

# Influence of the Network on the Interaction Parameter in System EPDM Vulcanizate–Solvent

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**ABSTRACT:** Swelling measurements in six organic solvents were carried out on samples of dicumyl peroxide crosslinked ethylene–propylene–diene (EPDM) having various crosslink densities. The Flory–Huggins interaction parameter  $\chi$  was determined for EPDM vulcanizates 312 and 812 as well as their mixture 312/812 using the Flory–Rehner equation. The results show that the  $\chi$  parameter for the crosslinked polymer is greater than for the uncrosslinked one and is a linear function of the crosslink density. The swelling behavior of the networks were also interpreted by the Flory–Erman theory using the structural factor  $F'_4$  to characterize the network and its behavior during the swelling. The obtained  $\chi$  values indicate that broadening of the molecular mass distribution, in the Gaussian region of distribution, mixture 312/812, increases interactions with solvents. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 991–999, 1997

## INTRODUCTION

The Frenkel–Flory–Rehner hypothesis<sup>1,2</sup> states that in swelling of crosslinked networks the elastic contribution and the mixing contribution to the free energy are equal. The chemical potential difference between the polymer solvent system and pure solvent is written<sup>2–5</sup>

$$(\mu_1 - \mu_1^0) = (\mu_1 - \mu_1^0)_{\text{mix}} + (\mu_1 - \mu_1^0)_{\text{el}} \quad (1)$$

At equilibrium swelling,  $(\mu_1 - \mu_1^0)$  vanishes and becomes

$$(\mu_1 - \mu_1^0)_{\text{mix}} = -(\mu_1 - \mu_1^0)_{\text{el}} \quad (2)$$

In terms of the Flory–Rehner expression for the chemical potential, eq. (2) becomes

$$\begin{aligned} \ln(1 - v_2) + v_2 + \chi v_2^2 \\ = \nu V_1 (v_2^{1/3} - (2/\phi)v_2) \end{aligned} \quad (3)$$

where  $v_2$  is the volume fraction of crosslinked polymer in the swollen state;  $\chi$ , the Flory–Huggins polymer/solvent interaction parameter;  $V_1$ , the molar volume of the solvent;  $\phi$ , the crosslink functionality; and  $\nu$ , the crosslink density of the polymer.

We note that the  $\chi$  parameter is generally accepted to be the same constant for the crosslinked and uncrosslinked polymer, i.e.,  $\chi_C = \chi$ . However, investigations of Mc Kenna and co-workers indicated<sup>6–8</sup> that the  $\chi$  parameter is a function of the crosslink density of the polymer. Furthermore, it should be mentioned that a considerable body of literature has dealt with the swelling activity parameter, which is obtained from measurements of the activities of the crosslinked and uncrosslinked polymers at constant vapor pressure. The Flory–Huggins  $\chi$  parameters obtained by swelling the vulcanizate in an excess of solvent are different

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from the values obtained from the measurement of the activities of the crosslinked polymer.

The chain-length distribution has different effects on the various properties used in the characterization of the network structure.<sup>9</sup> The experimental results in the area of rubberlike elasticity demonstrate that the distribution of network chain lengths can have a profound effect on elastomeric properties.<sup>10,11</sup> The systems of greatest interest are bimodal networks consisting of very short and relatively long chains. The resulting networks have a remarkably large modulus considering their high extensibility,<sup>12</sup> and this is considered to be due to the large numbers of short chains with very limited extensibility. Because of their limited extensibility, these chains give rise to striking departures from Gaussian behavior,<sup>13</sup> large upturns in the modulus, or reduced stress at high elongation. The elastic properties of the networks in the Gaussian region are also of interest in regard to establishing the relationships between the structure of a polymer network and its modulus and equilibrium degree of swelling. The prepared networks are studied with regard to their stress–strain isotherms in elongation and their swelling in a thermodynamically good solvent. The primary values of interest are the network modulus in the limits of large deformation and the degree of equilibrium swelling.

