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Interactions of various liquids with EPDM peroxide vulcanisates cured in the presence of coagents

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Summary

EPDM peroxide vulcanisates, cured in the presence of the coagent triallylcyanurate were swollen in various liquids and the Flory-Huggins parameters were determined. It was found that the presence of triallylcyanurate in the network did not influence the value of the X-parameter significantly. This result was explained by the fact that the coagent is not homogeneously distributed in the elastomer matrix. Furthermore, it was demonstrated that crosslink densities with highest accuracy could be calculated from equilibrium swelling data, using swelling agent-vulcanisate systems with low X-values.

Introduction

From our studies on EP(D)M peroxide vulcanisations in the presence of coagents, it was concluded that during the vulcanisation the coagent had been incorporated quantitatively in the network (1). The presence of a coagent in the vulcanisate might have an influence on network characteristics, such as swelling behaviour.

It has been reported, that the interactions of liquids with sulfur-cured elastomers are influenced by the composition of the curing system (2,3). During sulfur curing, sulfur bridges are formed, which shorten during the vulcanisation. In addition, vulcanisation results in grafting of polar accelerator residues. The ultimate length of the various crosslinks and the extent to which incorporation of the polar moieties takes place, depend on the composition of the sulfur vulcanisation system and the curing conditions. Thus, for two vulcanisates, cured to the same extent with different sulfur vulcanisation systems, the Flory-Huggins parameter (X), which is a measure for the interactions between a network and a swelling agent, will not be the same as a result of the different polarity of the networks.

The X-parameter for liquids with elastomers, cured with a peroxide, does not depend on the composition of the vulcanisation system, *i.e.* on the type of peroxide (4), which seems plausible because during the vulcanisation no polar groups are introduced into the network. However, addition of a coagent to the peroxide vulcanisation system might change this situation, due to incorporation of the coagent.

As an example of EP(D)M peroxide vulcanisations in the presence of coagents, the effect of triallylcyanurate (TAC) on the interactions of EPDM networks in various swelling agents will be described in this paper. Furthermore, the accuracy of determining the elastically active network chain density (μ_e) from equilibrium swelling experiments in various swelling agents will be discussed.

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Experimental

Materials

Dicumylperoxide (= DCP, Perkadox BC, *ex* Akzo, Deventer, The Netherlands) and triallylcyanurate (= TAC, *ex* Merck, Darmstadt, Germany) were purified by recrystallisation from methanol. Ethylene-propylene terpolymer (= EPDM, Keltan 4703, *ex* DSM, Geleen, The Netherlands, 54 wt% ethylene, 8 wt% ethylidene norbornene, M_n (GPC-DRI) = 90.000 g/mole) and the swelling agents benzene, chlorobenzene, *n*-heptane, cyclohexane, tetralin and decalin (*ex* Merck, Darmstadt, Germany) were used as received.

Sample preparation

The elastomer was mixed with DCP (0.3 - 2.0 wt%) and TAC (0 -2.5 wt%) on a laboratory mill. Dumb-bell shaped specimens were vulcanised in a hot press (185 °C, 5.5 min, 10 MPa) and used for both stress-strain and equilibrium swelling experiments.

Determination of Flory-Huggins parameters

The vulcanised samples were swollen in decalin by a factor 2-3, prior to the stress-strain experiments, in order to minimise intermolecular interactions. The elongation was measured discontinuously by increasing the load every 30 s. Measurements were repeated at least 3 times and μ_e was calculated from a Mooney-Rivlin plot (5). Next, Flory-Huggins parameters of the same vulcanisates in various liquids were calculated from their equilibrium swelling behaviour at 20 °C (5).

Results and Discussion

The calculated values of X for the various EPDM-swelling agent combinations are plotted in Fig. 1 as a function of v_2. It can be seen that for a given v_2 of an EPDM compound vulcanised in the presence of TAC, values for X were obtained, which differed not significantly from those of EPDM compounds, vulcanised without TAC.

