

The Utilization of Waste Latex Products in Styrene-Butadiene Rubber

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ABSTRACT

Waste latex products are converted to a processable material by a novel economical process developed in our laboratory. It contains rubber hydrocarbon of very high quality and is lightly cross-linked. Styrene-butadiene rubber is mixed with latex reclaim in different proportions. The mechanical properties are found to be improved up to 60 percent replacement of styrene-butadiene rubber by latex reclaim. The curing of styrene-butadiene rubber is found to be accelerated by the addition of latex reclaim. The processability study shows that the blends can be processed similar to SBR/NR blends.

Key Words: styrene-butadiene rubber, latex reclaim, waste latex products, processability, mechanical properties

INTRODUCTION

The recycling of scrap and used rubber has been practiced by the rubber industry for many years, almost entirely by conversion to reclaimed rubber (RR) [1-7]. Despite the obvious incentives to reduce compound cost and to conserve raw materials and energy, the use of reclaim constitutes only a very small percentage of raw rubber consumption. This is mainly due to the deterioration in technical properties [8-13].

In contrast to reclaim rubber, scrap latex products contain rubber hydrocarbon of very high quality which is only lightly cross-linked. Due to the unstable nature of the latex compound and the strict specifications in the quality of latex products such as condoms and examination gloves, the rejection

in the latex industry comes to as high as 10 to 15% of the rubber consumed. The rubber Research Institute of India has developed a process for reclaiming latex products [14], as has the rubber Research Institute of Malaysia [15, 16]. Recently, a novel economic procedure was developed for converting latex waste into a processable form (hereafter referred to as latex reclaim (LR)).

The blends of styrene-butadiene rubber (SBR) and natural rubber (NR) [17, 18] are used for many industrial applications such as tyre components, sporting goods, moulded and extruded products, footwear, sheetings etc.

This paper reports the study of vulcanization, physical properties and processing characteristics of the natural rubber latex reclaim and its blends with styrenebutadiene rubber.

EXPERIMENTAL

Materials

Styrene-butadiene rubber: SBR employed was of Synaprene 1502 grade obtained from Synthetics and Chemicals Bareilly, U.P., with Mooney viscosity (ML (1+4) 100 °C) value of 52.0.

Latex reclaim: prepared from waste latex gloves (waste gloves were supplied by AVT Rubber Products Ltd, Kakkanad), volatile matter -2.2%, ash content -2.2%, plasticity retention index P_o -40, with Mooney viscosity (ML(1+4) 100 °C) value of 54.

Additives: zinc oxide, stearic acid, mercapto benzothiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), sulphur, carbon black (HAF N 330), aromatic oil, Accinox ZC (N-1,3 dimethyl N'-phenyl p-phenylene diamine) were all commercial grades.

Equipment

Laboratory two roll mixing mill of size (15×33 cm) having a friction ratio 1:1.25 was used for mixing. The Goettfert Elastograph model 67.85, a micro-processor controlled rotorless durometer with a quick temperature distribution in the die or test chamber was also employed. In this instrument, a specimen of defined size was kept in the lower half of the cavity which was oscillated through a small deformation angle ($\pm 2^\circ$). The frequency was 50 oscillations per minute. The torque was measured on the lower oscillating half die. The optimum cure times of compounds were determined at 150 °C using the Elastograph.

The samples for tensile and tear strength measurements were held tight by two grips of Universal Testing Machine (UTM), with the upper grip being fixed.

The rate of separation of the power actuated lower grip was kept at 500 mm/min. The hardness of the samples was tested using Zwick 3114 Hardness Tester in accordance with ASTM D-2240 (1981). The test was carried out on samples of 300 mm diameter and 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation.

