_{1.5}$	P_2	P_1-PFM	$P_{1.5}$-PFM	P_2-PFM	R_{25}-PFM	R_{50}-PFM	R_{75}-PFM	R_{100}-PFM	R_{150}-PFM
NBR	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2
TMQ	1	1	1	1	1	1	1	1	1	1	1	1	1	1
DOP	6	6	6	6	6	6	6	6	6	6	6	6	6	6
MBTS	1	1	1	–	–	–	–	–	–	–	–	–	–	–
TMTD	0.5	0.5	0.5	–	–	–	–	–	–	–	–	–	–	–
Sulfur	1	1.5	2	–	–	–	–	–	–	–	–	–	–	–
HAF	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Peroxide (DCP)	–	–	–	1	1.5	2	1	1.5	2	–	–	–		
PETRA	–	–	–	–	–	–	5	5	5	5	5	5	5	5
Irradiation dose (kGy)										25	50	75	100	150

* phr = part per hundred part of rubber.