Stress-Relaxation Characteristics of Natural Rubber Modified with Phosphorylated Cashew Nut Shell Liquid Prepolymer

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ABSTRACT: The tensile stress-relaxation characteristics at room temperature of gum NR vulcanizates containing 10–20 phr of phosphorylated cashew nut shell liquid (PCNSL) prepolymer were studied at various strain rates and strain levels, in comparison with that containing the same dosage of 2-ethyl hexyl diphenyl phosphate and the unmodified sample. Modification of NR with 10–15 phr of PCNSL resulted in improvements in tensile properties along with a lower degree of stress relaxation at the higher strain rates and strain levels. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2183–2189, 1997

INTRODUCTION

Natural rubber (NR), endowed with a unique combination of physicomechanical properties,[1,2] has established an enviable position in the industrial market as an excellent engineering polymer.[3] However, it is often found necessary to modify it with various additives such as plasticizers and fillers to cater it to any specific service requirement. In many of its applications as engineering components, "long-term dimensional stability" under service conditions is an integral requirement, apart from others such as resistance to aging, solvents, chemicals, and oils. Mechanical properties of the vulcanizates such as modulus, strength, stiffness, stress–strain characteristics under various deformation modes, stress relaxation, and creep are some of the critical parameters in this respect.[4] Stress-relaxation characteristics of an elastomer under constant strain and at equilibrium conditions[5] is of particular importance in products such as oil seals and gaskets. High stress relaxation is undesirable in gaskets.[6] Similarly, a high degree of stress relaxation in oil seals may cause dimensional changes during service, leading subsequently to leakages and failure of the assembly.

Stress relaxation of a product is found to be dependent on various factors such as composition of the mix including the amount and type of fillers,[7–9] plasticizers and antioxidants,[10] nature and type of crosslinks,[11,12] crosslink density,[11–14] type and quantity of extra-network material arising from vulcanization,[15] and hysteresis behavior of the compound,[16] apart from the conditions of service or testing such as strain rate, strain level, and temperature.[17–21]

The potential of phosphorylated cashew nut shell liquid (PCNSL)[22] and phosphorylated cardanol prepolymer (PCP)[23] (oligomeric resins synthesized from CNSL and cardanol, respectively) as multifunctional additives for NR compounding has recently been reported.[24] At concentrations ranging from 5 to 20 phr, PCNSL was found to act as a plasticizer,[25] processing aid,[26] and tackifier[27] for NR. Improvements in tensile and tear strengths, elongation at break, resistance to fatigue failure, resistance to thermooxidative aging and decomposition, and flame resistance have

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been observed on modification of NR (SEV system) with 5–20 phr of PCNSL.[28,29] The PCNSL-modified NR vulcanizates showed a reduction in chemical crosslink density and a higher proportion of polysulfidic linkages compared to the unmodified sample.[30] The optimum combination of a variety of desirable properties as mentioned above and the excellent processability of NR modified with PCNSL (at 10 phr) gave an impetus for exploring the possibility of its usage for engineering applications.

Since "physical stress relaxation" at normal temperature is important with respect to engineering applications,[31] it was thought worthwhile to study the stress-relaxation characteristics of the PCNSL-modified NR vulcanizates. The stress-relaxation characteristics of PCNSL-modified NR vulcanizates in tension has been studied at various strain rates and strain levels, compared to that of the unmodified sample and that containing varying concentrations of a phosphatic plasticizer, viz., 2-ethyl hexyl diphenyl phosphate ("Santicizer 141"), the results of which are reported in this article.

EXPERIMENTAL

Materials

Cashew nut shell liquid (CNSL) conforming to Indian Standard (IS: 840 (1964)) was obtained from the M/s Vijaya lakshmi Cashew Factory, Quilon. PCNSL was synthesized by phosphorylating preheated CNSL with *o*-phosphoric acid at 175 ± 5°C for 4 h by a patented process.

2-Ethyl hexyl diphenyl phosphate ("Santicizer 141") was obtained from Monsanto Chemical Co., USA. Indian Standard Natural Rubber ("ISNR-5") was obtained from the Rubber Research Institute of India, Kottayam. Other chemicals such as zinc oxide, stearic acid, sulfur, mercaptobenzothiazole sulfenamide (MBT), and tetramethylthiuram disulfide (TMTD) were of the laboratory reagent grade.

