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Lac and Modified Lacs as Compounding Ingredients for Natural Rubber : Part I–Lac and Ethylene Glycol Modified Lac in Gumstock

B. B. KHANNA

Indian Lac Research Institute, Namkum, Ranchi 10

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The incorporation of shellac or ethylene glycol modified lac in natural rubber gumstock affects Mooney viscosity and scorch time favourably, indicating their possible use as processing aids and antiscorching agents. Shellac also enhances modulus, tear resistance and improves the ageing behaviour of rubber when MBT is the accelerator. With CBS as the accelerator, the addition of 2.5 parts shellac or ethylene glycol modified lac per 100 parts rubber increases modulus, tensile strength and resilience of the compositions. *Kusmi* shellac is slightly better than *Rangeeni* or *Platina* shellacs in affecting the mechanical properties of the natural rubber gumstock.

SHELLAC is a versatile natural resin and one of nature's bounties to India. It is of considerable importance to the economy of the country not only because it fetches Rs 10-15 crores per annum of foreign exchange, but also for its being a source of subsidiary income to some 4 millions of backward tribes people. Due to the development of several synthetics, it has to meet competition from them. Rubber industry is developing fast. If even a small amount of lac can be advantageously put into rubber compositions, it will open up vast avenues for its utilization and may also help in cutting down the import of resins needed by the rubber industry.

The practice of using shellac in rubber compounds appears to be quite old and can be traced back to as early as 1844. Thereafter, for a century, a number of patents were taken out and many claims regarding advantages of the use of shellac in rubber made[1-18]. After 1945 or so, however, very little work appears to have been done on the utilization of shellac in rubber, probably because India lacked the facilities to carry out the researches, while the outside countries started losing interest in shellac — it being an imported commodity for them. Only during the last decade, some studies[20-24] on its use in synthetic rubbers have been made. However, since Scott's work[19] carried out more than a quarter of a centruy back, no further study on the use of shellac in natural rubber has been made. As technology has made tremendous advances during these years, making better compounding ingredients and testing methods available, such a study was considered necessary. Also, a molecule of lac contains one carboxyl, five hydroxyls and one carbonyl group together with unsaturation[25]. It is, therefore, capable of being modified in a number of ways to give a host of products, viz. esters, ethers, metallic salts, etc. The present communication is the first in a series of papers reporting the results of studies on the effect of incorporation of these products and various types of lac into natural rubber.

Experimental procedure

Materials — The compositions of the various mixes prepared are given in Tables 1–3. *Platina* shellac

Table 1—Effect of incorporation of various types of shellac on the properties of natural rubber

[Base mix : Natural rubber (RMI), 100; zinc oxide, 4; sulphur, 2.5; stearic acid, 1; PBN, 1; and shellac, 10 parts]

Type of shellac added	Optimum cure time at 140°C min	Mooney No. ML_1+4 at (120°C)	Scorch time min sec	Modulus at 200% kg/cm²	Elongation at break %	Tensile strength kg/cm²	Tear resistance kg/cm	Durometer hardness	Impact resilience %	Fall in tensile strength on accelerated ageing for 120 hr %
				Accelerator, MBT (0.5%)						
None	30	18.0	8 0	8.5	800	110.0	33.1	36	74.3	93.7
Platina	45	16.5	18 12	7.4	610	73.5	35.0	35	65.3	77.5
Kusmi	45	16.25	17 45	10.0	700	85.7	37.0	36	67.0	71.5
Rangeeni	45	16.5	17 45	7.8	650	85.7	34.8	36	65.3	73.0
				Accelerator, CBS (0.5%)						
None	20	18.5	10 17	9.9	750	141.7	41.2	39	76.2	—
Platina	30	16.8	21 4	6.9	680	95.0	34.1	36	65.3	
Kusmi	30	17.0	19 35	11.1	600	110.8	37.0	38	67.0	
Rangeeni	30	16.5	21 10	8.3	630	98.3	33.8	39	67.0	

Table 2—Effect of incorporation of shellac and ethylene glycol modified lac on the properties of natural rubber using different curing systems

[Base mix : Natural rubber (RMI), 100; zinc oxide, 4; sulphur, 2.5; stearic acid, 1; PBN, 1; and accelerator, 0.5 part]

