

Characterization of the Network Structure of Hydroxyl Terminated Poly(butadiene) Elastomers Prepared by Different Reactive Systems

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ABSTRACT: Three types of hydroxyl terminated poly(butadiene) (HTPB) networks having different NCO/OH reactive group ratios were prepared using three different reactive systems (i.e., Desmodur N-100 pluriisocyanate, isophorone diisocyanate (IPDI)/trimethylol propane (TMP), and hexamethylene diisocyanate (HMDI)/TMP). Desmodur N-100 and TMP were used as polyfunctional reactants. The polymer–solvent interaction parameters (χ_1) for HTPB–tetrahydrofuran (THF) and HTPB–chloroform systems at 45°C were determined, using a vapor pressure osmometer (VPO), as 0.31 and 0.24, respectively. Equilibrium swelling values of the networks in THF and chloroform and the data obtained by osmometry were further used for the calculation of the mean number-average molecular weight between junction points (\bar{M}_c) of HTPB networks through the Flory-Rehner equation. The \bar{M}_c values of each network, which were calculated from the swelling data obtained in THF and chloroform using the corresponding χ_1 parameters for polymer–solvent systems, were found to be nearly the same. The changes in the mechanical, swelling, and the solubility properties of the networks prepared by three different reactive systems were followed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1129–1135, 1998

Key words: HTPB; propellant; network; molecular weight between junction points

INTRODUCTION

Poly(butadiene)-based prepolymers have been widely used in the rocket propellant technology as fuel and a polymeric binder. The best known ones are Carboxyl Terminated Poly(butadiene), CTPB, Hydroxyl-Terminated Poly(butadiene) (HTPB), and Poly(butadiene)-Acrylonitrile-Acrylic acid (PBAN). These are low molecular weight ($\bar{M}_n \cong 2000$ –3000 g/mol) liquid rubbers that have terminal allylic carboxyl or hydroxyl groups. In the preparation of a composite propellant, solid particulate oxidizer, burning rate catalyst, plasticizer, and

other minor additives are incorporated into the network via end linking of these functionally active prepolymers using low molecular reactants that have suitable functional groups and desired functionality. In rocket propellant technology, the widely used butadiene-based liquid prepolymer is hydroxyl terminated poly(butadiene) (HTPB). This liquid prepolymer has excellent physical properties such as low glass transition temperature, high tensile and tear strength, and resistance to degradation by numerous chemicals. Therefore, a lot of work has been devoted to the characterization of HTPB.^{1–5} The most commonly used reactants for end linking of HTPB prepolymer are di- or polyfunctional isocyanates, and the resultant network has the polyurethane structure.^{4–7}

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The HTPB prepolymer ideally contains two hydroxyl end groups. However, in the synthesis of HTPB via the free radical mechanism, which involves a random chain transfer process, some polymer chains are terminated as nonfunctional, monofunctional, or polyfunctional. Hence, the number average molecular weight, \bar{M}_c and sol fraction of networks strongly depend on the microstructure of HTPB chains. Therefore, various attempts have been devoted to the determination of the functional group's distribution over the HTPB prepolymer that are supplied from different sources.⁸⁻¹¹ It was reported by Baczek et al.⁹ that for HTPB samples having the number-average molecular weight of 2700 g/mol, a bifunctional prepolymer is the major component, and the average functionality increased with molecular weight.

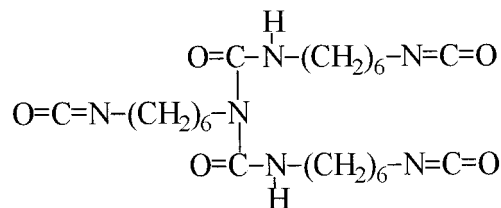
The determination of the thermodynamic solution properties of a polymer is an important aspect of the physico-chemical characterization of its network. The \bar{M}_c is the main characteristic parameter for a network, and in the end-linking reactions, its desired value is obtained by the optimization of the reactive groups ratio of two functional reactants to polyfunctional reactants. In the end-linking reactions, chain extension and branching can be controlled by adjusting the weight ratio of the two functional reactant to polyfunctional reactants.^{4,5,7} Therefore, the primary objective of this study is to determine the thermodynamic solution properties of HTPB in two different solvents; second, to compare the effect of the type of reactive system on the end-linking of HTPB chains; and last, to characterize the network structure of HTPB elastomers by following the swelling, solubility and mechanical measurements.

