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Polymer-Solvent Interaction Parameter for NR/SBR and NR/BR Blends

RANI JOSEPH, K. E. GEORGE, D. JOSEPH FRANCIS and K. T. THOMAS†

Department of Polymer Science & Rubber Technology Cochin University of Science & Technology, Cochin 682 022, India

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Polymer-solvent interaction parameters for the blends of natural rubber (NR) with styrene-butadiene rubber (SBR) and polybutadiene rubber (BR) are calculated using the Flory–Rehner equation by equating the network density of the vulcanizates in two solvents.

INTRODUCTION

Natural rubber/styrene-butadiene rubber blends and natural rubber/polybutadiene rubber blends are extensively used in the manufacture of tyres.[1] A knowledge of the polymer-solvent interaction parameters of these blends would be useful in the study of their network structure. A simple method suggested by Hayes[2] is used in this study for the calculation of the interaction parameters.

In the Flory–Rehner equation

$$-[\ln(1 - Vr) + Vr + \chi Vr^2] = \nu Vs(Vr^{1/3} - 2Vr/f)$$

Vr = Volume fraction of rubber in the swollen sample

† On leave from Rubber Research Institute of India, Kottayam 686 009.

ν = Number of effective network chains/cm^3 of rubber (the network density)
Vs = molar volume of the solvent and
f = functionality of the crosslinks (generally assumed to be 4)

Since ν should not change with change of solvent, swelling data from two solvents on samples of different network densities will provide solvable simultaneous equation for χ_1 and χ_2, the interaction parameters of the polymer in the solvents.

EXPERIMENTAL

The formulations used for preparing the vulcanizates for the swelling study are shown in Table I. The compounds were prepared on a laboratory mixing mill, taking care to mix the elastomers homogeneously. The cure curves of the compounds were taken on a Monsanto Rheometer model R.100 at 160°C. The compounds were vulcanized upto the respective optimum cure times, upto 90% of the optimum cure times and upto 80% of the optimum cure times on a steam heated laboratory hydraulic press at 160°C to get 3 sets of vulcanizates with different network densities for each compound.

LR grade benzene, toluene and isooctane were used for swelling studies without purification. Vulcanizate sample (1.0–2.0 g) was allowed to stand in an excess of benzene, toluene and isooctane

TABLE I
Formulations used for the preparation of the vulcanizates

	1	2	3	4	5	6	7	8	9
NR[a]	100	75	50	25	—	75	50	25	—
SBR[b]	—	25	50	75	100	—	—	—	—
BR[c]	—	—	—	—	—	25	50	75	100
DCP[d]	3	3	3	3	3	3	3	3	3

[a] $\bar{M}w = 7.70 \times 10^5$; Mooney viscosity, ML(1 + 4) at 100°C, 85.3, ISNR5 (Rubber Research Institute of India).
[b] 23.5% styrene; Mooney viscosity, ML(1 + 4) at 100°C, 49.2.
[c] 97% 1,4 (cis); Mooney viscosity, ML(1 + 4) at 100°C, 48.0.
[d] Di-cumyl peroxide (40%).

containing 0.1% phenyl-β-naphthylamine (PBN) at room temperature (30°C). After equilibrium swelling, the solvents containing PBN were replaced by respective pure solvents and after another two hours swelling was stopped. From the weights of the swollen specimen (a_1) and the specimen after drying for six days at room temperatures (a_2), the volume fraction of rubber in the swollen network (Vr) was calculated according to the relation

$$Vr = \frac{a_2 \times \frac{1}{\rho_r}}{a_2 \times \frac{1}{\rho_r} + (a_1 - a_2)\frac{1}{\rho_s}}$$

where ρ_r = density of rubber and ρ_s = density of solvent.

The Vr values obtained for the same vulcanizate in benzene and toluene were taken for the calculation of the interaction parameters of the polymers and polymer blends in benzene and toluene. The Vr values were substituted in the Flory–Rehner equation assuming no change in v with solvent. This gives an equation with χ_1 and χ_2, the interaction parameters in benzene and toluene as the unknowns. Since three vulcanizates of different network densities are available for each polymer or polymer blend, this procedure yielded three equations with χ_1 and χ_2 as the unknowns for each polymer or polymer blend. Solving these by linear regression gives the values of χ_1 and χ_2 for the particular polymer or polymer blend. The same calculation was repeated by comparing the values of Vr obtained for each vulcanizate with isooctane and toluene to get the interaction parameters in isooctane and toluene.

