

EFFECTS OF PROCESSING ADDITIVES ON THE PROPERTIES OF NATURAL RUBBER (NSR 20)

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Commercial sample of unprocessed natural rubber (polyisoprene) NSR 20 compounded into base polymer was processed into sheets using various vulcanizing and plasticizing additives. Physical testing of the vulcanized rubber samples was carried out on an Instron testing machine for tensile properties. Tests were also carried out to assess the effects of plasticizer additives on the rheological properties of the processed rubber. Tensile strength and modulus at break % increase steadily with increase in sulphur level up to 5 pphr (parts per hundred rubber) and fall gradually when sulphur level exceeds 10 pphr but elongation at break decreases accordingly. Dioctylsebacate (DOS) and Dioctyladipate (DOA) are quite effective as plasticizers in reducing the viscosity, T_g (glass transition temperature) and hardness of the rubber while Dibutoxyethoxyethyladipate (Bisoflex III) is less effective.

Key words: Natural rubber, Viscoelasticity, Vulcanization, Plasticization.

Introduction

Natural rubber (cis-1, 4 Polyisoprene) is a viscoelastic colloidal polymer which in its natural state possesses a number of undesirable properties namely, hardening in the cold and becoming 'tacky' in hot weather. Rubber appear to be highly elastic when handled, but when subjected to a tensile or compressive force for an appreciable length of time, their molecules slide past one another i.e. undergo viscous flow and on removal of the force, 100% recovery is not achieved (Anon 1986). These various undesirable effects can be corrected by the addition of certain chemical agents to the rubber mix in a process of vulcanization. Vulcanization introduces covalent crosslinks between the molecules and limit their relative movements making the rubber insoluble and infusible. It also prevents oxidation of the rubber by oxygen and ozone, a process that leads to premature ageing of the polymer. The chemistry of vulcanization is complex and has not been well understood throughout the years of its practice since its discovery in 1839 by Charles Goodyear. The profound effects of the process, however, are clear that it decreases the flow of rubber, increases its tensile strength and modulus but prevents extensibility (Austin 1985).

Experimental

In two separate experiments, the natural rubber base polymer NSR20 was first modified in one of the experiments by vulcanization and in the other by incorporation of certain plasticizers. The effects of these modifications were subsequently assessed on both the tensile and rheological properties of the polymer.

Vulcanization. The base rubber was modified using the recipe contained in Table 1.

Table 1
Vulcanization recipe for natural rubber NSR20

Ingredients	Parts per hundred base polymer (rubber) pphr	Role performed
Natural rubber (NSR20)	100.00	Base polymer
Carbon black(HAF)	40.00	Reinforcing filler
Aromatic oil(Durex 729)	5.00	To enhance miscibility of filler into rubber and speed up rate of mastication
Zinc oxide	2.00	Vulcanization activator
Stearic acid	2.00	An accelerator
N-isopropyl-N-phenyl-p-phenylenediamine (IPPD)	1.00	An antioxidant/antiozonant
N-cyclohexyl-2-benzthi-azly	0.50	Delay action accelerator
Sulphur	2.0-25.0	Vulcanizing/curing agent.

Before compounding, the commercial sample of natural rubber (NSR 20) used and the processing chemicals were tested to ensure their conformity to certain expected standards and specifications described elsewhere (Billmeyer 1971).

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After ascertaining the purity of all the ingredients shown in Table 1 they were compounded into the base polymer first by premasticating the rubber crump using 8" by 16" open two roll mill followed by master batching of the resultant masticated rubber which involved mixing of the rubber with other ingredients except the curatives. This was done on the same size of two roll mills used for premasticating. This stage was followed by mixing together the masterbatch and the curatives. Finally, vulcanization of the rubber mix was carried out in the laboratory on compression molding machine at 150°C and 150 psi for 15 min (Evans 1981).

Tensile testing of the vulcanized rubber. The rubber vulcanizates containing varying concentrations of the curing agent (sulphur) were subjected to the following tensile tests according to ISO standard using Dumbell specimen. (a) Tensile strength using Dunlop Tensiometer, (b) Modulus at 300% extension, (c) Elongation at break, (d) Hardness test using Wallace urometer. The results obtained from the tests are shown in Table 2.

