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Modified Lacs as Compounding Ingredients of Styrene-Butadiene Rubber: Part I — Epoxidized Lac in Gum Stock

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The processability as well as the performance and ageing characteristics of rubber compositions are known to be improved on incorporating resins as compounding ingredients. The relative effectiveness of shellac and epoxidized lac in improving the characteristics of styrene-butadiene rubber has been examined. The results obtained indicate that epoxidized lac brings about greater improvement in the modulus, tensile strength, tear resistance and hardness of the rubber than straight shellac. With both shellac and epoxidized lac, better results are obtained using CBS as the accelerator than with MBT.

THE advantages of incorporating resins in rubbers are well recognized. Among the benefits that resins confer to the rubbers are ease of processing and ability to produce light coloured, tough and light weight articles. Sometimes, resins also act as reinforcing agents and improve the ageing behaviour of rubber.

The possibility of using shellac in natural[1-7] and synthetic rubbers[8-12] has been explored by some workers. Modified lacs, such as lac ester[9,10] give more promising results in this respect. Epoxy resins have several desirable physical properties, such as good strength, excellent adhesion, high hardness and outstanding chemical resistance. Mika[13] investigated the possibility of using epoxy resins in synthetic rubber compositions. The modification of lac through the addition of epoxy resins lowers its acidity due to the reaction of the carboxyl group of lac with the epoxy group of the resin. This is desirable, as carboxylic groups are known to interfere in the vulcanization process. Similar modification was tried by Tripathi and coworkers[14] in the case of materials to be used in surface coatings.

The present paper presents the results of a study on the compounding of lac modified with epoxy resin with styrene-butadiene rubber (1502) in gum stock using two accelerators, cyclohexyl benzthiazyl sulphenamide (CBS) and mercaptobenzthiazole (MBT). The performance of the compounded rubber has been compared with that obtained using straight (unmodified) shellac.

Table 1 — Effect of incorporation of shellac or epoxidized lac on the properties of rubber

(*Base mix composition*: *Styrene-butadiene rubber*, 100; *zinc oxide*, 4; *sulphur*, 2; *stearic acid*, 1; *PBN*, 1; *and accelerator*, 1·5 *parts*)

Shellac or epoxidized lac added part/100 parts rubber	Optimum cure time (at 140°C.) *min.*	Modulus (at 200% elongation) *kg./cm.²*	Ultimate elongation %	Durometer hardness	Impact resilience %	Abrasion loss ml./1000 revolutions	Immersion behaviour (wt increase, %)* Benzene	Pet. ether
RESIN, SHELLAC; ACCELERATOR, MBT								
0	45	9·9	450	48	65·3	1·9	405	89
5	45	12·8	430	50	63·5	2·9	460	93
10	45	11·7	450	52	60·1	3·3	588	100
15	45	12·0	650	55	56·8	4·0	640	113
20	45	12·9	1100	58	53·5	5·0	700	130
RESIN, EPOXIDIZED LAC; ACCELERATOR, MBT								
5	45	13·5	400	51	67·0	2·9	471	86
10	45	13·0	490	54	60·1	3·6	618	98
15	45	12·4	690	57	56·2	4·1	665	110
20	45	12·3	1000	60	52·0	4·8	750	130
RESIN, SHELLAC; ACCELERATOR, CBS								
0	40	16·4	250	50	72·5	3·0	307	76
5	40	17·8	350	52	68·9	3·5	359	78
10	40	21·0	400	55	65·3	3·9	384	78
15	40	18·8	455	57	62·8	4·5	420	79
20	40	16·4	510	60	61·2	5·5	460	81
RESIN, EPOXIDIZED LAC, ACCELERATOR, CBS								
5	40	17·7	300	53	71·7	3·8	339	75
10	40	21·0	350	56	68·9	4·2	351	74
15	40	19·6	470	59	65·3	4·8	384	73
20	40	19·0	600	63	61·2	5·9	423	73

*The stock was immersed in the solvent for 96 hr at 25 ± 1°C.