For compression set the samples of 6.25 mm thick and 18 mm diameter were compressed to constant deflection (25%) and kept for 22 h at 70 °C in an air oven. The test was conducted according to ASTM D 395 (1982) method B. The samples were then taken out from the compression set apparatus and cooled at room temperature for 1/2 h and the final thickness was measured. The compression set was calculated as the following expression:

$$\text{compression set (\%)} = \frac{t_0 - t_1 \times 100}{t_0 - t_s}$$

where t_0 and t_1 the initial and final thickness of the specimen, respectively, and t_s as the thickness of the spacer bar used. The abrasion resistance was tested using samples of 10 mm thickness on a DIN Abrader under 10N load. Initially a pre-run was given for the sample and its weight was registered. The weight after 1 h run was also noted. The difference in weight would be the abrasion loss and expressed as volume loss (cm³/h) where m being the weight loss and ρ as the density of the sample.

The heat build up was determined according to ASTM D 623-67 (method A) using cylindrical samples of 2.5 cm height and 1.9 cm diameter. The oven temperature was kept constant at 50 °C. The stroke was adjusted to 4.45 mm and the load to 10.9 kg. The sample was pre-conditioned to the oven temperature for 2 min. The heat development at the base of the sample was sensed by hand.

The rebound resilience was measured using Dunlop tripsometer (BS 903 part 22, 1050). The samples were held in position by applying vacuum. The samples were conditioned by striking it six times using the indenter. The rebound resilience was calculated as:

$$\text{rebound resilience (\%)} = \frac{(1 - \cos \theta_2)}{(1 - \cos \theta_1)} \times 100$$

where θ_1 and θ_2 being the initial and final rebound angles, respectively, and θ_1 was 45° in all cases.

The processability of the compounds was evaluated using a Brabender Plasticorder model PL 3S. The torque rheometer was equipped by a device for measuring the torque generated due to

Table 1. Formulations for various proportions of SBR/LR.

Materials	A	B	C	D	E	F
SBR	100	80	60	40	20	0
LR	0	20	40	60	80	100
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
Carbon black	40	40	40	40	40	40
Aromatic oil	5	5	6	7	8	10
MBTS*	0.8	0.8	0.8	0.8	0.8	0.8
TMTD**	0.4	0.4	0.4	0.4	0.4	0.4
Sulphur	2.0	2.0	2.0	2.0	2.0	2.0
Accinox ZC	1.0	1.0	1.0	1.0	1.0	1.0

* mercapto benzothiazyl disulphide

** tetramethyl thiuram sulphide

the resistance of a material to flow under a pre-selected condition of shear and temperature.

Sample Preparation

The latex reclaim in the form of a sheet was masticated on a laboratory mixing mill and the SBR was added at different percentages. The blends were compounded according to ASTM-D 3182 (1982) as per the formulations given in Table 1. Latex reclaim was also compounded on a mixing mill as per formulations given in Table 1.

The optimum cure time (time to reach 90% of the maximum torque) of the compounds was determined on the Elastograph.

The compounds were then vulcanized up to their respective optimum cure times in an electric-

ally heated hydraulic press at 150 °C. Dumbbell shaped test specimens were punched out of these compression moulded sheets along the mill grain direction. The tensile properties were measured on a Zwick Universal Testing Machine Model 1445 using a cross-head speed of 500 mm/min according to ASTM D 412-80.

Angular test specimens were punched out of the compression moulded sheets and tear resistance of the blends was measured on the Zwick UTM according to ASTM D 624. Samples for compression set, hardness, abrasion resistance, heat build up and resilience were moulded and tested according to relevant ASTM standards. The ageing resistance of the vulcanizates was studied after ageing the samples at 100 °C for 24 and 48 h in a laboratory air oven.

In order to study the change in cross-link density during latex reclaiming, the average cross-link density ($\frac{1}{2} M_c$) was determined using the Flory-Rehner equation [19, 20].

Processability of the rubber compounds was evaluated at different temperatures (80, 100 and 120 °C) and at different shear rates (20, 40 and 60 rpm) on the Brabender Plasticorder.

RESULTS AND DISCUSSION

The cure characteristics of the compounds are shown in Table 2. This shows that the optimum cure time t_{90} (time for attaining 90% of the

Table 2. Cure characteristics and vulcanizate properties.