Rheological study of the plasticized rubber. Sequel to the measurement of the tensile properties of the vulcanized natural rubber NSR 20, the commercial sample of the polymer was modified using four plasticizers of varying proportions (Table 3) namely DOP (Dioctylphthalate), DOA (Dioctyladipate), DOS (Dioctyl sebacate) and Bisoflex III (Dibutoxyethoxyethyl adipate). Weighing, compounding and mixing processes were as described for the vulcanization process.

Determination of glass transition temperature, T_g and viscosity. The glass transition temperature of the samples was determined using thermal analysis scanning machine of the Toyo mechanical Rheovibron DDV-Type-II Viscoelastometer. Measurement of the loss tan. σ of samples under varying temperatures was taken until peaks were obtained in the value of this parameter usually associated with the temperature of glass-rubber transition. The viscosity of the samples was determined using Mooney viscometer by ASTM PI645.

Results and Discussion

The results of the effects of the curatives on tensile properties of natural rubber NSR20 are shown in Table 2.

Tensile strength and modulus at 300% extension show the same trend, both increase steadily with increase in sulphur content compared with the uncured (unvulcanized) rubber. They attain maxima in their values up to 10 pphr sulphur content and thereafter fall gradually when sulphur level exceeds that value. This observation is graphically shown for tensile strength values (Fig. 1).

The development is in agreement with the effect created by the increase in the network density introduced into the polymer by the curing agent (sulphur) since the network structure is supposed to reinforce intermolecular forces as a result of the bridging effect. The fall in these values after attaining this peak, however, can be attributed to the fact that during

Table 2
Effect of vulcanizing agents on the tensile properties on natural rubber (NSR 20)

Sulphur levels (pphr)	0	2.00	5.00	10.00	15.00	20.00	25.00
Tensile Strength (Mpa)	23.8	25.10	28.50	29.30	27.20	23.60	20.30
Modulus at 300% (Mpa)	7.6	8.32	9.02	9.40	8.70	7.60	6.50
Elongation at break, %	780.0	607.00	498.00	300.00	46.10	12.00	3.00
Hardness (shore)	53.50	57.50	64.50	69.00	74.00	79.00	82.00

Table 3
Effects of DOP and DOA on rheological properties of natural rubber (NSR20)

Formulation	1	2	3	4	5	6	7
DDP(pphr)	--	10	20	30	--	--	--
DDA(pphr)	--	--	--	--	10	20	30
Moony viscosity	52	38	28	23	34	27	18
T _g °C	-26	-34	-42	-46	-42	-54	-58
Hardness (IRHD)	54.4	46.4	41.4	36.4	44	40	34

Table 4
Effects of DOP and bisoflex III on rheological properties of natural rubber (NSR20)

Formulation	1	2	3	4	5	6	7
DOS(pphr)	--	10	20	30	--	--	--
Bisoflex III(pphr)	--	--	--	--	10	20	30
Moony viscosity	52	36	27	22	36	26	22
T _g °C	-26	-43	-52	-54	-38	-50	-57
Hardness (IRHD)	52.4	45.4	38.4	34.4	45	39	35

the curing reaction, only an optimum quantity of the curative is sufficiently and homogeneously soluble in the rubber mix to effect maximum impact. This value for sulphur-rubber mix has been found to be about 8pphr of sulphur (Gellings, Metherel 1991). Beyond this critical value, the excess sulphur curative crystallizes out from the rubber once a particular vulcanization temperature is attained. The excess sulphur has been shown to cause local concentration on the rubber which subsequently acts as vulcanization inhibitor leading to a reversion of the vulcanization process and a fall in these parameters.

There is a sharp drop in the value of elongation at break percent on vulcanization from 780% for the raw rubber to less than 50% at 15 pphr sulphur content before a gradual slowing down afterward (Table 2 and Fig. 2). Since vulcanization process is to introduce effectively sulphur-S-bridging groups all over the polymer structure, the treatment is expected to lead to a drastic fall in the polymer's extensibility as a result of the curtailment of the sliding of the molecules past each other by virtue of the curing agent. Furthermore, the chain entanglements which are present in the raw rubber become elastically effective when trapped between low degree of crosslinks, they can no longer unravel when the network is deformed. The gradual settling down in elongation at break percent values following the initial drastic fall can be due to excessive crosslinkage resulting from high sulphur level stiffening the molecules of the rubber. The excess sulphur present as curative as noted earlier crystallizes out at a critical temperature of vulcanization and this may become attached to the main chain as pendant groups. They present weak secondary interaction between neighbouring rubber chains that can lead to a reversion in network stiffness and additional source of hysteresis.