Experimental procedure

Materials — The compositions of the various mixes prepared are given in Table 1. Styrene-butadiene rubber (Synaprene 1502) was obtained from *Synthetics and Chemicals*, Barielly. Shellac (fresh *Rangeeni*) prepared by country (*bhatta*) process was used. It was powdered to 30 mesh. The epoxy resin used (Epikote 1001) was obtained from *Burmah Shell*, Calcutta. Epoxidized lac was prepared by fusing shellac and Epikote resin, taken in the ratio 7: 3 at 150 ± 1°C. for 15 min., cooling and powdering to 30 mesh. A typical sample had acid value 40·0, softening point 80-82°C. and melting point 90-93°C. All other chemicals were of commercial grade.

Mixing and vulcanization — Mixing was carried out in a two-roll mill having 35 × 15 cm. rolls revolving at 20 and 25 r.p.m. The stock was first heated to 40-45°C. Shellac was added at a roll temperature of 70°C. and epoxidized lac at 80°C. For the addition of sulphur and accelerator, the stock was cooled and the addition made at 45°C. After completion of mixing, the stock was cooled in running water.

Vulcanization was carried out at 140 ± 1°C. and 4000 lb./sq. in. pressure. The time for optimum cure was determined from the modulus-cure time curve.

Determination of characteristics of compounded rubber — Mooney viscosity was determined at 120 ± 1°C. according to ISO/R-289-1963 using a large rotor and a shearing disc viscometer. Scorch time was also estimated at the same temperature. The modulus, ultimate elongation and tensile strength of the stock were determined according to IS: 3400 (Part I)-1965 using dumb bell specimens.

The hardness was measured by means of Shore A durometer according to IS: 3400 (Part II)-1965. Tear resistance was estimated using unnicked 90° angle specimen according to ASTM designation D 624-54. Abrasion resistance was measured with the Akron-Croydon machine keeping the angle between the test specimen and the abrasive wheel at 20°. The abrasion loss is expressed as volume loss in ml. per 1000 revolutions of the abrasive wheel.

The impact resilience of the various mixes was measured with the Dunlop trypsometer and calculated using the relation

$$\frac{1-\cos \text{ angle of rebound}}{1-\cos \text{ original angle}} \times 100.$$

For studying the swelling behaviour of the various compositions, benzene and petroleum ether (b.p. 60-80°C.) were used. The percentage increase in weight obtained on immersing the specimens in the liquids at 25 ± 1°C. for 96 hr in the dark was determined.

Results and discussion

Optimum time for vulcanization — The results presented in Table 1 indicate that the time for optimum cure is independent of the proportion of shellac or epoxidized lac in the mix. Carboxyl groups tend to interfere in vulcanization, while hydroxyl groups accelerate it. Shellac has both these groups. Apart from shellac, zinc oxide (basic) and stearic acid (acidic) are present in the compositions. A host of reactions are possible between all these substances and possibly the effects of various reactions cancel out one another.

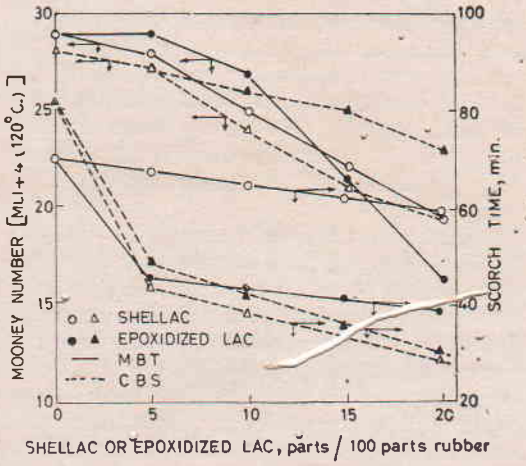

Fig. 1 — Effect of incorporating shellac or epoxidized lac in styrene-butadiene rubber on Mooney viscosity and scorch time of the resulting compositions

In the case of epoxidized lac, there is a reduction in the carboxyl content due to the reaction of some of the epoxy groups with the carboxyl group for lac[14] and this should result in acceleration of vulcanization, but this effect seems to be offset by the reaction of the residual epoxy group with the hydroxyl group of lac in the later stages, thereby lowering the hydroxyl content, which could otherwise have accelerated vulcanization.