The experimental results using the Flory–Rehner theory require the assumption of an affine nature for the junction point deformation. Using the structural factor  $F'_4$  along with the Flory–Erman theory,<sup>14,15</sup> it is possible to account for the departure from the affine model deformation. Originally, it was assumed that the  $F'_4$  for the affine model had a value of  $F'_4 = 1$ , which corresponds to a total suppression of crosslink fluctuations. These experimental results are then compared with theoretical predictions in order to elucidate the molecular aspects of rubberlike elasticity.

Swelling is a very important, although poorly studied, process in polymer chemistry. For this reason, in the present article, we describe our work on the studies of influence of the molecular mass distribution of uncrosslinked and crosslinked polymers as well as the structure of the polymer network on interactions in solvents.

## EXPERIMENTAL

The samples of randomly crosslinked ethylene–propylene–diene (EPDM, Keltan 312 and 812, 55

wt % ethylene, 4 wt % ethylenenorbornene) and the mixture of 312, 10 wt % and 812, 90 wt %, used in this study were prepared by peroxide curing, using the following amounts of Perkadox BC 40 (dicumyl peroxide 40 wt %): 0.5, 0.8, 1.2, 1.5, 2.5, 4.0, 6.8, and 8.0 phr. The compounds were molded on a laboratory two-roll rubber mill into sheets of the dimensions 144 × 215 × 2 mm and vulcanizates were cured 14 min at 443 K. The detailed composition of the samples was described in a previous study.<sup>16</sup>

The crosslink density of each sample and modulus at large deformation  $2C_1$  were determined by stress–strain measurements on unswollen dumbbell-shaped test specimens at room temperature and at the rate of 100 mm/min.<sup>17</sup> The molecular mass of the investigated polymers,  $M_n$ , and their distribution were determined by gel permeation chromatography (GPC). The measurements were carried out at 313.15 K on a Waters GPC apparatus utilizing four Styragel columns having nominal porosities of  $10^5$ ,  $10^4$ ,  $10^3$ , and 500 Å, respectively. Tetrahydrofuran was used as the solvent at the flow rate of about 0.5 cm<sup>3</sup>/min, as shown in Table I.

Swelling equilibrium measurements were carried out on each vulcanizate sample in six different solvents for 3–4 days at room temperature.<sup>16</sup> The extent of swelling was characterized by the volume fraction of the vulcanizate at swelling equilibrium  $v_2$ .

## RESULTS AND DISCUSSION

The results of equilibrium swelling of the vulcanizates in six organic solvents were calculated using the equation<sup>18</sup>

$$v_2 = \frac{m_2/\rho_2}{(m_2/\rho_2) + (m_1/\rho_1)} \quad (4)$$

where  $m_1$  and  $m_2$  are the solvent and specimen weights at equilibrium swelling, respectively, and  $\rho_1$  and  $\rho_2$  are the densities of the solvent and unswollen vulcanizate, respectively.

The stress–strain data were interpreted in terms of the reduced stress,  $[f^*]$  and the Mooney–Rivlin semiempirical equation<sup>3</sup>:

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \quad (5)$$

where  $2C_1$  and  $2C_2$  are constants and  $\alpha$  is the

**Table I Flory–Huggins Interaction Parameter of Uncrosslinked Polymer  $\chi_0$  and Slope  $\alpha_1$**

Solvents	Samples					
	312		812		312/812	
	$\chi_0$	$\alpha_1$	$\chi_0$	$\alpha_1$	$\chi_0$	$\alpha_1$
<i>n</i> -Heptane	0.417	0.414	0.430	0.423	0.415	0.231
Cyclohexane	0.369	0.362	0.387	0.374	0.359	0.253
<i>m</i> -Xylene	0.406	0.459	0.419	0.407	0.406	0.285
Toluene	0.481	0.546	0.477	0.569	0.476	0.357
Benzene	0.561	0.709	0.550	0.634	0.568	0.377
Tetrahydrofuran	0.503	0.982	0.508	0.610	0.508	0.472

Keltan 312:  $M_n = 95,000$ ,  $M_w = 313,000$ ,  $M_z = 747,000$ ,  $M_w/M_n = 3.3$ ,  $M(1 + 4)125^\circ\text{C} = 36$  (DSM catalog 1990).  
 Keltan 812:  $M_n = 135,000$ ,  $M_w = 435,000$ ,  $M_z = 1,005,000$ ,  $M_w/M_n = 3.2$ ,  $M(1 + 4)125^\circ\text{C} = 77$  (DSM catalog 1990).