EXPERIMENTAL

Materials and Characterization

The HTPB was purchased from Sartomer Company under the trade name of R-45M. The number-average molecular weight (\bar{M}_n) was determined as 2700 g/mol using vapor phase osmometry (VPO) with benzyl (MA = 210.2 g/mol) as the calibration standard. The OH equivalence of HTPB was determined as 0.71 mEq/g according to the method cited by Dee et al.¹² using *N*-methyl imidazole as an acetylation catalyst. The density of HTPB was determined as 0.900 g/cm³ at 25°C

and 0.888 g/cm³ at 45°C using a volume-calibrated pycnometer. Desmodur N-100 pluriisocyanate is a reaction product of hexamethylene diisocyanate with water. This product was kindly supplied by Bayer and used without further purification. Its molecular weight was determined as 610 g/mol by using VPO, and the equivalent weight was determined as 5.24 mEq/g using di-*n*-butyl-amine titration.¹³ The ideal formula of Desmodur N-100 is shown below.



Hexamethylene diisocyanate (HMDI) and isophorone diisocyanate (IPDI) were purchased from Fluka as better than 98% purity. Tri-methylol propane (TMP), which is a product of Aldrich, was used as a polyfunctional reactant. Its purity was better than 98%, and used as received. Tetrahydrofuran (THF) and chloroform used for the swelling tests were better than 99.9% purity. The densities of THF and chloroform were determined by picnometry to be 0.866 g/cm³ and 1.440 g/cm³, respectively, at 45°C.

Instrumentation

The tensile testing of HTPB elastomers was performed on a Tensilon (UTM II) tensile tester. The number-average molecular weight of HTPB and Desmodur N-100 and the polymer-solvent interaction parameter values for both HTPB-THF and HTPB-chloroform systems were determined by a Knauer type vapor phase osmometer (VPO).

Preparation of HTPB Networks

HTPB networks were obtained by the end-linking process of the HTPB chains via its terminal OH groups. For this process, three different reactive systems (i.e., Desmodur N-100 pluriisocyanate or a mixture of TMP with IPDI or HMDI) were used. To observe the effect of the type of reactive system on the swelling behavior, mechanical properties, and the sol fraction, HTPB networks were prepared as three sets consisting of three or four samples having different NCO/OH reactive group ratios. These sets are listed in Table I.

Table I The Composition of the HTPB Networks

NCO/OH Reactive Group Ratio	First Set (wt %)		Second Set (wt %)			Third Set (wt %)		
	HTPB	N-100	HTPB	TMP	IPDI	HTPB	TMP	HMDI
1.0	88.05	11.95	86.76	1.84	11.40	89.26	1.88	8.86
0.9	89.17	10.83	87.76	1.86	10.39	90.07	1.89	8.04
0.8	90.21	9.79	88.78	1.88	9.34	90.83	1.93	7.24
0.7	91.38	8.62	—	—	—	—	—	—

In the first set, Desmodur N-100 was used as pluriifunctional isocyanate. In the second and third sets, isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HMDI) were used as difunctional isocyanate, respectively, and trimethylolpropane (TMP) was used as polyfunctional reagent. The ratio in all compositions of the second and third sets were kept constant at 0.4, because the mechanical properties have been reported to be the best when the $\text{OH}_{\text{TMP}}/(\text{OH}_{\text{TMP}} + \text{OH}_{\text{HTPB}})$ ratio is 0.4.^{7,10} In the second and third sets, networks having a NCO/OH ratio of 0.7 could not be prepared, as they had poor physical properties.

To prepare the networks, the liquid HTPB was first degassed for 3 h under 200 mmHg vacuum at 65°C and mixed with a carefully weighed TMP for 15 min at 65°C. After addition of the required amount of isocyanate (IPDI or HMDI) and mixing an additional 3 min, the mixture was poured into Teflon-coated molds to form a flat film having a thickness of 0.7–1.0 mm. The molds were kept in an oven under nitrogen atmosphere at 65°C for 7 days. Desmodur N-100-cured HTPB networks were prepared according to the same procedure without TMP.