	A	B	C	D	E	F
Cure characteristics						
t_{10} (Scorch time, min)	2.8	2.6	2.3	1.8	1.4	1.2
t_{90} (Optimum cure time, min)	11.1	7.8	4.8	3.9	3.4	2.6
Vulcanizate properties						
Compression set (%)	22.86	22.06	21.36	20.86	20.48	20.21
Hardness (Shore A)	55	57	59	61	63	65
Abrasion resistance (cc/hr)	4.2	4.7	5.3	5.9	6.6	7.1
Heat build up (T °C)	35	34	33.08	32.67	32.16	31.24
Resilience (%)	44.86	45.61	45.82	46.11	46.56	46.92

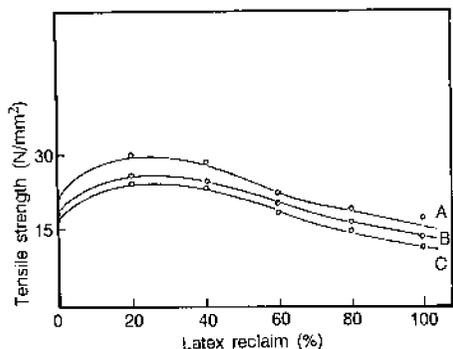


Figure 1. Variation in tensile strength with the percentage of latex reclaim. (A) original, (B) aged 24 h at 100 °C and (C) aged 48 h at 100 °C.

maximum torque) and scorch time t_{10} (time for attaining 10% of the maximum torque) decreases with the percentage of latex reclaim in the blends as shown in Table 2. This is possibly due to the presence of cross-linking precursors and/or unreacted curatives in the latex reclaim [2].

Figure 1 shows the variation in tensile strength with the amount of latex reclaim in the blends. The tensile strength first increases as in the case of styrene-butadiene rubber/rubber reclaim (SBR/RR) blend [21]. The tensile strength decreases when the percentage of latex reclaim in the blend is above 60 percent. This may be because

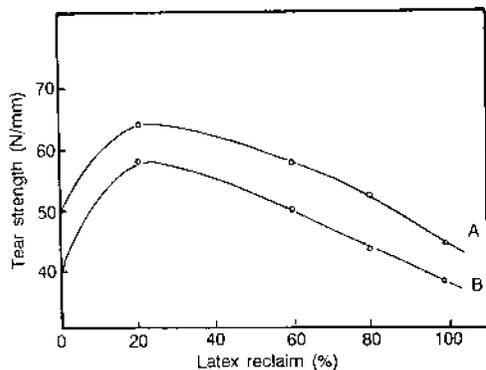


Figure 2. Variation in tear strength with the percentage of latex reclaim. (A) original, (B) aged 24 h at 100 °C.

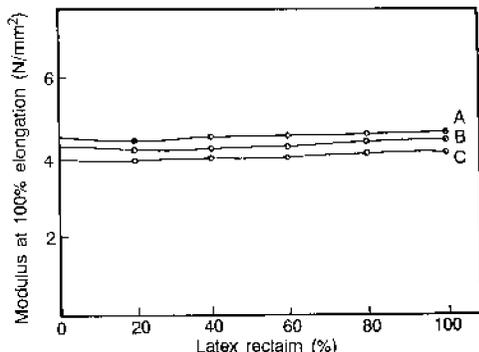


Figure 3. Variation in modulus at 100% elongation with the percentage of latex reclaim. (A) original, (B) aged 24 h at 100 °C and (C) aged 48 h at 100 °C.

latex reclaim forms a continuous phase [22] at this stage. The ageing resistance of the blends follows a similar pattern.

Figure 2 shows the variation in tear strength with the addition of latex reclaim. The tear strength increases and then decreases with the addition of latex reclaim. The ageing resistance of the samples containing latex reclaim is also comparable to that of SBR/RR blend up to 60% reclaim content as shown in Figure 2.