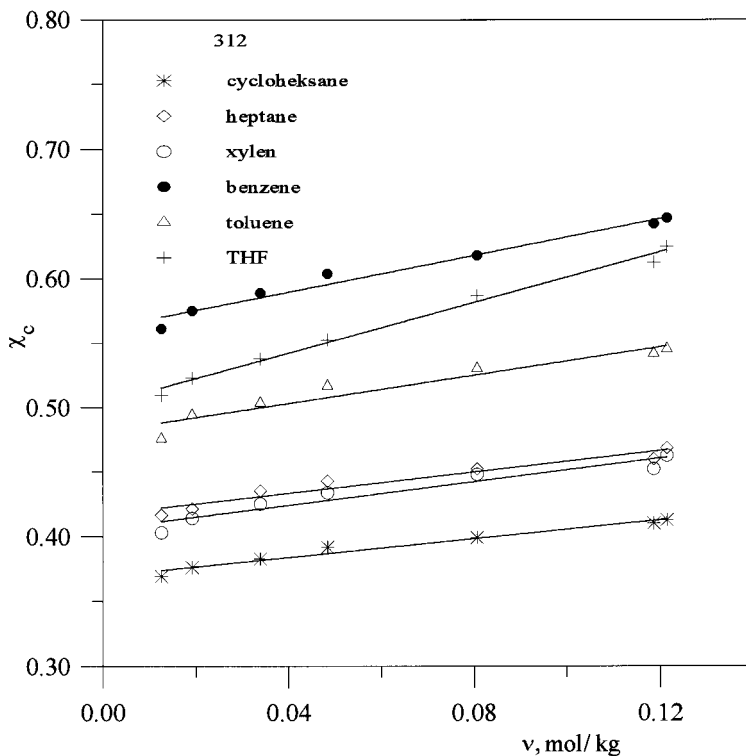
elongation ( $\alpha = L/L_i$ , where  $L$  and  $L_i$  are the stretched and unstretched lengths, respectively). Thus, reduced stress is plotted against reciprocal elongation to determine the crosslink density of the samples.

From the Flory–Rehner eq. (3) and the results of swelling in six solvents, the interaction parameters  $\chi_C$  for the crosslinked polymers were determined (Figs. 1–3). The dependence of the interac-

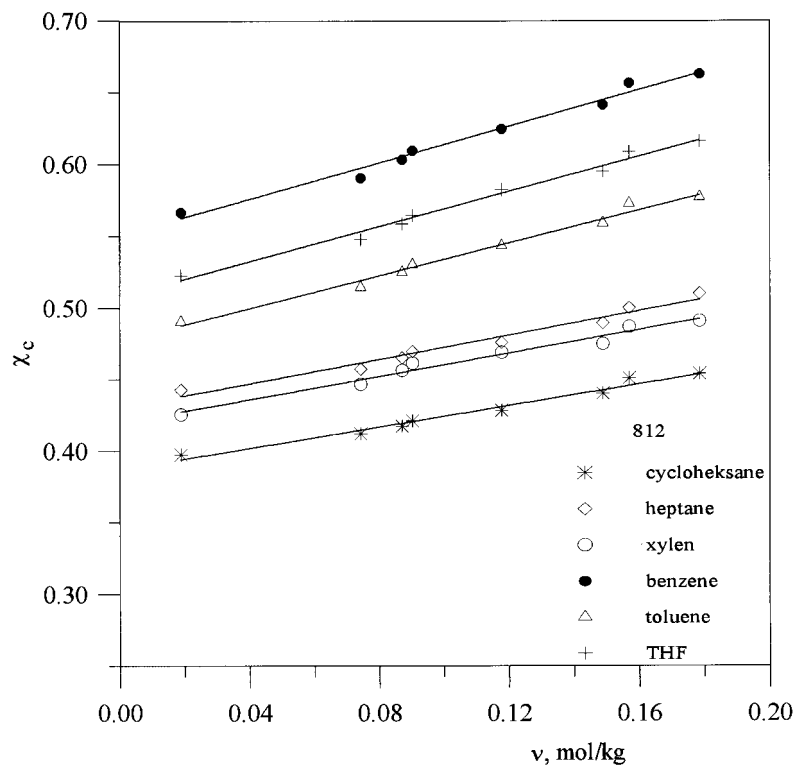
tion parameter  $\chi_C$  on the crosslink density is performed by the linear regression of the following equation, on the data for each solvent:

$$\chi_C = \chi_0 + \alpha_1\nu \tag{6}$$

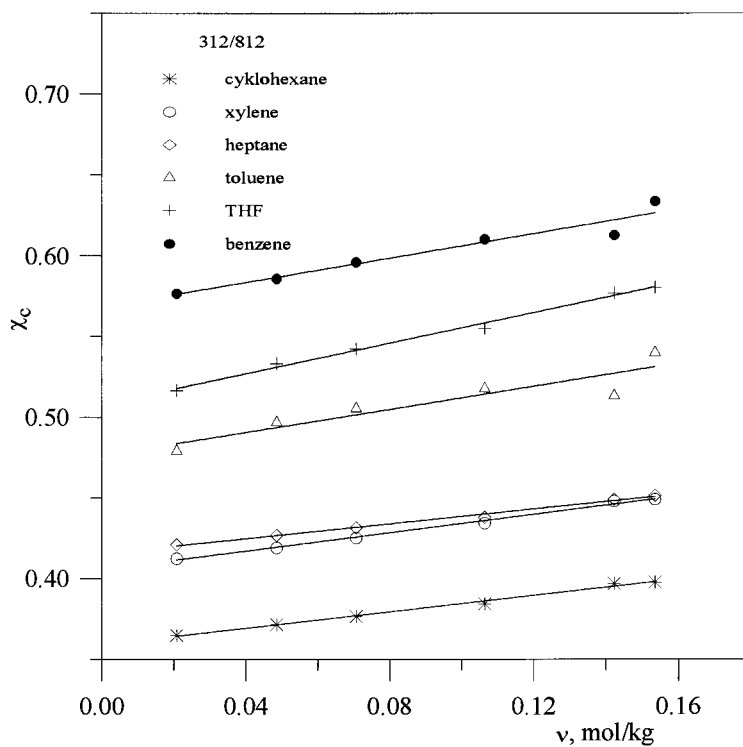
where  $\chi_0$  is the value of  $\chi$  in the uncrosslinked polymer in a dilute solution<sup>8</sup> and  $\alpha_1$  is a slope



**Figure 1** Dependence of  $\chi_C$  on crosslink density  $\nu$  for the vulcanizate 312 swollen in different solvents.



**Figure 2** Dependence of  $\chi_c$  on crosslink density  $\nu$  for the vulcanizate 812 swollen in different solvents.



**Figure 3** Dependence of  $\chi_c$  on crosslink density  $\nu$  for the vulcanizate 312/812 swollen in different solvents.