Methods

NR formulations as given in Table I were mixed on a two-roll mixing mill (size 150 × 300 mm) at a friction ratio of 1 : 1.12. Vulcanization characteristics of the formulations at 150°C were measured on an oscillating disk rheometer (Monsanto R-100) as per ASTM D-2084-81. Test specimens were molded on an electrically heated hydraulic press at 150°C and at the optimum cure times as determined above. Tensile properties of the vulcanizates were measured on a Zwick tensile tester (Model 1435) at a crosshead speed of 500 mm/min as per ASTM D-412-87 (Method A).

Stress relaxation of the vulcanizates at room temperature under constant tensile strain was measured on the Zwick tensile tester using dumbbell test specimens (die-C, ASTM D-412-87) at strain levels ranging from 50 to 150% and at the strain rates of 0.0208, 0.1042, and 0.2083 s^{-1}. The stress-relaxation characteristics of the vulcanizates were obtained by plotting the ratio σ_t/σ_0 against logarithm of time, σ_t and σ_0 being the stress at time t and initial stress, respectively.

RESULTS AND DISCUSSION

Tensile Properties

Results on the tensile modulus, tensile strength, and elongation at break of the different samples are given in Table II. The tensile modulus at different elongations of the PCNSL-modified NR vulcanizates decreased at a higher rate with increase in the concentration of PCNSL, as against that of the similar samples containing Santicizer. This indicates the higher degree of softening effect of the former, compared to the latter. The tensile strength of the PCNSL-modified NR vulcanizate reached a maximum of 16.70 MPa with 10 phr of PCNSL, whereas the maximum value for the Santicizer-modified NR vulcanizate (11.72 MPa) was obtained with 20 phr of the additive. The elongation at break of the PCNSL-modified vulcanizates were also considerably higher than that of the similar samples containing Santicizer. Normally, plasticizers are known to lower the modulus and tensile strength and increase the elongation at break of the base polymer. The reversal in these effects, particularly at low dosages of the plasticizer, has been referred to as an "antiplasticization" effect.[32] However, the increase in tensile strength of the PCNSL-modified NR vulcanizates does not seem to be due to antiplasticization, since during the whole range of concentration from low to high, the PCNSL-modified NR vulcanizates showed a lower tensile modulus, higher tensile strength, and higher elongation at break.[28]

The higher tensile strength and elongation at

Table I Formulations

	Mix Code (phr)						
Ingredients	U	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}
NR	100	100	100	100	100	100	100
ZnO	10	10	10	10	10	10	10
Stearic acid	2	2	2	2	2	2	2
Sulfur	2	2	2	2	2	2	2
MBT	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PCNSL	—	10	15	20	—	—	—
Sancticizer	—	—	—	—	10	15	20

break of the PCNSL-modified NR vulcanizates was supposed to be partly due to the probable formation of an "entangled network structure" between PCNSL and NR.[30] Besides, the possibility for H-bonding between the phosphate groups of the adjacent molecules of PCNSL and interactions between the unsaturated side chain of PCNSL and the unsaturations of the isoprene main chain has also been proposed. The absence of similar unsaturation sites and hydroxyl groups suitable for H-bonding in 2-ethyl hexyl diphenyl phosphate rules out the possibility for similar interactions in the Santicizer-modified NR vulcanizates.

Stress-relaxation Characteristics

Effect of Dosage of Plasticizer

The stress-relaxation plots of the different vulcanizates at a strain level of 150% and strain rate of 0.2083 s^{-1} are given in Figure 1. The amount, time, and rate of stress relaxation at equilibrium conditions are given in Table III.