CHARACTERIZATION OF ELASTOMERS

The equilibrium swelling degrees of the networks were determined to calculate the mean number-average molecular weight between junction points (\bar{M}_c). The swelling tests were performed in THF and chloroform gravimetrically at 45°C. Small pieces of dry HTPB elastomers (0.3–0.4 g) were weighed and kept in THF or chloroform until equilibrium was attained. The swelling ratio of HTPB networks and the volume fraction of polymer in equilibrium state were calculated according to the following equation,

$$1/v_{2m} = q_v = 1 + (w_2/w_1 - 1)\rho_2/\rho_1 \quad (1)$$

where q_v is the swelling ratio by volume, w_1 and w_2 are weights of the samples in the dry and swollen state respectively, ρ_1 and ρ_2 are the densities of the solvent and the polymer (at 45°C, $\rho_1 = 1.440 \text{ g/cm}^3$ for chloroform, $\rho_1 = 0.886 \text{ g/cm}^3$ for THF and $\rho_2 = 0.888 \text{ g/cm}^3$ for HTPB). v_{2m} is the volume fraction of the polymer in the swollen gel at equilibrium. The equilibrium swelling degree of HTPB networks determined in THF and chloroform are given in Table II.

Sol fraction of the elastomers was extracted with toluene in a Soxhlet apparatus for 24 h. The extracted samples were deswollen in methanol and dried under vacuum. The sol fractions of HTPB elastomers prepared using three reactive systems at different NCO/OH ratios are listed in Table II.

Tensile Stress–Strain Measurements

Elastomeric test specimens were punched from the cured slab using a die prepared in accordance with ASTM D 412-68. The tensile stress–strain measurements were performed at room temperature at a crosshead speed of 5 mm/min. These measurements were made for six samples of each composition having different NCO/OH ratios, and the results were averaged.

RESULTS AND DISCUSSION

Determination of \bar{M}_c from Swelling Measurements

\bar{M}_c of a network is a main characteristic parameter that serves as a reference in describing a network structure. Therefore, as an initial attempt to characterize the network structure of HTPB elastomers using the data obtained from the swelling measurements, the polymer–solvent

Table II Extraction, Swelling, and Mechanical Measurement Results of HTPB Elastomers Prepared by Three Different Reactive Systems

Run No.	Reaction System	NCO/OH Reactive Group Ratio	Sol Fraction wt (%)	q_v in THF	q_v in Chloroform	Elongation at Break (%)	Ultimate Tensile Stress (MPa)	Young's Modulus (MPa)	\bar{M}_c^a (g/mol)	\bar{M}_c^b (g/mol)	\bar{M}_c^c (g/mol)
1	Desmodur N-100	1.0	10.6	5.4	6.1	90	0.63	1.18	3800	3800	5650
2	Desmodur N-100	0.9	12.8	6.8	7.3	97	0.43	0.79	5900	5300	8500
3	Desmodur N-100	0.8	20.8	8.3	9.4	140	0.35	0.48	9000	9000	14,000
4	Desmodur N-100	0.7	26.5	10.5	11.7	150	0.13	0.24	14,300	13,400	27,800
5	IPDI/TMP	1.0	3.3	5.3	5.9	157	0.78	1.04	3500	3500	6400
6	IPDI/TMP	0.9	5.3	8.0	9.1	172	0.67	0.74	8500	8350	9000
7	IPDI/TMP	0.8	19.4	13.7	15.9	560	0.58	0.32	24,000	24,000	21,000
8	HMDI/TMP	1.0	3.2	5.3	5.9	75	0.76	1.06	3500	3500	6300
9	HMDI/TMP	0.9	8.22	9.1	9.6	97	0.44	0.71	10,800	9900	9400
10	HMDI/TMP	0.8	21.6	14.2	16.3	410	0.34	0.30	25,300	25,300	22,300

^a Calculated from the Flory-Rehner equation using swelling data obtained in THF.

^b Calculated from the Flory-Rehner equation using swelling data obtained in chloroform.