**Table II** Values of Flory–Huggins Interaction Parameter Using Flory–Rehner and Flory–Erman Equations

Solvents	Samples					
	312		812		312/812	
	$\chi_{F-R}$	$\chi_{F-E}$	$\chi_{F-R}$	$\chi_{F-E}$	$\chi_{F-R}$	$\chi_{F-E}$
<i>n</i> -Heptane	0.388	0.4136	0.393	0.443	0.391	0.410
Cyclohexane	0.328	0.366	0.334	0.398	0.331	0.358
<i>m</i> -Xylene	0.357	0.389	0.369	0.426	0.364	0.416
Toluene	0.448	0.464	0.461	0.491	0.456	0.468
Benzene	0.536	0.541	0.555	0.567	0.545	0.549
Tetrahydrofuran	0.482	0.493	0.501	0.523	0.492	0.501

of the line. The results of such an analysis are presented in Table I. The values of  $\chi_0$  are almost the same for samples 312 and mixture 312/812 for the same solvent, but differ for sample 812. This occurrence can be also noticed when the crosslinked samples were considered. For instance, the value of  $\chi_C$  for the samples 312-0.5, 812-0.5, and 312/812-0.5 in cyclohexane are  $\chi_C = 0.366$ ,  $\chi_C = 0.398$ , and  $\chi_C = 0.358$ , respectively (Table II). It should be emphasized that the content of ethylene can vary in the EPDM polymer and that it has a strong influence on the polymer property. Investigated samples 312 and 812 and the mixture 312/812 differ between themselves in molecular mass distribution before crosslinking, which affects the molecular mass distribution after crosslinking. In this way, in the mentioned samples, all other parameters which influence the interactions of polymer–solvent are eliminated.

On the basis of the theory of random crosslinking described by Treloar,<sup>3</sup> the gel point corresponds to the state in which the number of crosslinks is exactly one-half the number of original molecules  $M_n$ . That gives the value of one crosslink per molecule, which is obvious from the equation<sup>19</sup>

$$\frac{X}{N} = \left( \frac{M_n}{M_d} \right) f \quad (7)$$

where  $X/N$  is the number of crosslinks per molecule;  $M_n$ , the number molecular mass of the polymer;  $M_d$ , the molecular mass of dicumyl peroxide (DCP); and  $f$ , the quantity of DCP in phr. From these calculations, it follows that for sample 312-0.5 the formation of 0.7 crosslinks per molecules is possible, while for sample 812-0.5, one crosslink

per molecule with the same quantity of DCP (0.2 phr) is formed. Furthermore, from this follows that the crosslink density is not the same as for samples 312 and 812. Sample 812 with a higher molecular mass  $M_n$  and narrow molecular mass distribution (Mooney viscosity greater than of sample 312, Table I) has a higher crosslink density than that of sample 312, which results in lower swelling. Considering now samples 812 and mixture 312/812 in the similar way, according to eq. (7), there is 0.97 crosslink per molecule for sample 312/812, which can be neglected when compared with 812. This indicates that they have the same crosslink density in the network. However, sample 312/812 has higher elasticity (lower modulus) and better swelling, which causes lower interaction parameters for sample 312/812 than for sample 812. The results of swelling and the stress–strain measurement indicate that the extent of molecular mass, and particularly its distribution, has a great influence on a polymer network and its properties.

The values of the Mooney–Rivlin constant  $2C_1$  are given in Table III. Since  $2C_1$  represents the modulus in the limit of large elongation, it serves as a measure of the elastic effectiveness of network chains. The presented values of  $2C_1$  show that adding a small amount, 10 wt %, of sample 312 into mixture 312/812 causes broadening of the molecular mass distribution and significantly enlarges the limited chain extensibility of the mixture in the Gaussian region of distribution.

Besides the crosslink density and the modulus, there is another parameter that describes the polymer network: the structural factor  $F'_4$ . Precisely, it characterizes the network efficiency of the crosslinks in the network and depends on