The increase in the network density occasioned by the excessive crosslink also explains the steady increase observed in

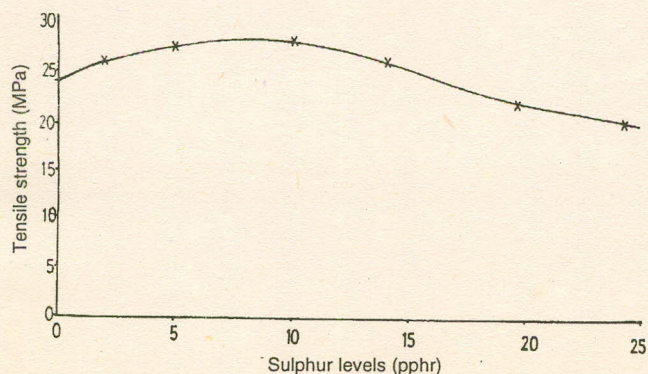


Fig 1. Graph of tensile strength (MPa) versus sulphur level (pphr).

the values of the hardness of the vulcanized rubber over the unvulcanized one.

Effects of plasticizers on rheological properties. Plasticizers are low molecular weight diluents which are added to polymers during processing to lubricate their molecular chains and enhance flow which is often measured in terms of the viscoelastic properties of the polymer. The four commercial plasticizers used in this study i.e. DOA, DOS, DOP and Bisoflex III seem to produce parallel effects on the glass transition temperature T_g , the viscosity index and the hardness of the modified polymer (Tables 3 and 4). The effect of the plasticization treatment on the viscosity of the modified rubber is also shown by the graph (Fig. 3).

During the plasticization, intermolecular forces are effectively reduced by the chemical additives leading to the increased apparent free volume and hence a reduction in T_g , viscosity and hardness of the polymer. The comparative parallel performance of the plasticizers on the rubber may also be

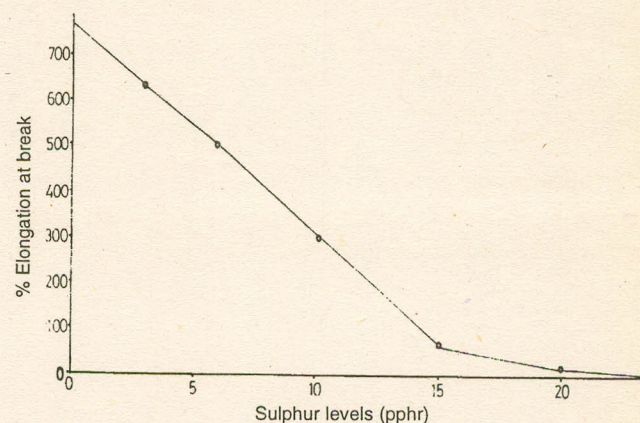


Fig 2. Elongation at break (%) versus sulphur level (pphr).

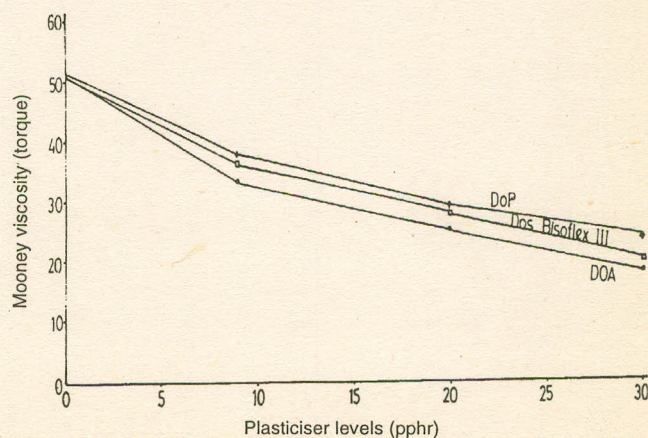


Fig 3. Graph of Mooney versus plasticisers level (pphr).

attributed to a possible similarity in their solubility parameters (Lewis 1986).

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