RESULTS AND DISCUSSION

Figure 1 and Figure 2 show the values of interaction parameters of the polymers and polymer blends in benzene and toluene obtained by comparing the swelling data in benzene and toluene and Figure 3 and Figure 4 show the values of interaction parameters in isooctane and toluene by comparing the swelling data in isooctane and toluene. The interaction parameters of NR and SBR in isooctane and toluene using the latter system are fairly in agreement with

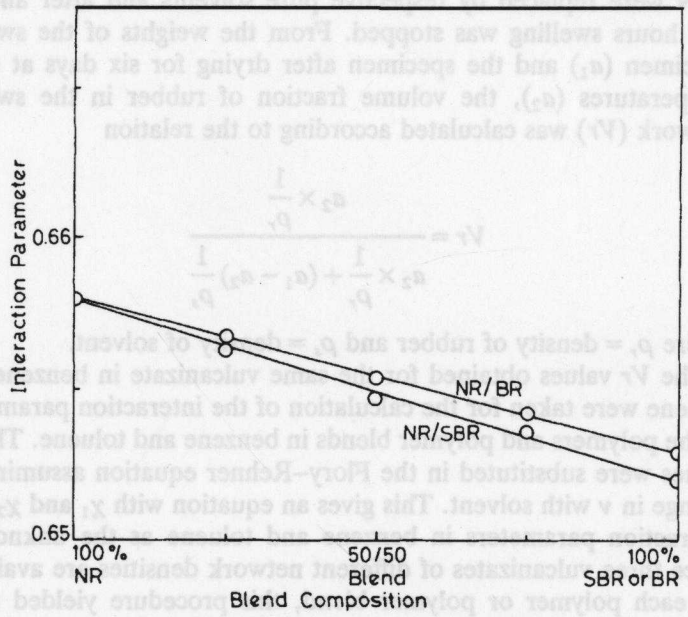

FIGURE 1 Interaction parameters of NR/SBR and NR/BR blends in benzene (benzene-toluene system).

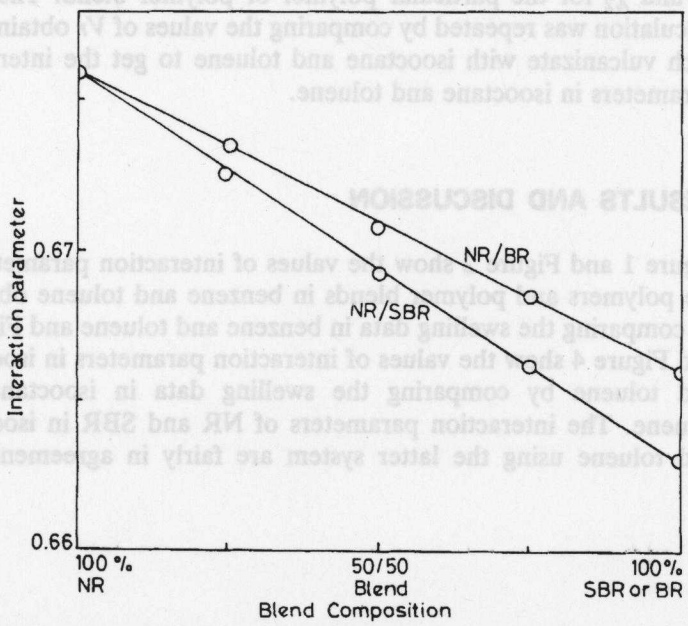

FIGURE 2 Interaction parameters of NR/SBR and NR/BR blends in toluene (benzene-toluene system).

