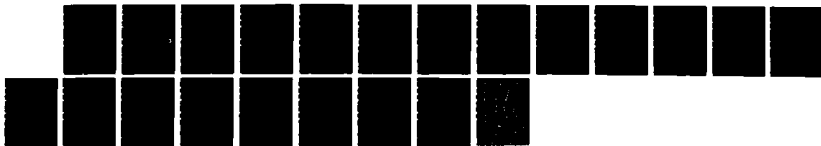RUBBER-MODIFIED PPOXIES: INTERFACIAL TENSION AND
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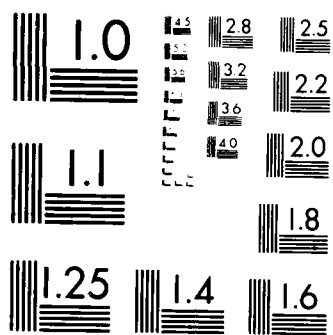UNCLASSIFIED

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Tension and Morphology

Technical Report No. 2.

J. E. Sohn, J. A. Emerson, P. A. Thompson, and J. T. Koberstein
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RUBBER-MODIFIED EPOXIES:
INTERFACIAL TENSION AND MORPHOLOGY

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ABSTRACT

The interfacial tension between carbomethoxy-terminated butadiene-acrylonitrile copolymers and an epoxy resin as a function of temperature and copolymer composition is investigated. Using a digital image processing technique, the shape of a pendant drop of the epoxy in the copolymer is determined. Analysis of the drop shape is performed by profile discrimination and subsequent robust shape analysis. The data are used to examine the relationship between interfacial tension and particle size of the dispersed copolymer phase in rubber-modified epoxy resins. The value of the apparent Flory-Huggins interaction parameter is estimated from the data.

Introduction

The fracture properties of glassy polymers can be improved via the addition of reactive butadiene-acrylonitrile copolymers to the glassy matrix.[1] [2] [3] These rubber-modified resins have been studied for over a decade, with most of the work focusing on modified epoxy resins.[4] [5] [6] [7] [8] Toughness improves on increases in the volume fraction of the dispersed rubber phase,[1] [9] the epoxy-rubber compatibility,[3] [7] and depends on the particle size distribution of the dispersed phase.[3] [10] Most studies have focused on liquid systems where phase separation occurs during the curing process. Typically, the variables studied include rubber composition and concentration, composition and concentration of the curing agent(s), cure time and temperature, and time to gelation.

One system variable which has received little attention to date is the interfacial tension between the rubber and the epoxy. According to classical nucleation theory, the critical nucleus size is directly proportional to the interfacial tension. The interfacial tension also

appears as a parameter in a recent model[11] which predicts the particle size, composition and volume fraction in rubber-modified epoxy resins. Deliberate adjustment of the rubber/epoxy interfacial tension may therefore comprise a means for the control of the dispersed rubber phase morphology and subsequently the material fracture properties.

The interfacial tension between rubber and epoxy can be systematically altered through the use of carbomethoxy-terminated butadiene-acrylonitrile copolymers of varying compositions. In this communication we report measurements of the interfacial tension between an epoxy resin and these rubbers as a function of temperature. These data, together with experimental determinations of dispersed rubber particle sizes, are used to explore the relationship between interfacial tension and rubber phase morphology in rubber-modified epoxy thermosets.

Experimental

The rubber/epoxy interfacial tension was determined by measurement and analysis of pendant drop profiles of one component in the other. The analysis of pendant drop profiles is a well established method for the determination of interfacial tension between two liquid phases;[12] and its application to polymers has been described by Wu.[13]

Pendant and sessile drop profiles result from the balance of forces owing to gravity and surface or interfacial tension. Bashforth and Adams expressed this balance as[14]

$$2 + B\frac{z}{a} = \frac{1}{R/a} + \frac{\sin\phi}{x/a}, \tag{1}$$

where the shape factor B is given by $B = \frac{a^2 \Delta \rho g}{\gamma}$, with a the radius of curvature at the drop apex, R the radius of curvature at coordinate (x,z), ϕ the angle between a tangent to the drop profile and the horizontal axis, $\Delta\rho$ the mass density difference between the fluid and the surrounding medium, g the gravitational constant, which is negative for a pendant drop configuration, and γ the interfacial tension.

