Thermally stimulated depolarization study of natural rubber and polystyrene mixtures

M. Topić* **and Z. Veksli**
Ruđer Bošković Institute, POB 1016, 41001 Zagreb, Croatia
(Received 23 March 1992)

The glass transition of natural rubber (NR) in a mixture with polystyrene (PS) was investigated by global thermally stimulated depolarization current (t.s.d.c.) measurements and by the partial polarization technique. The experiments were carried out on samples with different NR/PS ratios and different PS particle dispersion. The activation energy (E_α) and the approximate number of dipoles (N) which take part in α relaxation were determined. A simple method for approximating the $N(E_\alpha)$ distribution was proposed. The results show that the presence of PS significantly decreases N as well as the width of the distribution. The agglomeration of PS particles reduces their activity. The specific influence of PS is expressed most at low PS concentrations. The results confirm the existence of attractive interactions at the NR–PS interfaces.

(Keywords: thermally stimulated depolarization; glass transition; mixtures; interface; activation energy distribution; natural rubber; polystyrene)

INTRODUCTION

Multiphase polymers are combinations of two or more polymers which can be mixed on a molecular scale or can form a two-phase structure. Thermoplastic elastomers are examples of multiphase polymers prepared from immiscible or semi-immiscible blends, block copolymers and interpenetrating networks[1,2]. Thermodynamic incompatibility leads to the 'domain' morphology often desired to combine the properties of each phase. However, the properties depend on the structure, the size and shape of the domains and the mode of mixing. The mixing is controlled by the interfacial tension. The mechanical properties are also determined by the interface and adhesion at the interface which enables efficient transfer of stress between the polymer components. Two polymers do not often exhibit adequate adhesion and in such cases suitable chemical agents are added. However, phase morphology control without chemical reactions to form interpenetrating phases seems to offer an appropriate procedure for preparing immiscible thermoplastic elastomers with the desired combination of properties of the two polymers[3]. The central feature in the characterization of immiscible polymer mixtures is morphology which is essential for understanding structure–property relationships.

In a recent paper[4], the preparation of a series of mixtures of natural rubber (NR) and polystyrene (PS) from emulsions was described. The influence of the NR/PS composition as well as the effect of agglomerated PS latex particles were investigated by mechanical stress–strain and n.m.r. spin–spin relaxation measurements. Also, preliminary investigations of thermally stimulated depolarization current (t.s.d.c.) measurements were carried out. The results obtained showed an evident influence of the interface.

This paper reports the study of the NR–PS system in the temperature region of the glass transition of NR using different t.s.d.c. measurements.

EXPERIMENTAL

The NR in the form of latex of ~60% dry rubber was a commercial sample of Malaysian origin. PS latex was prepared by emulsion polymerization. The preparation has been described elsewhere[4]. NR–PS mixtures were prepared by mixing the NR latex with PS water emulsion, followed by drying and annealing in a vacuum at 333 K for 7 days. The residual styrene monomer was removed during the drying. Such a procedure gives a NR–PS film with a homogeneous distribution of the components. Some of the samples were prepared using the previously dialysed PS latex. In the course of the extensive dialysis the emulsifier was partly removed which reduced surface activity and brought about the agglomeration of the latex particles[5].

The t.s.d.c. measurements were performed on 1 mm thick samples using aluminium evaporated electrodes (diameter 13.6 mm). The samples were placed in the shielded cell filled with dry nitrogen. The measurements were carried out in the following way: discharge by heating up to 303 K with the short-circuited electrodes, polarization by the electric field $E_p = 12\,\mathrm{kV\,cm^{-1}}$ at a temperature $T_p = 213$ K for 20 min, cooling to 183 K under the same field, relaxation at 183 K in the short-circuited state for 30 min and depolarization by heating at a rate of $2\,\mathrm{K\,min^{-1}}$. For experiments with partial polarization the procedure was modified as follows: polarization at T_p for 5 min, cooling to $T_p - 5$ K

---

* To whom correspondence should be addressed

0032-3861/93/102118-04

under E_p for ~5 min, cooling to 183 K in the short-circuited state and relaxation at 183 K in the short-circuited state for 20 min. The current was measured by a Keithley 616 electrometer.