Table III Mooney–Rivlin Constant  $2C_1$  of EPDM Samples

	Samples															
	312-0.5	312-0.8	312-1.2	312-1.5	312-2.5	312-4.0	312-6.8	312-8.0	812-0.5	812-0.8	812-1.2	812-1.5	812-2.5	812-4.0	812-6.8	812-8.0
$\nu$ (mol/kg)	$8.255 \times 10^{-2}$	$1.256 \times 10^{-2}$	$1.915 \times 10^{-2}$	$3.388 \times 10^{-2}$	$4.829 \times 10^{-2}$	$8.059 \times 10^{-2}$	0.118	0.120	$1.879 \times 10^{-2}$	$7.407 \times 10^{-2}$	$8.703 \times 10^{-2}$	$9.025 \times 10^{-2}$	0.117	0.149	0.1569	0.1784
$2C_1$ (MPa)	0.0349	0.0532	0.0811	0.1052	0.2045	0.3413	0.4589	0.5099	0.0796	0.3137	0.3686	0.3822	0.4981	0.6302	0.6644	0.7546
$\nu$ (mol/kg)	$1.237 \times 10^{-2}$	$2.073 \times 10^{-2}$	$4.848 \times 10^{-2}$	$7.070 \times 10^{-2}$	0.106	0.142	0.154		$1.879 \times 10^{-2}$	$7.407 \times 10^{-2}$	$8.703 \times 10^{-2}$	$9.025 \times 10^{-2}$	0.117	0.149	0.1569	0.1784
$2C_1$ (MPa)	0.0524	0.0878	0.2053	0.2994	0.4504	0.6028	0.6505		0.0796	0.3137	0.3686	0.3822	0.4981	0.6302	0.6644	0.7546

their degree of fluctuations. Structural factor  $F'_4$  has been used with the Flory–Erman theory to determine the departure from the affine deformation in investigated samples, using equation

$$M_c = \frac{F'_4 \rho_2 V_1 [(2/\phi)v_2 - v_2^{1/3}]}{\ln(1 - v_2) + v_2 + \chi v_2^2} \quad (8)$$

The studied samples were swollen in six solvents at 296 K to the equilibrium swelling and average values of  $F'_4$  for the investigated tetrafunctional networks were obtained (Table IV). Thus, the values of  $F'_4$  indicate departure from the affine deformation assumed in the Flory–Rehner theory,<sup>2,5</sup> and this is especially significant for vulcanizate 812 which shows the lowest value of  $F'_4 = 0.69$  and for mixture 312/812 which shows the highest value of  $F'_4 = 0.87$ . Using this approach, the  $\chi$  parameters obtained from the Flory–Rehner theory were corrected to allow deviations from affine behavior. From the results of the present study, it is obvious that the values of the interaction parameters are changed by correction with  $F'_4$  (Table II). When swelling is taken into account using any of these methods, Flory–Rehner or Flory–Erman, the difference in the interaction parameters is obvious for same solvent and vary from sample to sample. For example, values of  $\chi_C$  for samples 312, 812, and 312/812 marked as 0.8 in heptane are 0.419, 0.458, and 0.415, respectively, which can be seen in Figures 4 and 5. The value for sample 812 differs considerably (the upper line in Figures 4 and 5).

It should be pointed out that the investigated networks have a molecular mass between crosslinks in the range of  $M_C \cong 2.803$  kg/mol for sample 812 and  $M_C \cong 60.568$  kg/mol for sample 312-0.5. It is of importance to note that samples marked as 0.5 are under the gel point and that samples 0.8 and samples 1.2 are less crosslinked, while samples 6.8 and 8.0 are highly crosslinked (Table III). Their dependence on swelling is shown in Figure 6, where it is shown that the swelling intensity can be divided into two parts and approximated with two lines: the first part, low crosslink density, when the networks are under and around gel point, and the second part when the networks are moderately and highly crosslinked.