The interfacial tensions were obtained experimentally by regression of this equation on

the experimental drop profile. Images of the drop profile were recorded digitally by feeding the output of a video camera to a Tecamar Video Van Gogh frame grabber resident in a microcomputer. Discrimination of the drop profile (*i.e.* edge detection) was accomplished by global thresholding. A piece-wise rotationally-resistant smoothing routine was then applied to minimize discretization effects in the profile. The comparison of Eq. (1) and the experimental profiles was effected with a robust shape comparison algorithm based on repeated median concepts.[15] [16] These analysis procedures have been discussed in detail in previous communications.[17] [18]

The carboxy-terminated butadiene-acrylonitrile copolymers (CTBNs) used in these studies, prepared by a process that yields polymers with lower polydispersity compared to the commercially available CTBNs, were provided by B.F. Goodrich Company. The methyl esters of the carboxy-terminated copolymers were prepared by refluxing the copolymer in methanol, with reaction progress monitored by infrared spectroscopy. The epoxy resins used were derived from the diglycidyl ether of bisphenol A. For interfacial tension measurements, Epon® 828 (Shell Chemical) was used ($n \sim 0.1$). The structures of these materials are shown in Figure 1.

The acrylonitrile content of the copolymers and their solubility parameters, both obtained from technical information of B F. Goodrich Company, are given in Table 1. The material densities, also given in Table 1, were determined over the range of 25-95°C with digital density meters manufactured by Mettler Instrument Corporation that are capable of measuring density as a function of temperature to five significant figures. The accuracy of these measurements is critical to the determination of the interfacial tension, since the important quantity is the density difference between the two materials. Since this difference is often small, greater measurement accuracy yields more accurate interfacial tension values. The molecular weights of the elastomers were determined from gel permeation chromatographic data, calibrated from polystyrene standards, and are given in Table 2.

TABLE 1. Properties of CTBNs and Epoxy

Material	%Acrylonitrile	Solubility Parameter (δ)	$\rho(T)$
X162	0	8.04	$0.92792 + 6.2695 \times 10^{-4}T$
X8	18	8.77	$0.96776 + 6.1081 \times 10^{-4}T$
X13	27	9.14	$0.98521 + 5.7453 \times 10^{-4}T$
Epon 828	-	10.9	$1.18773 + 7.2290 \times 10^{-4}T$

TABLE 2. Molecular Weights of CTBNs

CTBN	M_w	M_N	$P = M_w/M_N$
X162	9100	5400	1.68
X8	8900	5300	1.68
X13	7300	5900	1.23

These same materials were used in the preparation of solid rubber-modified epoxy resins. The morphology of these rubber-modified epoxy resins as a function of composition was described by Romanchick et al.[19] Table 3 shows the average particle diameter of the dispersed rubber phase as a function of copolymer composition for 10 wt% copolymer. It was found that as the acrylonitrile content of the copolymer decreases, the size of the domains of the dispersed phase increases.

TABLE 3. Morphology vs copolymer composition

CTBN in epoxy	% Acrylonitrile in Copolymer	Average Diameter μm Dispersed Phase
X162	0	0.35
X8	18	0.30
X13	27	0.29*

* 200-500Å domains also present

Results

The surface tensions of several copolymers were determined as a function of tempera-
ture over the range 25-100°C (Figure 2). Esterifying the carboxylic acid end groups results in
a decrease in the surface tension, which may be explained by the existence of a hydrogen
bond network in the carboxylic acid terminated copolymers that causes the copolymer to
behave as though it had a much greater molecular weight. Evidence for such a network was
provided by the observation of a significantly higher viscosity for the carboxy-terminated
material. With the methyl ester terminated copolymer, no such network exists, and the poly-
mer behaves as a low molecular weight polymer. The temperature dependence of the surface
tension for the four samples is ~ $-0.1 dyne/cm°C$, consistent with temperature dependencies
observed in other polymer systems (most dependencies are ~ $-0.06 dyne/cm°C$).[13] Weaver
determined the surface properties of several epoxy systems and found the temperature depen-
dence of the surface tension to be $-0.11 dyne/cm°C$.[20] The values of the surface tension as
well as the temperature dependencies are consistent with reported values in many polymeric
systems.[13]

The interfacial tension of three copolymer-epoxy pairs was determined at 55°C; the
results are given in Table 4. As the acrylonitrile content of the copolymer increases, the
interfacial tension decreases. This is reasonable based on solubility parameter arguments, in
that the copolymer's solubility parameter approaches that of the epoxy as the acrylonitrile

content increases, and the two materials become more compatible.