Mooney viscosity and scorch time — The data presented in Fig. 1 show that Mooney viscosity falls continuously with increase in the concentration of both shellac and epoxidized lac. The factors contributing to plasticization brought about by shellac are the presence in it of (i) resin part of low molecular weight, (ii) wax (4-5·5 per cent), and (iii) quinone dyes which might act as radical acceptors[15] during the mastication of rubber.

The scorch time falls with increase in the concentration of shellac and epoxidized lac. Epoxidized lac tends to be more scorchy than shellac, because some of the carboxyl groups which can interfere in vulcanization are blocked in it. However, when CBS is used as the accelerator, epoxidized lac is less scorchy than shellac, as the acid and the amine derived by the decomposition of CBS react with the epoxide, thereby leaving less of it to block the carboxyl group of lac.

Modulus and ultimate elongation — Both shellac and epoxidized lac increase the value of modulus (Table 1). With MBT as the accelerator, the optimum value of modulus is obtained at a concentration of 5 parts/100 parts rubber, while with CBS, this is achieved only using 10 parts of shellac or epoxidized lac/100 parts rubber. Epoxidized lac brings about greater increase in the value of modulus than shellac.

The ultimate elongation increases on the addition of shellac or epoxidized lac. The simultaneous increase in the values of modulus and elongation is a unique feature, as most of the reinforcing agents which increase the value of modulus reduce the extent of elongation. This is probably due to the dual character of shellac. Its plasticizing effect increases the extent of elongation, while a number of reactive groups present in it possibly lead to some sort of bonding between its molecule and the

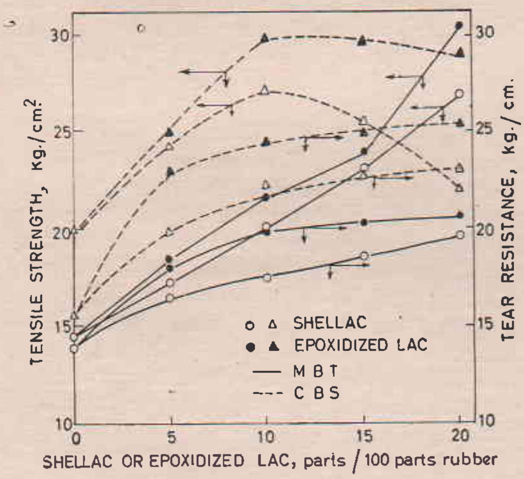

Fig. 2 — Effect of incorporating shellac or epoxidized lac in styrene-butadiene rubber on the tensile strength and tear resistance of the resulting compositions

rubber molecule resulting in increase in stiffness and thereby the modulus.

Tensile strength and tear resistance — A marked increase in the tensile strength and tear resistance of rubber is brought about by the incorporation of shellac or epoxidized lac; epoxidized lac is more effective in this respect (Fig. 2). While with MBT, tensile strength increases continuously with increase in the concentration of shellac or epoxidized lac, with CBS, it increases up to a concentration of 10 parts shellac or epoxidized lac/100 parts rubber and then declines. The tear resistance becomes more or less constant after the incorporation of 10 parts of shellac or epoxidized lac/100 parts rubber.

Hardness, abrasion resistance and impact resilience — An appreciable increase in the hardness of rubber is observed on the addition of shellac or epoxidized lac, the improvement with the latter being more noticeable. The increase in hardness accompanied by a fall in Mooney plasticity of rubber on the addition of shellac or epoxidized lac is in distinct contrast to the normal experience with filler compositions, where increase in hardness brings about simultaneous increase in Mooney viscosity.

The abrasion loss increases with increase in shellac or epoxidized lac loading whichever the accelerator used.

The stock becomes less resilient on the addition of shellac or epoxidized lac; the improvement in this respect is more with epoxidized lac than with shellac.

Swelling — Epoxidized lac reduces the swelling of rubber in petroleum ether when CBS is the accelerator.

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