Figure 3 shows the variation in modulus with the amount of latex reclaim and the retention in modulus with ageing. There is only a marginal inc-

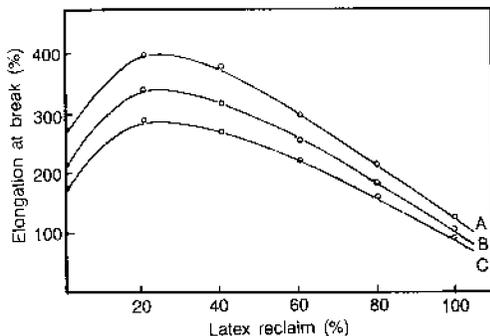


Figure 4. Variation in elongation at break with the percentage of latex reclaim. (A) original, (B) aged 24 h at 100 °C and (C) aged 48 h at 100 °C.

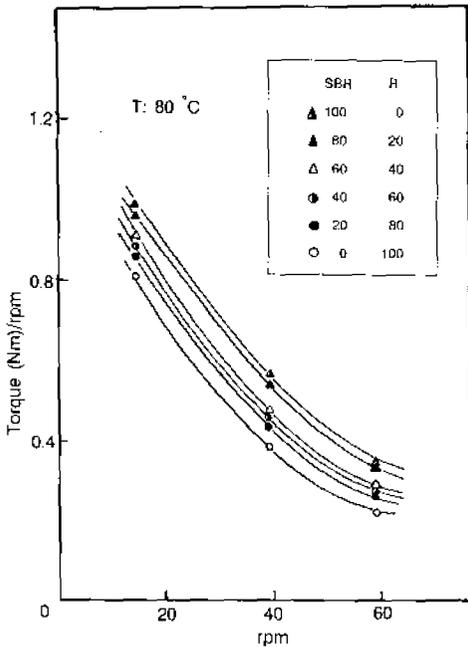


Figure 5. Variation in viscosity (torque/rpm) with shear rate (rpm) for SBR/LR blends at 80 °C.

rease in modulus with the addition of latex reclaim. This may be attributed to the increased amount of cross-link density in the blends [22]. The higher cross-link density in the blends containing latex reclaim may be due to only part of the cross-links present in the latex reclaim breaking during the reclaim preparation.

Figure 4 shows the variation in elongation at break with the addition of latex reclaim and its retention after ageing. The reduction in elongation at break at higher percentages of latex reclaim may also be due to the increased cross-link density in the blends.

The hardness increases with increase in the amount of latex reclaim as it has been expected (Table 2). The compression set decreases with the addition of latex reclaim (Table 2) which further confirms the increased cross-link density in the blends.

Table 3. Power law index for SBR/LR filled blends.

Blend composition (percentage of latex reclaim)	Power law index		
	Temperature		
	80 °C	100 °C	120 °C
0	0.316	0.284	0.273
20	0.298	0.276	0.261
40	0.282	0.264	0.253
60	0.251	0.246	0.230
80	0.224	0.218	0.204
100	0.196	0.184	0.176

The resilience (Table 2) slightly increases with increasing amount of latex reclaim as in the case of SBR/NR blends [23].

The abrasion resistance registers only marginal changes initially and decreases at higher concentrations of latex reclaim (Table 2). The variation in heat build up is inversely proportional to that of resilience as expected.

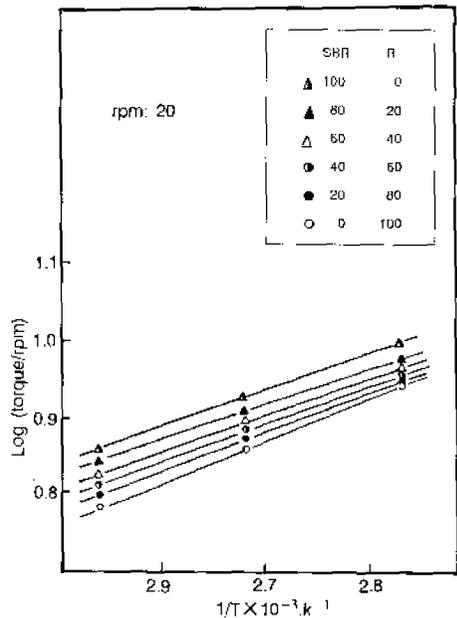


Figure 6. Variation in torque with rpm for SBR/LR blends at 80 °C.