The above results show the comparatively lower degree of stress relaxation for the vulcanizates containing 10–15 phr of either PCNSL or Santicizer. Upon increasing the content of plasticizers to 20 phr, the extent and rate of stress relaxation increases to considerably higher values, similar to that of the unmodified vulcanizate. In unfilled NR vulcanizates at normal temperatures, the rate of stress relaxation has been shown to be strongly dependent on the degree of crosslinking of the vulcanizates.[33] The higher stress relaxation of the vulcanizates containing 20 phr of the plasticizer may be due to the presence of higher proportions of "extra-network materials" as a result of lower degree of crosslinking, which may contribute to stress relaxation as reported earlier.[15] The formulations containing 10–15 phr of PCNSL or Santicizer may find applications as seals or gaskets, whereas those containing 20 phr of the plasticizers may be used as sealants for joints. In the application as a sealant, the higher stress-relaxation characteristics reduces the maximum stress in various joint configurations.[34]

Effect of Strain Rate and Strain Level

The effect of an increase in the strain rate from 0.0208 to 0.2083 s^{-1} and strain level from 50 to 150% on the stress-relaxation characteristics of

Table II Tensile Properties of the Vulcanizates

	Mix Code						
Parameter	U	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}
Modulus-100% (MPa)	0.87	0.52	0.42	0.23	0.68	0.63	0.60
Modulus-200% (MPa)	1.72	1.10	0.83	0.38	1.40	1.29	1.18
Modulus-300% (MPa)	—	1.65	1.30	0.55	2.27	2.09	1.97
Tensile strength (MPa)	2.16	16.70	15.67	7.26	2.66	2.38	11.72
Elongation at break (%)	240	1060	1170	1340	310	330	840

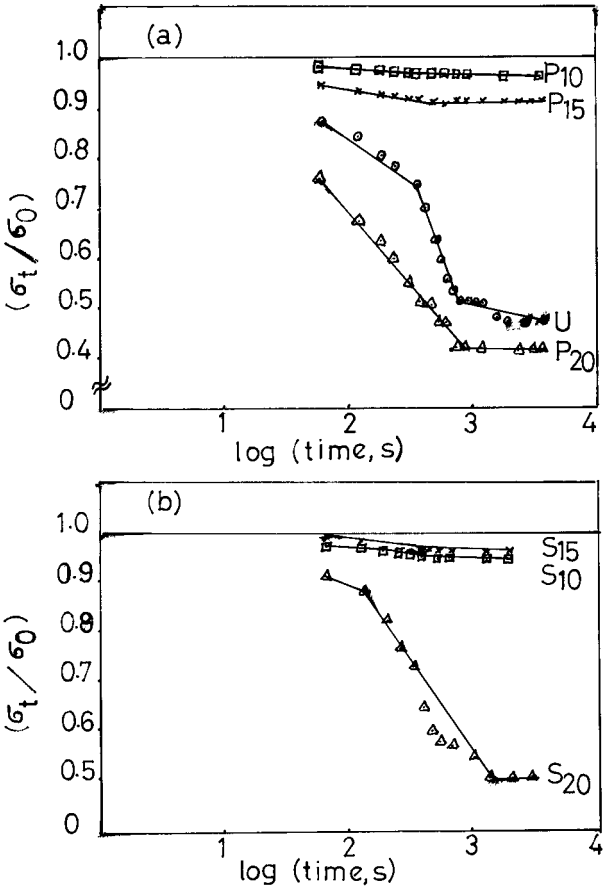

Figure 1 Stress-relaxation characteristics of NR vulcanizates containing various dosages of PCNSL/Santicizer: (a) unmodified and PCNSL-modified; (b) Santicizer-modified. Strain rate = 0.2083 s^{-1}; strain level = 150%.