RESULTS AND DISCUSSION

T.s.d.c. measurements

T.s.d.c. measurements were carried out on samples with different NR/PS (w/w) ratios. The characterization of a mixture of 70/30 NR/PS by d.s.c. showed two glass transitions at 207 and 375 K, confirming the two immiscible components[6]. In order to obtain a clean α relaxation peak, produced by the NR component, a $T_p = 213$ K was chosen. A study of high temperature glass transition, belonging to PS, by t.s.d.c. was impossible because of the electrical conductivity of NR. The t.s.d.c. results in the temperature region of the α peak of pure NR are shown in *Figure 1*, curve R. The temperature of the maximum of the obtained peak is ~213 K. Curves B and C are related to mixtures having NR/PS ratios of 70/30 and 50/50, respectively. It can be seen that the addition of PS decreases the maximum current (I_m) of the dipolar relaxation, while the maximum temperature (T_m) is practically unchanged.

In order to discuss how many NR dipoles take part in α relaxation in the mixtures, the relative number of dipoles per sample (N) is approximated by the equation[7–9]:

$$N = I_m \times T_m \tag{1}$$

The results for N for pure NR and for different mixtures are shown in *Figure 2a* (open circles). A better insight into the influence of the presence of PS can be obtained taking into consideration the specific number of dipoles (N'), which are related to a weight unit of NR in the samples studied. Therefore:

$$N' = I_m \times T_m / p \tag{2}$$

where p is the weight fraction of NR in a sample. The N' values are shown in *Figure 2a* (solid circles). The results show that the number of NR dipoles is significantly decreased by the presence of PS. One can assume an inhibiting influence of PS on the relaxation mechanism in NR. The specific values additionally show that the inhibiting influence increases very slightly and is almost constant with increase in PS concentration.

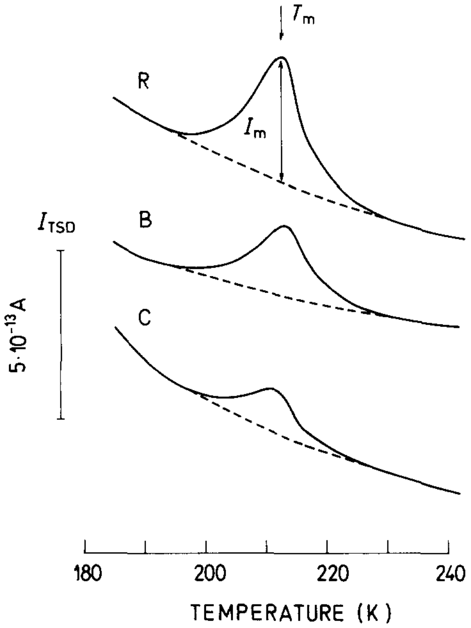

Figure 1 T.s.d.c. *versus* temperature, in the region of glass transition for samples with different NR/PS (w/w) ratios: (R) pure NR; (B) 70/30; (C) 50/50. $E_p = 12$ kV cm^{-1}, $T_p = 213$ K

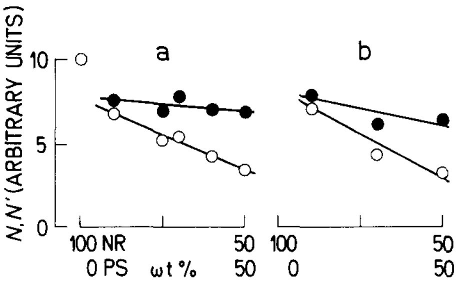

Figure 2 Number of dipoles in NR taking part in α relaxation *versus* sample content: (○) N approximated by equation (1); (●) N' calculated according to equation (2). Influence of PS dispersion: (a) original PS latex; (b) dialysed PS latex

The results presented in *Figure 2b* are for samples prepared using agglomerated PS. Taking into consideration that the agglomeration of PS particles reduced their surface area one should expect a smaller interface activity of PS. However, the results in *Figure 2b* show the same tendency as those in *Figure 2a*. Thus the expected influence of the agglomeration on the number of dipoles is not confirmed.