TABLE 4. Interfacial Tension vs Copolymer Composition at 55°C

System	% Acrylonitrile in copolymer	$\gamma(dyne/cm)$
X162-epoxy	0	1.52
X8-epoxy	18	0.58
X13-epoxy	27	0.55

Williams *et al.* modeled the segregation of a dispersed phase during a thermoset polymerization.[11] [21] The free energy change for the formation of spherical domains is given by

$$\Delta G = (4/3)\pi r^3 \Delta G_N + 4\pi r^2 \sigma, \qquad (2)$$

where r is the radius of the dispersed domains, ΔG_N the free energy change involved in the separation of a dispersed phase of any composition, and σ the surface tension. ΔG reaches a maximum for the critical radius r_c, and

$$r_c = \frac{2\sigma}{|\Delta G_N|}. \qquad (3)$$

Particles of size r_c or larger are thermodynamically stable and grow spontaneously. When nucleation is the controlling factor, the particle size is thus expected to be directly proportional to the interfacial tension, as we observe in our data.

Williams *et al.*[21] on the other hand, concluded that growth was the controlling process, and that interfacial tension had practically no effect on the final particle size distribution. In their modelling, they varied their experimentally determined value of the interfacial tension by a factor of four, and found no significant changes in the final particle size distribution. The accuracy of their interfacial tension measurements are doubtful however. Their reported pure component surface tensions $(1-3\times10^{-4}Nm^{-1}$ for the X13 rubber used in our study) are unreasonably low, falling two orders of magnitude lower than those we have measured (Figure 2) and those typically observed for other polymers.[13] In addition, the use of Antanoff's rule, that is the interfacial tension is equal to the difference in pure component surface

tensions, is generally unwarranted for polymeric systems.[13] The results of their simulations must therefore be considered within this context.

Wu investigated the interfacial and rheological effects on the formation of a dispersed phase in incompatible polymer blends during melt extrusion.[22] The relationship for the master curve obtained is

$$\frac{G\eta_m a}{\gamma} = 4p^{\pm 0.84}, \tag{4}$$

where G is the shear rate, a the particle diameter, η_m the matrix viscosity, η_d the dispersed-drop viscosity, and $p = \eta_d/\eta_m$. Thus the dispersed-drop size is directly proportional to the interfacial tension, in agreement with nucleation theory and the results described herein.

The apparent direct relationship between interfacial tension and particle size that we have observed is not conclusive however. In changing the interfacial tension, we have also changed the interaction parameter, as reflected in the variation of solubility parameters for the series of rubbers (Table 1). A full simulation employing some model such as that of Williams et al. is required to resolve the independent effects of the interaction parameter and interfacial tension, and their importance in controlling the rubber particle size.

The effect of temperature on interfacial tension was studied using two rubbers, one with no acrylonitrile (carbomethoxy-terminated PBD), the other containing 18 wt% acrylonitrile. Plots of interfacial tension versus temperature are shown in Figure 3. As the temperature increases, the interfacial tension decreases linearly for both pairs, with a value of ~ 0.01 dyne/cm°C for both systems. This value compares favorably with those found in other polymer pairs, such as PDMS/PBD.[18]

Interfacial tension can be calculated from the surface tensions of the two phases by harmonic-mean or geometric-mean equations.[13] However, a better picture of the interfacial region can be determined by using a statistical thermodynamic theory (mean-field theory) based on the energy of mixing contribution to the interfacial tension, as given by Helfand and Tagami.[23] For infinite molecular weight, they obtained the expression

$$\gamma = (\chi/6)^{1/2}\rho_0 bkT, \tag{5}$$

where χ is the Flory-Huggins interaction parameter, b the effective statistical segment length, and ρ_0 the average monomer density. The theory was extended by Helfand and Sapse to remove the restriction of property symmetry of the polymers yielding[24]

$$\gamma = kT\alpha^{1/2}[\frac{\beta_A + \beta_B}{2} + \frac{1}{6}\frac{(\beta_A - \beta_B)^2}{\beta_A + \beta_B}], \tag{6}$$

where α is the interaction density parameter given by $\alpha = \rho_0\chi$ and $\beta_i = \rho_i b_i^2$. The statistical segment length b is calculated from $b = m^{1/2}(r_0/M^{1/2})$, where m is the mass of a monomer unit, r_0 the unperturbed end-to-end distance, and M the molecular weight.