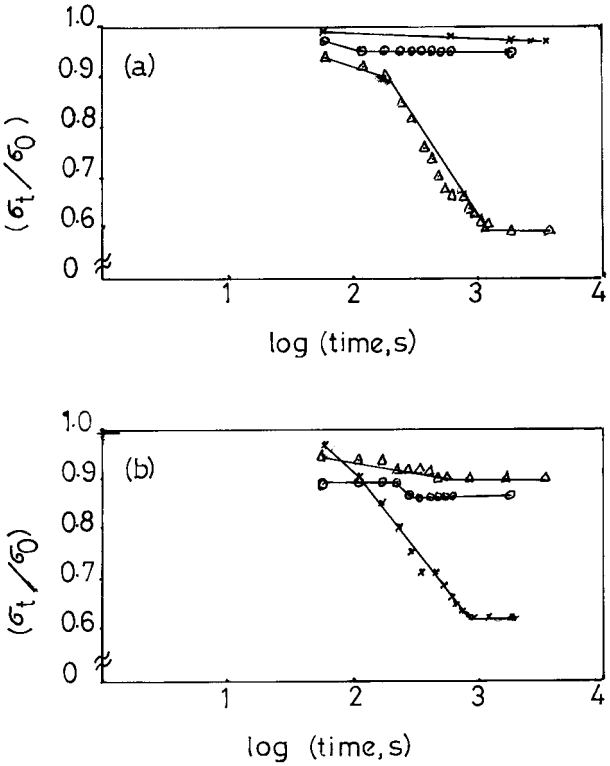

Figure 2 Stress-relaxation characteristics of NR vulcanizates at various strain levels: (a) unmodified; (b) PCNSL (10 phr)-modified. Strain levels = 50, 100, and 150%; strain rate = 0.0208 s^{-1}.

the unmodified and PCNSL-modified NR vulcanizates are shown in Figures 2–4 and Table IV. The results show that the extent and rate of stress relaxation of the vulcanizates are independent of the strain rate and strain levels. This is in accordance with the observation of Gent on the independence of rate of stress relaxation on the degree of deformation of unfilled NR vulcanizates, at extensions below 200%.[35] Chasset and Thirion also observed that in unfilled NR vulcanizates at normal temperatures the rate of stress relaxation was substantially independent of the type and degree of deformation.[33] However, the NR vulcanizate containing 10 phr of PCNSL shows a low extent and rate of stress relaxation at the various strain rates

Table III Effect of Dosage of PCNSL/Santicizer on the Stress-relaxation Characteristics of Gum NR Vulcanizates[a]

Parameter	Mix Code						
	U	P_{10}	P_{15}	P_{20}	S_{10}	S_{15}	S_{20}
Stress-relaxation time (s)	1500	1800	300	720	540	360	1200
Stress relaxation[b] (%)	53	5	9	59	6	4	49
Rate of stress relaxation (%/s)	0.035	0.003	0.030	0.082	0.011	0.011	0.041

[a] Strain rate = 0.2083 s^{-1}; strain level = 150%.
[b] Steady values.

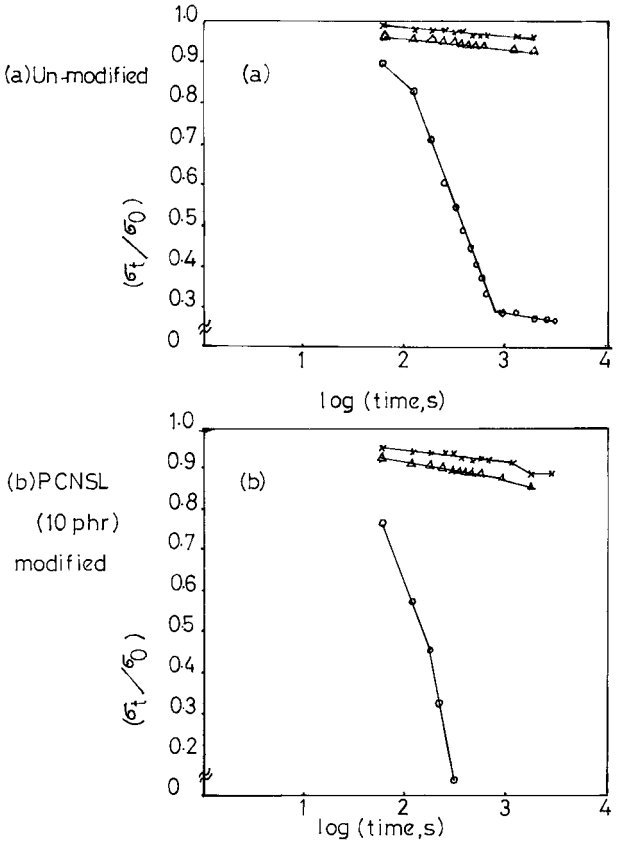

Figure 3 Stress-relaxation characteristics of NR vulcanizates at various strain levels: (a) unmodified; (b) PCNSL (10 phr)-modified. Strain levels = 50, 100, and 150%; strain rate = 0.1042 s^{-1}.

and strain levels. Thus, at the strain rate of 0.2083 s^{-1} and 150% elongation, the PCNSL-modified NR vulcanizate showed 5% stress relaxation at the rate of 0.003%/s as against 53 and 0.035%/s, respectively, for the unmodified sample.