^c Calculated from the mechanical measurements.

interaction parameters of HTPB-THF and HTPB-chloroform systems (χ_1) were determined using the VPO method. Although VPO is not an absolute equilibrium method to determine the molar mass of the polymer, and consequently the thermodynamic data on polymer-solvent system, it has been reported that the data obtained by the VPO are satisfactorily in agreement with the data obtained by other absolute and equilibrium techniques such as membrane osmometry and Cahn electrobalance.¹⁴ It has been established in the literature that the solvent activity of a polymer solution can be calculated using the following equation,¹⁵

$$-\ln a_1 = \Delta R M_1 / 1000 K \quad (2)$$

where a_1 is solvent activity, ΔR is electrical resistance recorded by VPO, M_1 is the molecular weight of solvent, and K is the calibration constant of the osmometer that was determined using benzyl (MW = 210) as the calibrating substance. According to the Flory-Huggins theory^{16,17} the activity of the solvent in a polymer solution can be written as

$$\ln a_1 = \ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2 \quad (3)$$

where, v_2 is volume fraction of polymer, x is the number of chain segments in a polymer molecule, assuming that the chain segments have approximately the same volume as the solvent molecules, and χ_1 is the Flory-Huggins interaction parameter of the polymer-solvent system. The following equation can be derived from the eqs. (2) and (3).

$$-\Delta R M_1 / 1000 K = \ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2 \quad (4)$$

The χ_1 parameter of the HTPB-THF and HTPB-chloroform systems were calculated as 0.31 and 0.24, respectively, at 45°C using the data from the VPO measurements in the eq. (4).

The \bar{M}_c value of the HTPB networks were calculated by the following Flory-Rehner equation,¹⁸⁻²² using the data from the VPO and swelling experiments given in Table II

$$\bar{M}_c = -v_1 \rho (v_{2m}^{1/3} - 2v_{2m} / \Phi) / [\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] \quad (5)$$

where \bar{M}_c is the number-average molecular weight between junction points, v_1 is solvent molar volume, ρ is the density of the HTPB networks, Φ is the functionality of the network ($\Phi = 3$), and v_{2m} is the volume fraction of polymer in swollen gel at equilibrium. The \bar{M}_c values evaluated by swelling measurements in both THF and chloroform using the Flory-Rehner equation are given in Table II.

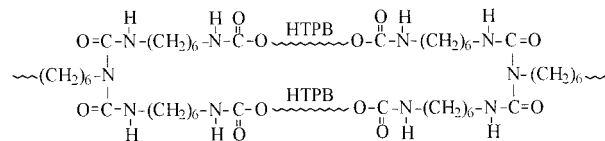
In conformity with the difference in χ_1 parameters of HTPB-THF and HTPB-chloroform systems, the swelling of the HTPB networks in THF and chloroform is significantly different (Table II). In spite of this difference, the \bar{M}_c values of the HTPB networks having the same HCO/OH ratio were found to be nearly the same using the equilibrium swelling results in both THF and chloroform. These results can be considered as a proof for the correct determination of the interaction parameters of both the HTPB-chloroform and the HTPB-THF systems.

As was stated above, VPO is not an absolute method for the determination of molar mass. Hence, the χ_1 parameter was determined from the solution behavior of the HTPB prepolymer, not from the network chain. If we consider the main contribution to the elastic free energy of the networks is due to the HTPB part of the network chains, neglecting this uncertainty does not cause a remarkable ambiguity in \bar{M}_c values of the networks.

It can clearly be seen from the data given in Table II that the chain length between junction points (\bar{M}_c) of the networks are strongly affected by the NCO/OH reactive groups ratios. For each of three sets shown in Table I, the \bar{M}_c values increase as the NCO/OH reactive groups ratios decrease. When the NCO/OH reactive group ratios are 1.0 and 0.9, the \bar{M}_c values of the networks are not appreciably influenced by the type of reactive systems. But for the NCO/OH ratio of 0.8, Desmodur N-100 end-linked elastomer has a smaller \bar{M}_c value than those of IPDI/TMP and HMDI/TMP end-linked elastomers. This can be explained by considering that in IPDI/TMP and HMDI/TMP end-linked systems, the ratio of the difunctional reactant (IPDI or HMDI) to the polyfunctional one (TMP) increases as the total NCO/OH ratio decreases (see Table I). These result in chain extension simultaneously with branching reactions. Therefore, the junction point densities can easily be controlled by changing the amount of TMP in the network forming reaction

of HTPB with IPDI/TMP and HMDI/TMP reactive systems.