Shellac or ethylene glycol modified lac added parts/100 parts rubber	Optimum cure time (at 140°C) min	Mooney No. ML_1+4 (at 120°C)	Scorch time min sec	Modulus at 200% kg/cm²	Elongation at break %	Tensile strength kg/cm²	Tear resistance kg/cm	Durometer hardness	Impact resilience %
Resin, shellac; accelerator, MBT									
0	30	19.0	8 0	8.5	800	110.0	33.1	37	74.3
2.5	30	18.5	9 10	9.0	780	100.1	36.9	37	72.5
5.0	30	18.0	10 50	9.5	750	94.3	36.0	36	70.7
7.5	40	17.0	14 0	9.8	730	90.2	35.5	36	68.9
10.0	45	16.5	17 45	10.0	700	85.7	37.0	36	67.0
Resin, ethylene glycol modified lac; accelerator, MBT									
2.5	30	18.5	9 0	6.8	820	105.4	29.6	35	65.3
5.0	30	18.0	10 10	6.7	800	99.9	26.5	35	63.5
7.5	30	17.0	12 15	6.6	780	94.5	26.0	36	61.8
10.0	30	16.0	15 5	6.6	760	87.8	25.2	37	60.1
Resin, shellac; accelerator, CBS									
0	20	18.5	10 17	9.9	750	141.7	41.2	39	76.2
2.5	20	18.0	12 2	12.5	700	144.6	37.2	38	79.9
5.0	30	17.5	14 5	10.7	650	132.1	37.0	37	70.7
7.5	30	17.5	16 35	10.7	630	122.4	36.8	37	68.9
10.0	30	17.0	19 35	11.1	600	110.8	37.0	38	67.0
Resin, ethylene glycol modified lac; accelerator, CBS									
2.5	20	18.0	11 30	13.7	700	148.5	37.6	40	79.9
5.0	30	17.5	13 10	10.5	650	119.4	27.6	38	72.5
7.5	30	17.5	14 45	10.7	650	103.7	27.4	38	72.5
10.0	30	17.0	16 50	10.8	630	100.1	27.0	36	70.7

Table 3—Effect of incorporation of shellac and ethylene glycol modified lac on the properties of natural rubber using a sulphur-less curing system

[Base mix : Natural rubber (RMI), 100; zinc oxide, 4; stearic acid, 1; PBN, 1; and TMTD, 2.5 parts]

Shellac or ethylene glycol modified lac added parts/100 parts rubber	Optimum cure time (at 140°C) min	Mooney No. ML_1+4 (at 120°C)	Scorch time min sec	Modulus at 200% kg/cm²	Elongation at break %	Tensile strength kg/cm²	Tear resistance kg/cm	Durometer hardness	Impact resilience %
Resin, shellac									
0	20	18.8	10 48.5	12.1	600	150.0	30.9	35	78.9
2.5	30	18.5	10 25	12.4	600	121.5	30.6	30	74.3
5.0	30	18.5	10 00	12.3	580	110.2	30.4	31	72.5
7.5	30	18.2	9 40	12.3	550	100.1	30.3	31	70.7
10.0	30	18.0	9 01	12.1	500	88.7	30.1	31	68.9
Resin, ethylene glycol modified lac									
2.5	20	18.0	10 20	12.1	600	128.8	29.4	30	74.3
5.0	30	17.0	10 01	10.7	700	127.0	26.5	31	72.5
7.5	30	16.2	9 40	7.1	750	126.0	23.4	31	70.7
10.0	30	15.5	9 05	6.8	720	120.3	22.0	31	68.9

Table 4 — Properties of various types of lac

	Platina	*Kusmi*	*Rangeeni*
Life under heat, min	26	68	51
Fluidity, mm	32	104	79
Hot alcohol insolubles, %	0.3	0.8	1.06
Wax, %	Nil	3.9	4.7
Colour index	1.1	10	16

(dewaxed, decolorized) was obtained from Angelo Bros., Calcutta and was machine made. *Rangeeni* and *Kusmi* shellacs were prepared by the country (*bhatta*) process. The properties of the three types of shellac used are given in Table 4. These were powdered to 30 mesh before compounding.