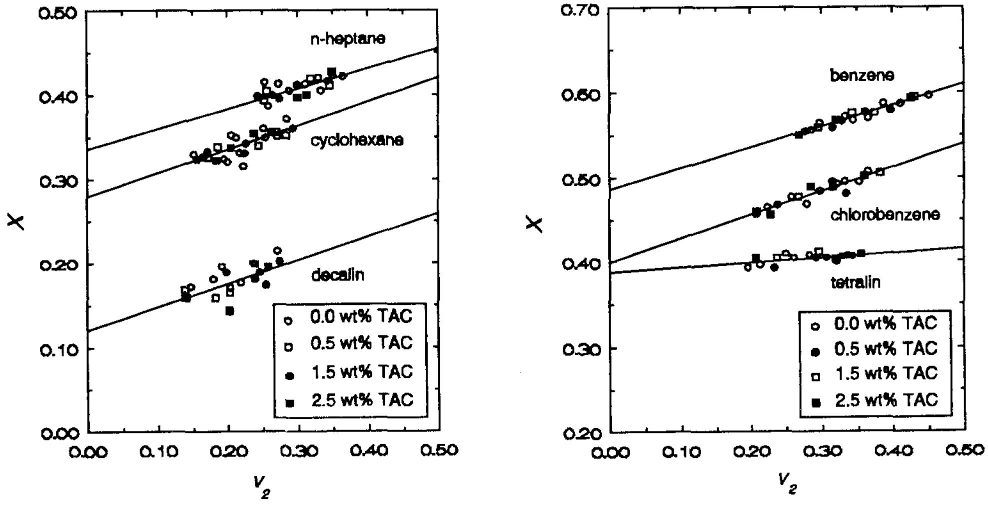

Figure 1 Influence of TAC on the relationship between X and v_2, for the interaction of peroxide cured EPDM-TAC networks with various swelling agents (20 °C).

Fig. 1 shows that, although the EPDM network had been modified by covalent binding of more than 2 wt% of a polar species, no significant change of the network-liquid interaction had occurred. These results are in contrast with those of studies on the influence of sulfur and grafted sulfur accelerator residues on network-liquid interactions (2,3).

This discrepancy can be explained by considering the different vulcanisate morphologies. Accelerated sulfur vulcanisation yields a network with a homogeneous distribution of sulfur bridges (and pendant accelerator residues), resulting from the reversible nature of the crosslinking reactions. Therefore, when using different types of sulfur curing systems or by changing the concentration of sulfur and sulfur accelerators, the bulk polarity of the networks will be different. For a peroxide cure in the presence of TAC a different situation exists. The coagent is dispersed in domains, whereas the peroxide is more or less dissolved in the elastomer-coagent blend (6,7). The heterogeneous blend structure will not change during the vulcanisation and the elastomer matrix is crosslinked in the same way as in the absence of TAC, whilst spots with high crosslink density exist locally near coagent domains. Thus, the bulk polarity of the vulcanisates only slightly changes by the presence of the coagent, which explains the negligible effect of the presence of TAC on the network-liquid interaction characteristics, as expressed by X.

The data in Fig. 1 clearly illustrate the absence of an effect of the coagent on the network-swelling agent interaction, which was observed with all the swelling agents. The accuracy in determining X becomes better with increasing X values, which is obvious when using *e.g.* benzene. This is probably the reason why benzene has often been used as a swelling agent for determining the crosslink density of EPDM networks (8-11). However, not only the accuracy of X, but also the sensitivity of μ_e for the value and the error of X governs the overall accuracy for determining the crosslink density of networks.