Assuming perfect end linking of HTPB chains (which means no loops, no dangling chains, and at least three or more network functionalities) with Desmodur N-100 pluriifunctional reactant, the network structure can be represented as follows,



The \bar{M}_c value of this structure was calculated as 3100 g/mol by taking the mean number-average molecular weight of the HTPB chains and the HMDI part of Desmodur N-100 into consideration. The network structure obtained by Desmodur N-100 at a NCO/OH = 1.0 reactive group ratio resembles the aforementioned perfectly end-linked structure. From the swelling experiments, the \bar{M}_c value of the network was calculated as 3800 g/mol (run 1, in Table II). If we take into account the approximation involved in both the Flory-Rehner equation^{23,24} and the determination of the χ_1 parameter using the VPO method, the agreement between these two values is striking.

The determination of the sol fraction is an important aspect of the characterization of any end-linked network. The HTPB chains are incorporated into the network by the reactions of their end groups. The data given in Table II show that the sol fraction of network is directly related to the average chain length between junctions (\bar{M}_c). Considering all compositions, the sol fraction increases as \bar{M}_c increases. This can be explained on the basis that, as the HCO/OH reactive groups ratio decreases, the amount of unreacted HTPB chains increases, reacting only at one end or chain extended rather than intermolecularly end linked. Thus, the decrease in NCO/OH reactive group ratio leads to an increase in the number of HTPB chains that are located as dangling chains or unreacted chains in the network, and subsequently, a decrease in the number of the constituent chains in the network and an increase in the quantity of the sol fraction is observed. The amounts of extractable polymer in the networks are illustrated in Figure 1 as a function of \bar{M}_c . It is interesting to note that for each of the three reaction systems, the change of sol fraction with \bar{M}_c is almost linear.

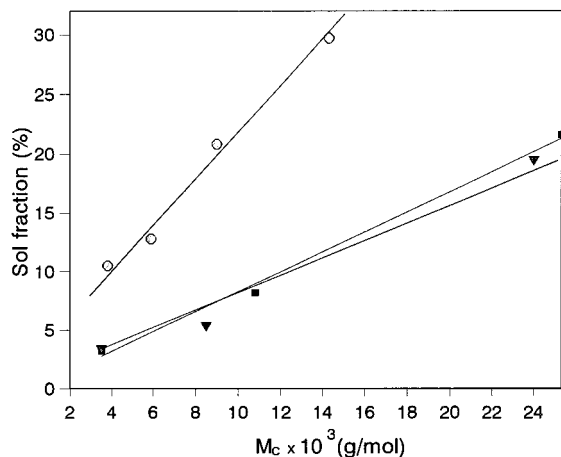


Figure 1 Plot of \bar{M}_c vs. sol fraction of the HTPB networks prepared by three different reactive system. (\bar{M}_c values were calculated using the swelling data obtained in THF). (○) Desmodur N-100, (▽) IPDI/TMP, (■) HMDI/TMP.

As can be seen in Table II, a trend is apparent when the elongation at break values are compared to the data obtained from swelling experiments with the increasing \bar{M}_c , elongation increases also. The tensile stress–strain properties of polymer networks are known to be strongly dependent on the length of the elastically effective network chains. It can clearly be observed from the \bar{M}_c values of the networks that, with the increasing \bar{M}_c , longer chains between junction points, a more elastic network, an increase in the quantity of sol fraction, greater swelling and lower Young's modulus take place. The relationship between the \bar{M}_c and elongation at break values of the HTPB networks prepared using three different reactive systems are illustrated in Figure 2. It is interesting to note that while Desmodur N-100 end linking of HTPB chains brings about a linear change in the elongation of networks with their \bar{M}_c values, for the networks prepared by IPDI/TMP and HMDI/TMP reactive systems nonlinear changes were observed (Fig. 2).