Partial polarization technique

The investigation of the activation energies (E_α) of α relaxation is important for characterizing mixed polymers, because the glass transition reflects various interacting phenomena. The most popular method for determining E_α is the initial rise method[10,11]. However, its application on the global t.s.d.c. curves of distributed α processes is not suitable. The results for the E_α obtained in such a way are limited to the low energy region and cannot characterize the entire process[9]. Better results can be achieved by performing partial polarizations within narrow temperature ranges[12] and instead of one activation energy a series of energies are calculated.

The partial t.s.d.c. curves of pure NR in the region of the glass transition are shown in *Figure 3*. The parasitic current was subtracted[9] and the curves represent the net t.s.d.c. In order to characterize the whole transition three characteristic curves were obtained by using three different temperature ranges for partial polarization. Curve I in *Figure 3* is a low energy curve obtained with the lowest possible T_p which still produces a curve big enough to apply the initial rise method and to determine E_α(I). Curve II is the maximum amplitude curve to determine E_α(II). Curve III is a high energy curve obtained with the highest T_p which still produces a curve suitable for determining E_α(III). Similar partial analyses with three such characteristic curves for a sample of 50/50 NR/PS are shown in *Figure 4*. In comparison with the curve for pure NR (*Figure 3*) the I_m is significantly decreased. The whole temperature range of α relaxation is rather narrow and the temperature windows for polarization of 5 K touch each other.

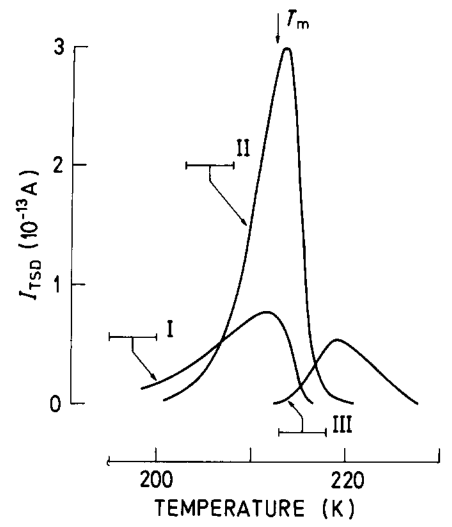

Figure 3 T.s.d.c. *versus* temperature obtained by partial polarization in pure NR ($E_p = 12$ kV cm^{-1}). Horizontal lines show the temperature of application of E_p: (I) curve obtained in the lower temperature region; (II) maximum amplitude curve; (III) higher temperature curve

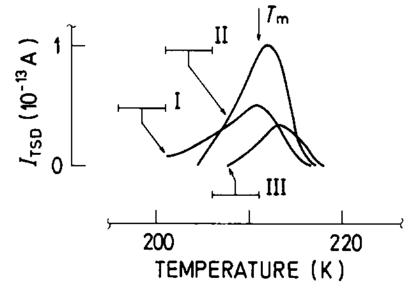

Figure 4 T.s.d.c. *versus* temperature for the mixture with 50/50 NR/PS. Partial polarization as in *Figure 3*

From the analysis of the partial curves in *Figures 3* and *4* it follows that the recorded curves are always shifted toward the higher temperature values in relation to the temperature range of polarization. This is because the temperature obtained from the recorded curve is not the real temperature of the sample due to the temperature gradient caused by a finite heating rate. However, the T_p at the beginning of the temperature range, in which E_p was applied, was the real sample temperature, stabilized before application of E_p. As a consequence the maximum amplitude curve was obtained by T_p which was always $\sim$5 K below T_m.

The partial curves can be used to calculate the number of dipoles N(I), N(II) and N(III) by using equation (1) and N' (I), N'(II) and N'(III) by using equation (2).

Knowing the numbers of dipoles and the related energies, the energy distribution function $N(E_\alpha)$ can be approximated. By taking the logarithmic values of N the exponential shape of the distribution can be transformed into a linear one[8], which enables the distribution to be constructed simply as a triangle.