The lower stress relaxation of the PCNSL-modified NR vulcanizate may be explained in terms of the molecular theory for viscoelasticity.[36] Accordingly, the application of a stress to the polymer molecule will cause distortion by altering the equilibrium conformation to a less probable one, resulting in a decrease in the entropy and a corresponding increase in the free energy of the system. If the stress is maintained, strain relief is sought by converting the excess free energy into heat, thereby stimulating the thermal motion of the segments back to their original positions, resulting in stress relaxation. The reduced crosslink density of the PCNSL-modified vulcanizate necessitates a greater number of "coordinated segmental motions of the polymer chains" for stress relaxation. The higher crosslink density of the unmodified NR vulcanizate permits a greater number of modes of relaxation for its chain segments involving a lower degree of cooperation between each, resulting in a higher rate of stress relaxation.

CONCLUSIONS

The present study leads to the following conclusions:

1. Modification of NR with 10–15 phr of PCNSL results in improved tensile properties along with a lower degree of stress relaxation (at higher strain rates and strain levels) compared to the unmodified sample. Although the rate of stress relaxation for the vulcanizates containing 10–15 phr of Santicizer is comparable to that containing

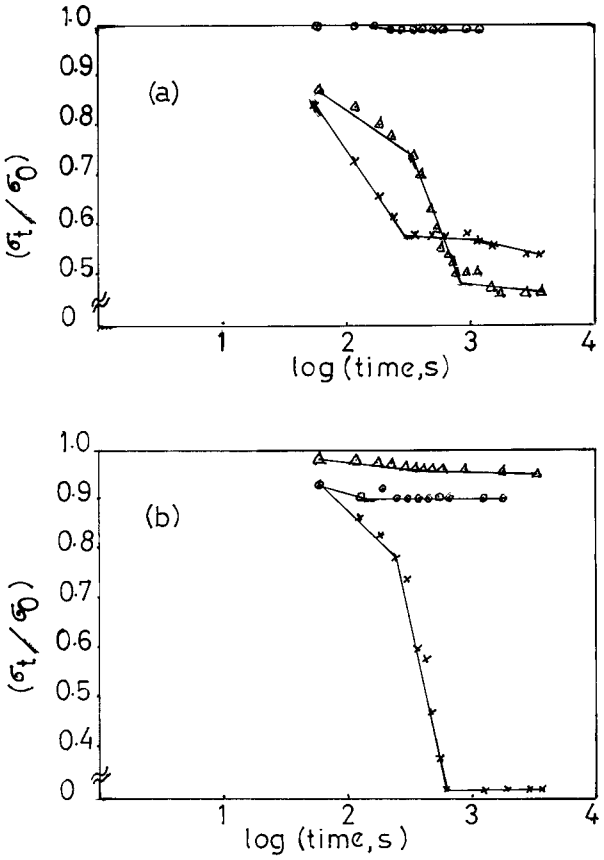

Figure 4 Stress-relaxation characteristics of NR vulcanizates at various strain levels: (a) unmodified; (b) PCNSL (10 phr)-modified. Strain levels = 50, 100, and 150%; strain rate = 0.2083 s^{-1}.

Table IV Effect of Strain Rate and Strain Level on the Stress Relaxation of Unmodified and PCNSL-modified NR Vulcanizates

		Mix Code			
		U	P_{10}	U	P_{10}
Strain Rate (s^{-1})	Strain Level (%)	Stress Relaxation (%)		Rate of Stress Relaxation (%/s)	
0.0208	50	5	13	0.042	0.036
	100	3	37	0.002	0.044
	150	40	10	0.032	0.021
0.1042	50	73	—	0.041	—
	100	4	11	0.008	0.006
	150	8	14	0.004	0.008
0.2083	50	1	10	0.004	0.042
	100	46	68	0.017	0.103
	150	53	5	0.035	0.003

similar dosages of PCNSL, their tensile properties are lower.

2. The increase in dosage of PCNSL or Santicizer to 20 phr results in a significant increase in the extent and rate of stress relaxation.
3. At strain levels ranging from 50 to 150% and strain rates ranging from 0.0208 to 0.2083 s^{-1}, the stress-relaxation characteristics of unmodified and PCNSL-modified NR vulcanizates are independent of each other.

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