Some authors<sup>20,21</sup> also assumed that the reason why the  $\chi$  parameter differs for crosslinked and uncrosslinked polymer is because there are differences between interaction parameters for junctions and network chains. As the investigated net-

**Table IV Flory–Huggins Interaction Parameter and Structural Factor  $F'_4$  at Affine Deformation**

Solvent	Samples			
	EPDM	312	812	312/812
	$\chi$ Flory–Rehner	$\chi$ Flory–Erman	$\chi$ Flory–Erman	$\chi$ Flory–Erman
<i>n</i> -Heptane	0.380 + 0.083 $v_2$	0.399 + 0.162 $v_2$	0.406 + 0.231 $v_2$	0.393 + 0.141 $v_2$
Cyclohexane	0.321 + 0.120 $v_2$	0.353 + 0.185 $v_2$	0.370 + 0.238 $v_2$	0.342 + 0.168 $v_2$
<i>m</i> -Xylene	0.340 + 0.210 $v_2$	0.367 + 0.265 $v_2$	0.380 + 0.315 $v_2$	0.377 + 0.192 $v_2$
Toluene	0.429 + 0.218 $v_2$	0.439 + 0.273 $v_2$	0.440 + 0.325 $v_2$	0.435 + 0.260 $v_2$
Benzene	0.489 + 0.286 $v_2$	0.483 + 0.346 $v_2$	0.473 + 0.398 $v_2$	0.484 + 0.329 $v_2$
Tetrahydrofuran	0.459 + 0.230 $v_2$	0.458 + 0.305 $v_2$	0.457 + 0.346 $v_2$	0.459 + 0.276 $v_2$
$F'_4$	—	0.81	0.69	0.87

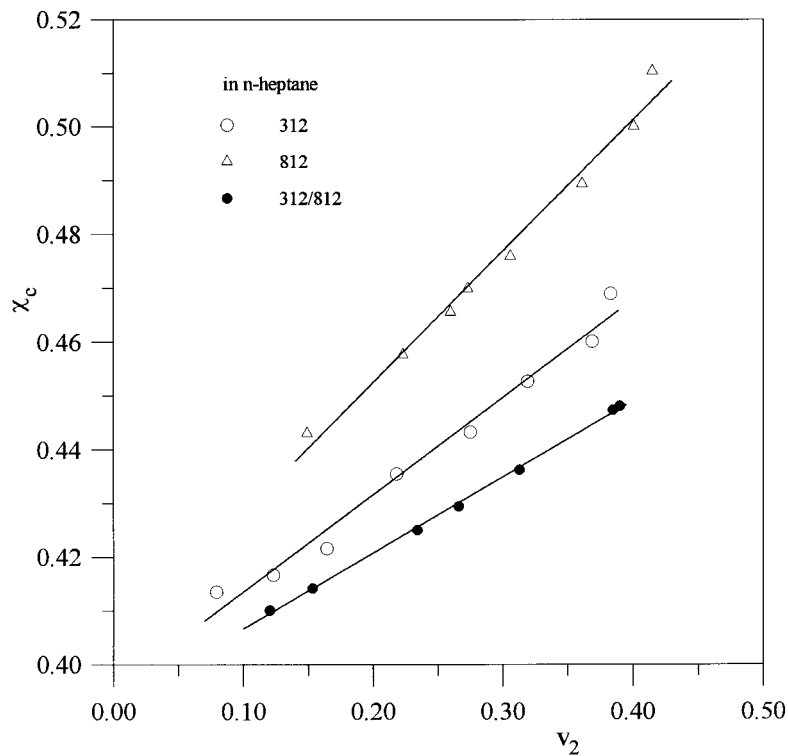
works have quite a variety of junction densities, the swelling of such systems in six solvents did show the change of interactions with the change of the crosslink density.