The distribution functions for E_α for samples with different NR/PS contents are shown in *Figure 5*. The function R is related to the sample of pure NR. The values of ln N were normalized to ln N(II) = 10. In order to make a reliable comparison among different systems the normalization was performed with the same factor for all the ln N and ln N' values in *Figure 5*. The distributions were characterized by widths β or β' at heights equal to 80% of the maximum value; β is related to N, while β' is related to N' (*Table 1*).

For a better insight the obtained widths are shown in *Figure 6*. The following conclusions can be drawn:

1. Sample R (pure rubber) has the biggest width.
2. The widths decrease with increase in PS content.
3. The influence of PS is mainly manifested in the suppression of the higher energy region.
4. The agglomeration of the PS particles by the dialysis procedure increases the widths for samples with the same NR/PS content.

The specific behaviour of NR due to the addition of PS, which is reflected by β', shows another very interesting aspect. That is, the decrease in β', e.g. the specific influence of PS, is most pronounced in the sample with the minimum amount of PS and successively decreases with increase in PS content. The systems with agglomerated PS follow the same tendency, but always with a wider distribution, on average 24%.

In a recent paper[9], an attempt was made to express the difference between the 'highest' and the 'lowest' E_α

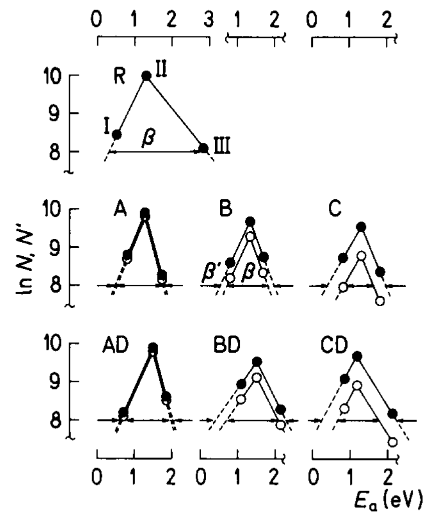

Figure 5 Distribution of the activation energy in the glass transition of NR in NR–PS mixtures: (○) related to $N(E_\alpha)$; (●) related to $N'(E_\alpha)$; (I) determined from lower temperature t.s.d.c. curves; (II) determined from maximum amplitude curves; (III) determined from higher temperature curves. NR content (wt%): (R) 100; (A) 90; (B) 70; (C) 50. (AD), (BD) and (CD) are related to dialysed PS. β, Distribution widths at 80% of the maximum value; β' corresponds to the specific distribution $N'(E_\alpha)$

Table 1 Activation energy distribution $N(E_\alpha)$ in the glass transition of NR in NR–PS mixtures

	R	A	B	C	AD	BD	CD
NR (wt%)	100	90	70	50	90	70	50
Ln N (I)	8.46	8.68	8.18	7.95	8.07	8.55	8.32
(II)	10.00	9.77	9.27	8.78	9.77	9.12	8.93
(III)	8.11	8.14	8.34	7.59	8.51	7.89	7.43
Ln N' (I)		8.79	8.58	8.72	8.19	8.95	9.09
(II)		9.89	9.67	9.55	9.89	9.52	9.70
(III)		8.26	8.74	8.36	8.62	8.29	8.20
E_α (eV) (I)	0.53	0.84	0.82	0.83	0.70	1.10	0.87
(II)	1.31	1.28	1.34	1.32	1.50	1.52	1.20
(III)	2.85	1.74	1.70	1.82	1.86	2.16	2.15
β (eV)	2.65	1.21	1.10	0.78	1.30	1.42	1.09
β' (eV)		1.29	1.44	1.55	1.42	1.91	2.00

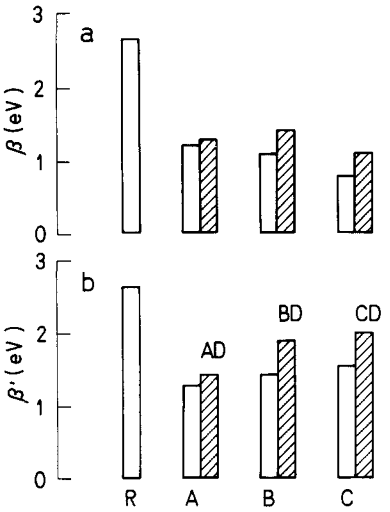

Figure 6 Block diagram comparison of results from *Figure 5*: (a) β values; (b) β' values