Table 4. Activation energy of viscous flow for SBR/LR filled blends.

Blend composition (percentage of latex reclaim)	Activation energy (cal/mol)		
	rpm		
	20	40	60
0	2.67	1.99	1.44
20	2.23	1.56	1.26
40	1.86	1.34	1.18
60	1.43	1.19	1.11
80	1.24	1.07	1.04
100	1.08	0.97	0.95

The average cross-link density of the latex gloves (4.42×10^{-5} g mol/cm³) was found to decrease during the reclaiming process. The average cross-link density of the latex reclaim was found to be 2.35×10^{-5} g mol/cm³.

The processability studies were done on all compounds given in Table 1. Figure 5 illustrates

the effect of viscosity (torque/rpm) of the blends with shear rate at a temperature of 80 °C. The blends are highly pseudoplastic as expected. It may also be observed that the addition of latex reclaim up to 20% does not change the viscosity of SBR significantly.

Figure 6 shows the variation of torque with rpm. The power law index was calculated as the slope of the log (torque) vs. log (rpm) lines [24, 25]. Variation of the power law index with temperature (80, 100 and 120 °C) for the blends is shown in Table 3. The value of the power law index increases with increase in temperature and with the percentage of latex reclaim, which means that the blends become more Newtonian as expected.

Figure 7 permits the calculation of activation energies of viscous flow for SBR/LR blends. In order to understand the influence of temperature on viscosity of the blends at a particular shear rate, the Arrhenius plots at constant rpms were obtained.

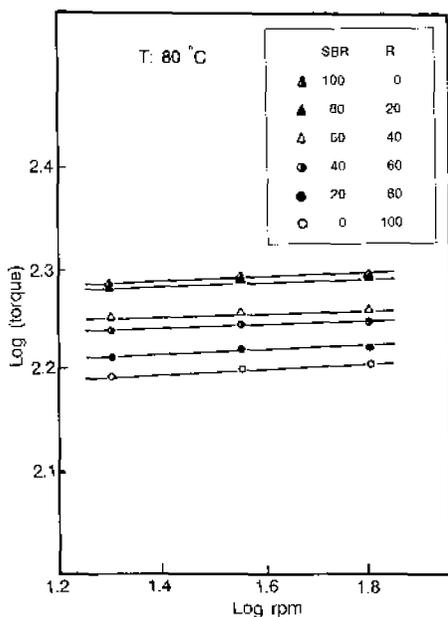


Figure 7. Variation in viscosity (torque/rpm) with temperature for SBR/LR blends.

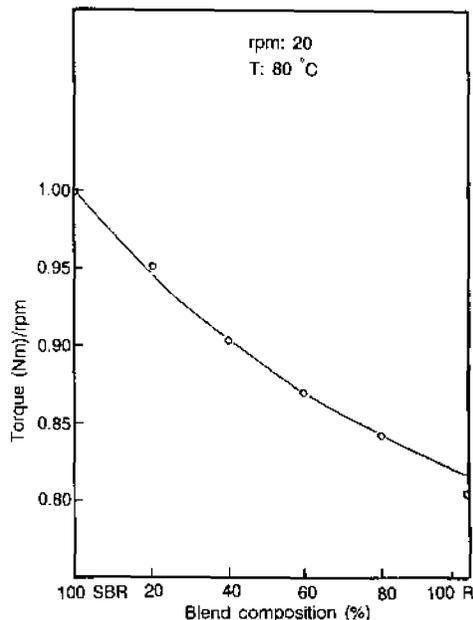


Figure 8. Variation in viscosity (torque/rpm) with blend composition for SBR/LR blends.

ed [26]. In Figure 7, logarithm of torque/rpm is plotted as a function of reciprocal temperature. The activation energy (E) of flow, calculated from the slope of these lines is given in Table 4. It provides valuable information on the sensitivity of the material towards the change in temperature. From the table it is clear that all the blends have an activation energy intermediate between those of the components.