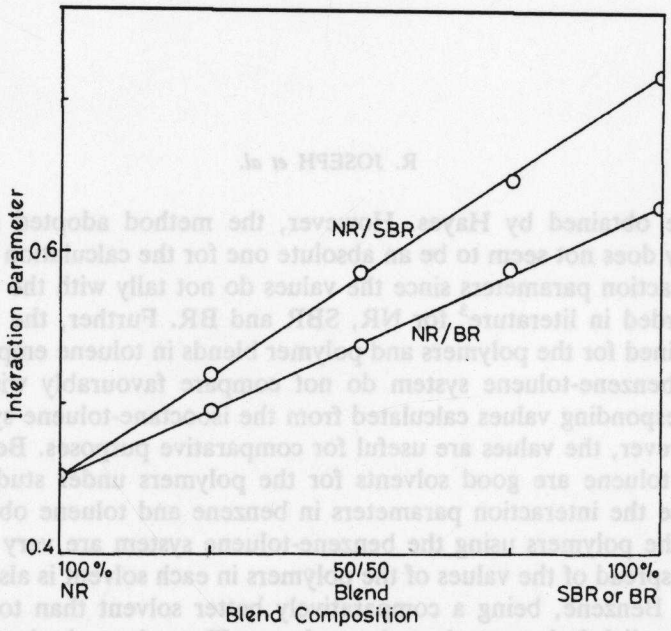

FIGURE 3 Interaction parameters for NR/SBR and NR/BR blends in isooctane (isooctane-toluene system).

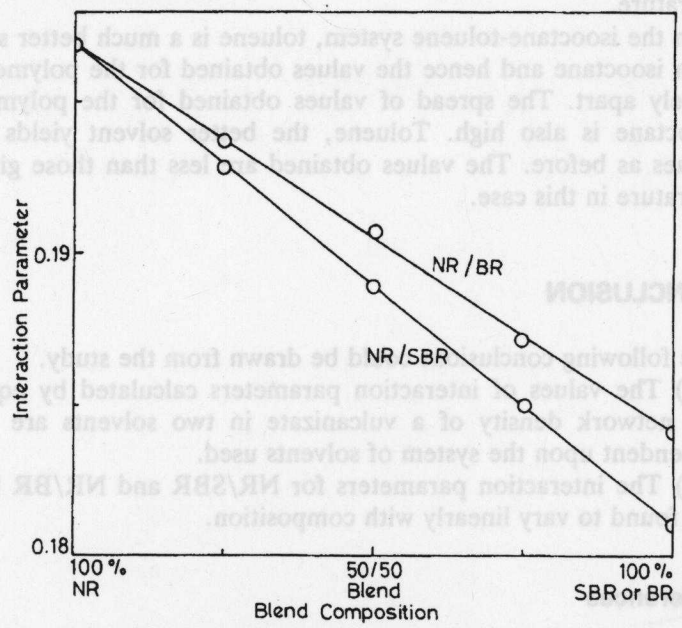

FIGURE 4 Interaction parameters for NR/SBR and NR/BR blends in toluene (isooctane-toluene system).

those obtained by Hayes. However, the method adopted in the study does not seem to be an absolute one for the calculation of the interaction parameters since the values do not tally with the values recorded in literature[3] for NR, SBR and BR. Further, the values obtained for the polymers and polymer blends in toluene employing the benzene-toluene system do not compare favourably with the corresponding values calculated from the isooctane-toluene system. However, the values are useful for comparative purposes. Benzene and toluene are good solvents for the polymers under study and hence the interaction parameters in benzene and toluene obtained for the polymers using the benzene-toluene system are very close. The spread of the values of the polymers in each solvent is also very low. Benzene, being a comparatively better solvent than toluene, yields slightly lower values than toluene. The values obtained with the benzene-toluene system are higher than those given in the literature.

In the isooctane-toluene system, toluene is a much better solvent than isooctane and hence the values obtained for the polymers are widely apart. The spread of values obtained for the polymers in isooctane is also high. Toluene, the better solvent yields lower values as before. The values obtained are less than those given in literature in this case.

CONCLUSION

The following conclusions could be drawn from the study.

1) The values of interaction parameters calculated by equating the network density of a vulcanizate in two solvents are highly dependent upon the system of solvents used.

2) The interaction parameters for NR/SBR and NR/BR blends are found to vary linearly with composition.

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