The error in μ_e for a single measurement equals the sum of the partial errors of X and the polymer volume fraction of the swollen network (v_2), assuming no error in the molar volume of the swelling agent (V_1) and T, respectively (Eq. 1).

$$\Delta\mu_e = \Delta v_2(\delta\mu_e/\delta v_2)_X + \Delta X(\delta\mu_e/\delta X)_{v2} \qquad (1)$$

Δv_2 is correlated with the accuracy of weighing and was taken as ± 0.004. The partial derivatives $(\delta\mu_e/\delta v_2)_X$ and $(\delta\mu_e/\delta X)_{v2}$ were obtained from differentiation of the Flory-Rehner equation (5). The deviation of X had to be determined from partial differentiation of X to v_2 and μ_e, respectively.

$$\Delta X = \Delta\mu_e(\delta X/\delta\mu_e)_{v2} + \Delta v_2(\delta X/\delta v_2)_{\mu e} \qquad (2)$$

The partial derivatives $(\delta X/\delta\mu_e)_{v2}$ and $(\delta X/\delta v_2)_{\mu e}$ were also obtained by differentiation of the Flory-Rehner equation, whereas $\Delta\mu_e$ was estimated from the error in the stress-strain experiments. This error is largely determined by the error in determining the original cross section and the initial length of the samples, being similar in all experiments. It was assumed that $\Delta\mu_e/\mu_e$ amounted to ± 4%.

From this analysis the relative error in μ_e was determined as a function of v_2 for a number of swelling agents (Fig. 2).

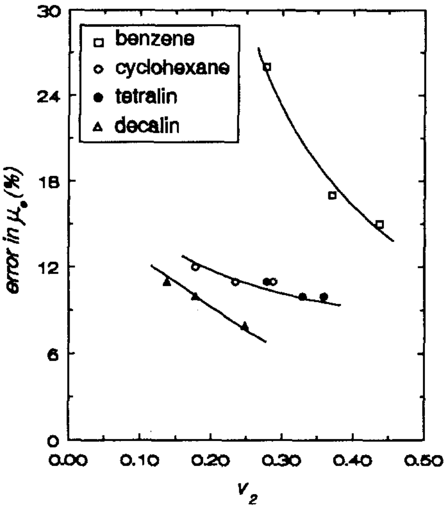

Figure 2 Dependence of the relative error of μ_e on v_2, calculated from equilibrium swelling data in various liquids.

The results clearly show that crosslink densities of EPDM vulcanisates could be determined with a high accuracy when decalin was used as swelling agent, in spite of the relatively scattered data obtained for the relation between X and v_2.

Conclusions

The results of the experiments described in this paper show that the presence of the coagent TAC in EPDM networks did not influence the X-parameter for several elastomer-liquid systems. This result was explained by the fact that the coagent is concentrated in domains, thus having only a marginal influence on the bulk polarity of the network. Therefore, we assume that other coagents have also no influence on the network-liquid interactions, provided the elastomer-coagent system is phase separated. Furthermore, it was demonstrated that different swelling agents for determining the crosslink densities of vulcanisates yielded values of μ_e with a different accuracy. In general, it can be stated that crosslink densities with highest accuracy will be obtained, when vulcanisate-liquid systems with a low X-parameter are used.

References

1. Dikland HG (1992) PhD thesis, University of Twente, Enschede, The Netherlands
2. Moore CG, Trego BR (1964) J Appl Polym Sci 8: 1957
3. Saville B, Watson AA (1967) Rubber Chem Technol 40: 100
4. Loan LD (1963) J Appl Polym Sci 7: 2259
5. Dusek K, Prins W (1969) Adv Polym Sci 6: 1
6. Ahne H, Wiedenmann R, Kleeberg W (1975) Rubber Chem Technol 48: 878
7. Dikland HG, Sheiko SS, Möller M, van der Does L, Bantjes A, accepted for publication in Polym Comm
8. Barton AFM (Ed) (1990) Handbook of polymer-liquid interaction parameters and solubility parameters, CRC Press, 2nd ed., Boca Raton, Ann Arbor, Boston
9. Flisi U, Crespi G (1968) J Appl Polym Sci 12: 1947
10. Hassan AM, Ray LN Jr (1971) J Appl Polym Sci 15: 145
11. Bykadorov NU, Dobryakov ND, Pestov AG, Rubanova RA, Shreibert AI (1973) Funkts Org Soedin Polim, 148

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