Figure 8 shows the variation in viscosity of the blends with composition. The viscosity decreases with the amount of latex reclaim as expected in the case of SBR/NR blends.

CONCLUSION

The latex reclaim derived from waste latex products is found to have good rubber hydrocarbon. The curing of SBR/LR blends is found to be faster than SBR/NR blends. The latex reclaim can improve the mechanical properties of SBR vulcanizates upto about 60 percent. The processability of SBR/LR blend is found to be similar to that of SBR/NR blend.

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REFERENCES

1. Harshat A. A., *Environ. Sci. Technol.*, **6**, 5, 412, 1972.
2. Phadke A. A., Bhattacharya A. K., Chakraborty S. K. and De S. K., *Rubber Chem. Technol.*, **56**, 726, 1983.
3. Acetta A. and Vergnaud J. M., *Rubber Chem. Technol.*, **54**, 302, 1981.
4. Acetta A. and Vergnaud J. M., *Rubber Chem. Technol.*, **55**, 961, 1982.
5. Phadke A. A., Chakraborty S. K. and De S. K., *Rubber Chem. Technol.*, **57**, 19, 1984.
6. Kazarnowicz M. C., Osmundson E. C., Boyle J. P. and Savage R. W., Meeting of the Rubber Division, American Chemical Society, Cleveland, Ohio, Oct. 4-7, 1977; *Rubber Chem. Technol. (Abstract)*, **51**, 386, 1978.
7. Peterson L. E., Moriarty J. T. and Bryant W. C., *ibid.*
8. Burgoyne M. D., Leaker G. R. and Kretic Z., *Rubber Chem. Technol.*, **49**, 376, 1976.
9. Le Beau D. S., *Rubber Chem. Technol.*, **40**, 217, 1967.
10. Kalinichenko V. N., Blokh G. A., Vasker A. Ya. and Sulyaeva, *Int. Polym. Sci. Technol.*, **11**, 7, T87, 1984.
11. Burford R. P. and Pittolo M., *Rubber Chem. Technol.*, **55**, 1233, 1982.
12. Wolk R. H., *Rubber Age*, **104**, 103, 1972.
13. Kwabata N., Murkami T. and Yamashita S., *Int. Polym. Sci. Technol.*, **7**, 5, 29, 1979.
14. Claramma N. M., Kuriakose Ba. and Thomas E. V., Presented to the International Conference on Rubber and Rubber-like Materials, Jamshedpur, India, November 6-8, 1986.
15. Aziz Y., *High Quality Reclaimed Rubber from Latex Waste*, Presented at the Plastic-Rubber Institute Seminar, Kuala Lumpur, Malaysia, 4th August 1990.
16. Aziz Y., *Utilization of Reclaimed Rubber from Latex Glove Factory Rejects*, Presented at Polymer 90, Kuala Lumpur, Malaysia, 23rd September 1990.
17. Shundo M., Imoto M. and Minoura Y., *J. Appl. Polym. Sci.*, **10**, 930, 1966.
18. Gardiner J. B., *Rubber Chem. Technol.*, **43**, 370, 1970.
19. Flory P. J. and Rehner J., *J. Chem. Phys.*, **11**, 512, 1943.
20. Saville B. and Watson A. A., *Rubber Chem. Technol.*, **40**, 100, 1967.
21. Swor R. A., Jensen L. W. and Rudzol M., *Rubber Chem. Technol.*, **53**, 1215, 1980.
22. George R. S. and Joseph R., *Die Angew. Macromol. Chem.* In press.
23. Brown R. J., Knill R. B., Kerscher J. F. and Todd R. U., *Rubber Chem. Technol.*, **35**, 546, 1962.
24. Blyler L. L. and Daane J. H., *Polym. Eng. Sci.*, **7**, 178, 1967.
25. Lee G. C. N. and Purdon J. R., *Polym. Eng. Sci.*, **9**, 360, 1969.
26. Goodrich J. F. and Porter R. S., *Polym. Eng. Sci.*, **7**, 45, 1967.