**CONCLUSIONS**

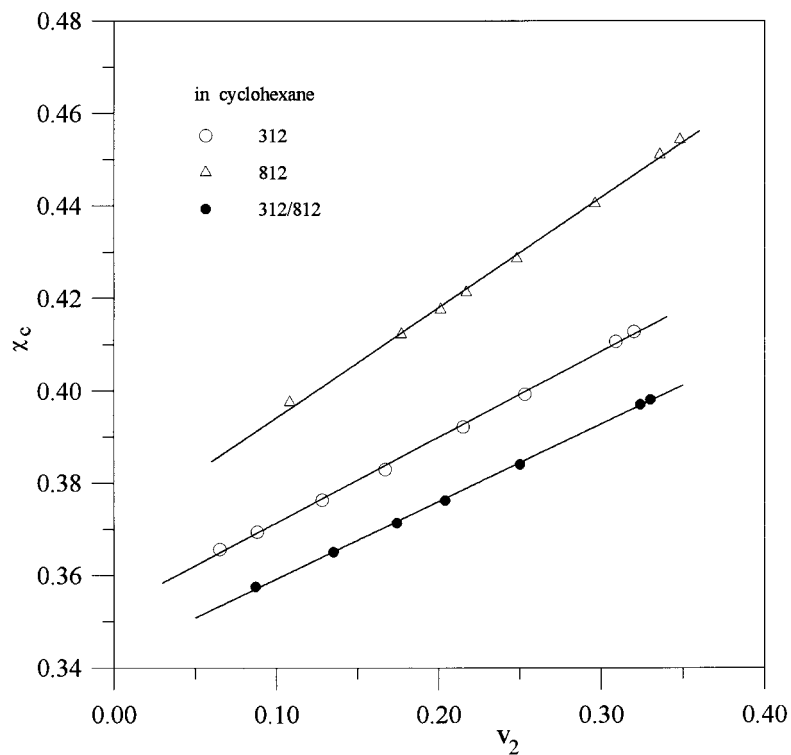
The EPDM vulcanizates were swelled in six good solvents and the interaction parameters were de-

termined as a measure of molecular interactions between polymer and solvent. From the results of swelling and elastic modulus, it can be concluded that extent of the molecular mass of uncross-linked polymer and particularly its distribution have a significant influence on the network property.

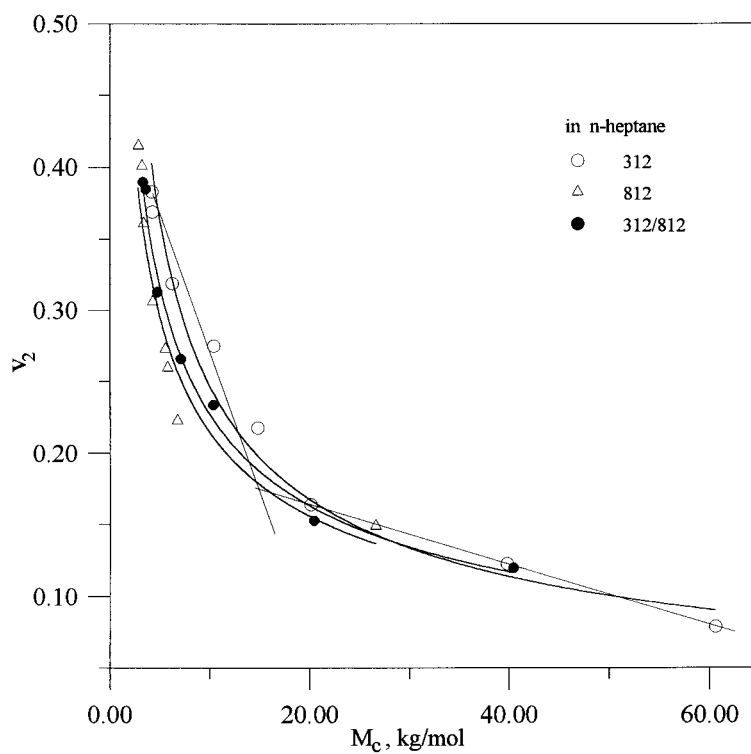
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**Figure 4** Dependence of  $\chi_C$  with volume fraction of vulcanizates in swollen state  $v_2$  for samples 312, 812, and 312/812 swollen in *n*-heptane.



**Figure 5** Dependence of  $\chi_c$  with volume fraction of vulcanizates in swollen state  $v_2$  for samples 312, 812, and 312/812 swollen in cyclohexane.



**Figure 6** Dependence of volume fraction of vulcanizates in swollen state  $v_2$  with molecular mass between crosslink  $M_C$  for samples 312, 812, and 312/812.



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