Determination of \bar{M}_c via Mechanical Measurements

The \bar{M}_c value or the molecular weight of the chain section between junction points in the network can be calculated from the theory of rubber elasticity.^{20,25,26} It has been proven that the modulus of elasticity or the shear modulus values obtained by the stress–strain measurements are very useful to measure the crosslinking density of the network. The elongation behavior of the dry test

specimen was inferred by the following equation^{20,25,26}:

$$\sigma = G(\lambda - \lambda^{-2}) = (\rho RT/\bar{M}_c)(\lambda - \lambda^{-2}) \quad (6)$$

Here, σ is the tensile stress that is based on the cross-section of the unstretched dry sample, λ is the ratio of the final length to the original length of the test specimen, ρ is the density of the polymer, \bar{M}_c is the number-average molecular weight of the network chains between junction points, and G is shear modulus. The Young's modulus (E) can be calculated from the initial slope of the stress–strain curve and putting $G = E/3$ in eq. (6), the number-average molecular weight between junction points (\bar{M}_c) of a network can be calculated.

The \bar{M}_c values of the HTPB networks were also characterized through the tensile stress–strain measurements using eq. (6). The results are listed in Table II, in which the \bar{M}_c values of the elastomers determined by the tensile stress–strain measurement are inconsistent with the values recorded by the equilibrium swelling measurement. This inconsistency seems to be quite reasonable because the network defects (i.e., loops and entanglements) play a minor role in the stress–strain behavior of the HTPB elastomers.²⁷

The equilibrium swelling data in the case of Desmodur N-100–reacted systems were generated by the elasticity theory using the \bar{M}_c values obtained from the tensile stress–strain measure-

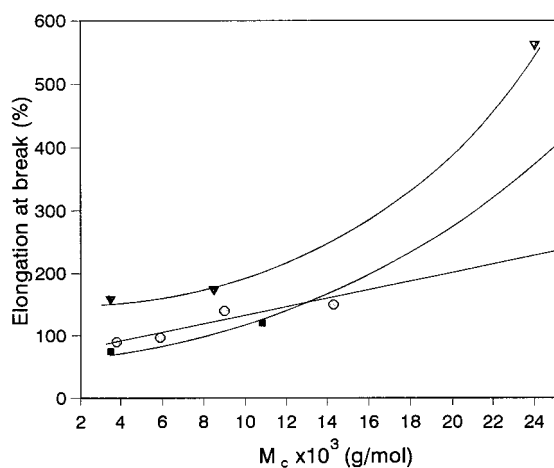


Figure 2 The relationship between \bar{M}_c and elongation at break point of HTPB networks prepared by three different reactive system. (\bar{M}_c values were calculated using the swelling data obtained in THF). (○) Desmodur N-100, (▽) IPDI/TMP, (■) HMDI/TMP.

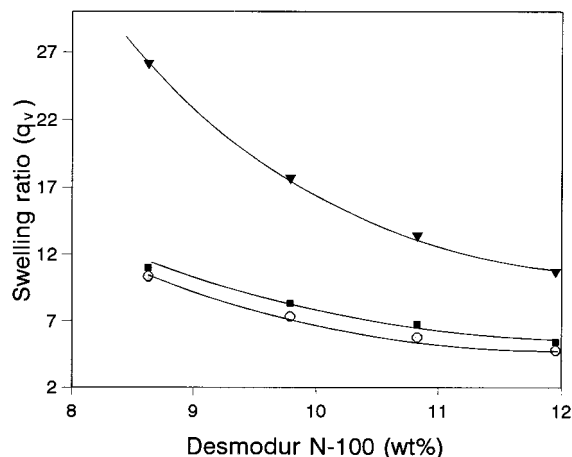


Figure 3 The comparison of the observed swelling ratios with predicted values in the case of Desmodur N-100. (○) Affine model, (■) observed values (in THF), (▽) Phantom model.

ments. According to the elasticity theory, for isotropic swelling of a perfect three-functional network, the following equations can be written^{18,27}:

for the affine network model:

$$\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2 + v_1 \rho / \bar{M}_c (v_{2m}^{1/3} - 2v_{2m}/3) = 0 \quad (7)$$

for the phantom network model:

$$\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2 + (v_1 \rho / 3 \bar{M}_c) v_{2m}^{1/3} = 0 \quad (8)$$

The plots of the predicted and observed swelling values vs. weight percentages of Desmodur N-100 (Fig. 3) reveal that the observed swelling data are everywhere between the prediction of the phantom model and the affine model. Interestingly, the observed swelling values are in close agreement with those predicted by the affine model.

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