The reaction between lac and ethylene glycol was carried out at 180 ± 2°C using conc. sulphuric acid as the catalyst. A Dean and Stark separator was used for driving out the water of reaction; other details were the same as reported by Gidvani[26]. A typical sample of ethylene glycol modified lac thus prepared had acid value 34.0 and hydroxyl value 205.4.

Mixing and vulcanization — Mixing was carried out in a two-roll mill having 35 × 15 cm rolls revolving at 20 and 25 rpm. Rubber was masticated at 45–50°C and the ingredients were then added. Shellac or ethylene glycol modified lac was added prior to the accelerator and sulphur at a roll temperature of 70–75°C. For the addition of sulphur and accelerator, the stock was cooled and the addition made at 45–50°C. Thereafter the stock was taken out and cooled in running water.

Vulcanization was carried out at 140 ± 2°C and 4000 lb/sq in pressure for a specified period. The time at which the tensile strength became maximum was taken as the time for optimum cure.

Testing — Mooney viscosity was determined according to I S : 3660 (Part I–NR : 8)-19 using a large rotor. The temperature of the platens was, however, kept at 120°C to reduce the duration of the experiment. Scorch time was also estimated at the same temperature.

The modulus, elongation at break and tensile strength were determined according to IS : 3400 (Part I)-1965 using dumb bell specimens. The hardness was measured using 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.

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

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

Accelerated ageing test was carried out according to IS : 3400 (Part IV)-1965 in an air oven maintained at 100 ± 1°C.

The properties of shellac were studied according to IS : 16–1956.

Results and discussion

Time for optimum cure — The time for optimum cure is enhanced by the addition of all the three types of shellac to the same extent using any one of the accelerators (Table 1). When ethylene glycol modified lac (hereafter referred to as modified lac) is incorporated, there is no increase in the time of optimum cure with MBT, while an increase is noticed with CBS and TMTD (Tables 2 and 3).

A possible reason for the increase in the time of optimum cure can be the acidity of shellac (acid value 70–72), as carboxyl groups are known to interfere with vulcanization[27]. Modified lac having reduced acid value (34.0) behaves somewhat better than straight shellac in this respect.

Mooney viscosity and scorch time — The Mooney viscosity falls regularly with progressive increase in the concentration of lac or modified lac, indicating their plasticizing effect, which is nearly same with various types of lac and a little more with the modified lac. As lac resin and its modified forms have low molecular weights (1000) and contain long paraffin chains, they act as lubricants and thereby increase plasticity and tackiness.

The scorch time is enhanced with the addition of lac or modified lac with MBT or CBS, the effect being a little more pronounced with the former, while with TMTD, a slight reduction is noticed. The useful antiscorching effect noticed with these resins is a welcome feature.

Modulus and elongation at break — Out of three types of lac tested, only *Kusmi* enhances the modulus on using MBT or CBS, while it remains constant with TMTD. Also the modulus increases with the use of modified lac, when CBS is the accelerator, the optimum value being obtained at a concentration of 2.5 parts/100 parts rubber.

The elongation at break shows a progressive decrease with the incorporation of shellac or modified lac, indicating that their incorporation has a stiffening effect on rubber.

Tensile strength and tear resistance — Using CBS as the accelerator, the incorporation of 2.5 parts shellac or modified lac/100 parts rubber has a beneficial effect on the tensile strength, while with MBT, an increase in tear resistance is noticed with the progressive addition of shellac, *Kusmi* shellac showing the best behaviour in this respect. Using TMTD, the tear resistance is constant when shellac is incorporated.

Hardness and resilience — Hardness remains constant or falls slightly on the addition of shellac. When modified lac is incorporated using MBT, hardness shows a slight increase.

Impact resilience increases on the incorporation of 2.5 parts shellac or modified lac/100 parts rubber when CBS is the accelerator.

Accelerated ageing — The incorporation of shellac has a beneficial effect on accelerated agening (Table 1). Here again, *Kusmi* shellac shows the best behaviour.

Summarizing, it can be concluded that the three varieties of lac tested behave more or less alike in influencing the mechanical properties of natural rubber gumstock, *Kusmi* shellac showing slightly superior behaviour than *Rangeeni* or *Platina*. Its better performance can be attributed to its superior life under heat and flow (Table 4), which enables its thorough dispersion during compounding. Modified lac does not show any appreciable improvement over shellac in affecting the mechanical properties of the resultant compositions, but makes the stocks more tacky.

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