that could be observed during the glass transition in epoxy resin. It was found that the difference, ΔE_α, decreased with increase in the attractive interactions and bondings. Therefore, a significant decrease in ΔE_α occurred in the cured resin. ΔE_α was a measure for flexibility of the dipole groups in the mixed systems. It is obvious that a construction of the approximated distribution $N(E_\alpha)$ of the glass transition and determination of the distribution widths represent a more precise way to consider the possible interactions between the components. The decrease of β with increase in PS concentration is a consequence of the existing and growing interface area. The interface sites with attractive interactions cause, to some extent, the immobility of the electric dipoles in NR. The agglomeration of PS particles, as shown earlier, has no influence on the global number of relaxing dipoles but is marked with increase in β. The agglomeration decreases the interacting surface acting in the same way as a decrease in PS concentration.

CONCLUSIONS

An investigation of the t.s.d.c. curves in the range of the glass transition of NR for a series of samples with different NR/PS ratios and different PS particle dispersion was performed. The number of dipoles in a sample N, which take part in α relaxation, was approximated on the basis of the maximum current and maximum temperature of the obtained curves. It was found that the presence of PS significantly reduced N which decreased almost linearly with increase in PS concentration. The specific number of dipoles N', which was related to a weight unit of NR, also decreased with PS concentration but only very slightly. It seemed that N' was practically constant in relation to the NR/PS ratio. The influence of the agglomeration of PS particles was not observed.

More peculiarities were found by the method proposed for characterizing the glass transition approximating $N(E_\alpha)$ distributions as triangles. Three characteristic t.s.d.c. curves were obtained by use of partial polarization: the minimum energy curve, the maximum amplitude curve and the maximum energy curve. The corresponding E_αs were determined by the initial rise method and the Ns were approximated for each of the partial curves. The comparison of the distribution widths, at heights equal to 80% of the maximum values, for a series of samples showed the increase of β with increase in PS concentration and with the decrease of the NR–PS interface. The specific influence of PS related to a weight unit of NR and expressed through β' is most pronounced in the systems with low PS content. As a decrease of β is an indication of attractive phenomena one can conclude that there exist attractive interactions at the interfaces of the two phases.

ACKNOWLEDGEMENTS

The authors are grateful to Professor S. Popović for critical reading of the manuscript and to Mr S. Valić for help in the sample preparation.

REFERENCES

1 Legge, N. R., Holden, G. and Schroeder, G. E. (Eds) 'Thermoplastic Elastomers', Hanser Publishers, New York, 1987
2 Silverstain, M. S. and Narkis, M. *J. Appl. Polym. Sci.* 1987, **33**, 2529
3 Paul, D. R. and Barlow, J. W. *J. Macromol. Sci. Rev. Macromol. Chem.* 1980, **C18**, 109
4 Valić, S., Šincek-Pećanić, V., Topić, M., Andreis, M., Ranogajec, F. and Veksli, Z. *Rubber Chem. Technol.* in press
5 Schlueter, H. in 'Copolymers, Polyblends and Composites' (Ed. N. A. J. Platzer), American Chemical Society, Washington DC, 1975, p. 99
6 Malavašič, T. personal communication, 1992
7 Bucci, C. and Fieschi, R. *Phys. Rev. Lett.* 1964, **12**, 16
8 Kovarskii, A. L., Mansimov, S. A. and Buchachenko, A. L. *Polymer* 1986, **27**, 1014
9 Topić, M., Moguš-Milanković, A. and Katović, Z. *Polymer* 1991, **32**, 2892
10 Garlick, G. F. J. and Gibson, A. F. *Proc. Phys. Soc. (London)* 1948, **60**, 574
11 Wanderschueren, J. and Gasiot, J. in 'Topics in Applied Physics' (Ed. P. Bräunlich), Vol. 37, Springer-Verlag, Berlin, 1979, p. 163
12 Nishinari, K., Chatain, D. and Lacabanne, C. *J. Macromol. Sci. Phys.* 1983, **B22**, 529