Figure 4 shows the theoretical and the experimental relationships of the temperature dependence of the interfacial tension for the two polymer pairs. The interaction parameter was estimated from the solubility parameters according to the regular solution expression

$$\chi = \frac{(\delta_A - \delta_B)^2}{\rho_0 kT}, \tag{7}$$

where δ_i is the solubility parameter of component i (Table 1). The statistical segment length b was estimated using the value of $r_0/M^{1/2}$ for PBD. The theory overestimates the interfacial tension by a factor of four, and the predicted temperature dependence is opposite from that determined experimentally.

As an alternative to the use of Eq. (7), we also applied the Helfand-Tagami theory directly to the experimental interfacial tension data to obtain an apparent interaction parameter.

The temperature dependence of the apparent interaction parameters (Figure 5) was well represented by a relationship where both entropic and enthalpic contributions are considered:

$$\chi = \chi_H/T - \chi_S. \tag{8}$$

The values of χ_S and χ_H as determined from plots of apparent χ vs $1/T$ (Figure 5) are given in Table 5 for two rubber-epoxy pairs, along with values previously obtained for the pair PBD-PDMS. The generally good agreement between the values given in Table 5 and

those reported by Round and McIntyre as referenced by Helfand[25] show that both entropic and enthalpic contributions are necessary for correct temperature dependence of the interfacial tension. These apparent χ parameters are also in reasonable agreement with those determined by Williams *et al.*[21] from cloud point measurements on an epoxy system based on a rubber similar to X13. (see Table 5)

The Helfand-Tagami theory assumes infinite molecular weight for the two components, however, the materials studied here have low molecular weights (Table 2). Nevertheless, reasonable agreement is found between the temperature dependence of the interfacial tension when the Flory-Huggins interaction parameter is comprised of both entropic and enthalpic terms.

TABLE 5. Entropic and enthalpic contributions to temperature dependence

System	χ_S	χ_H
X162-epoxy	0.278	109.9
X8-epoxy	0.312	104.6
PBD-PDMS[a]	0.25	126
Rubber - epoxy[b]	0.336	69 45

[a] Reference 18
[b] Reference 21

Summary

The interfacial tension between an epoxy resin and butadiene-acrylonitrile copolymers are determined, using digital image processing techniques and a recently developed robust statistical algorithm. The effects of copolymer composition and temperature on the interfacial tension are explored. The interfacial tension is found to correlate with the morphology of the two phase system: increasing acrylonitrile content of the copolymer results in a decrease in the interfacial tension and a corresponding decrease in the domain size of the dispersed rubber phase in the epoxy matrix. The Flory-Huggins interaction parameter χ was estimated and best agreement for the temperature dependence requires both enthalpic and

entropic contributions.

Acknowledgments

List of Figures

Figure 1. Chemical structures of the epoxy resin and the butadiene-acrylonitrile copolymers.
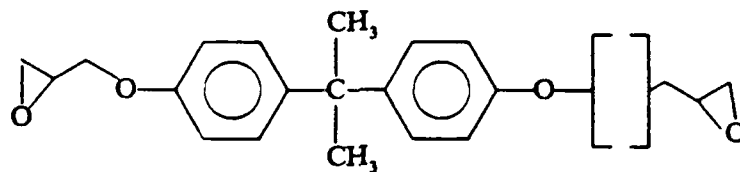
Butadiene-acrylonitrile copolymer

$$ROOC \left[\left[CH_2CH = CHCH_2 \right]_x \left[CH_2CHCN \right]_y \right]_z COOR$$
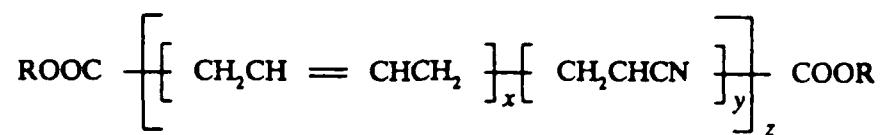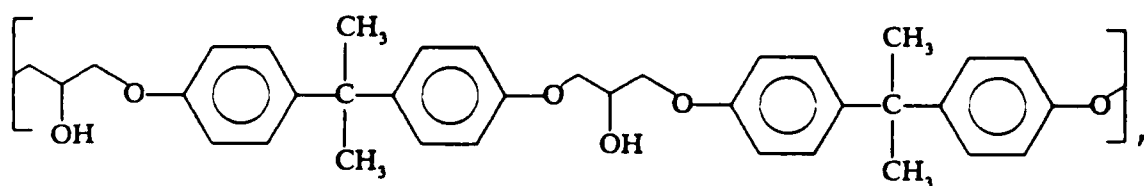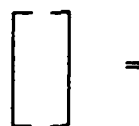
Epoxy

where

$$\left[\quad \right] =$$

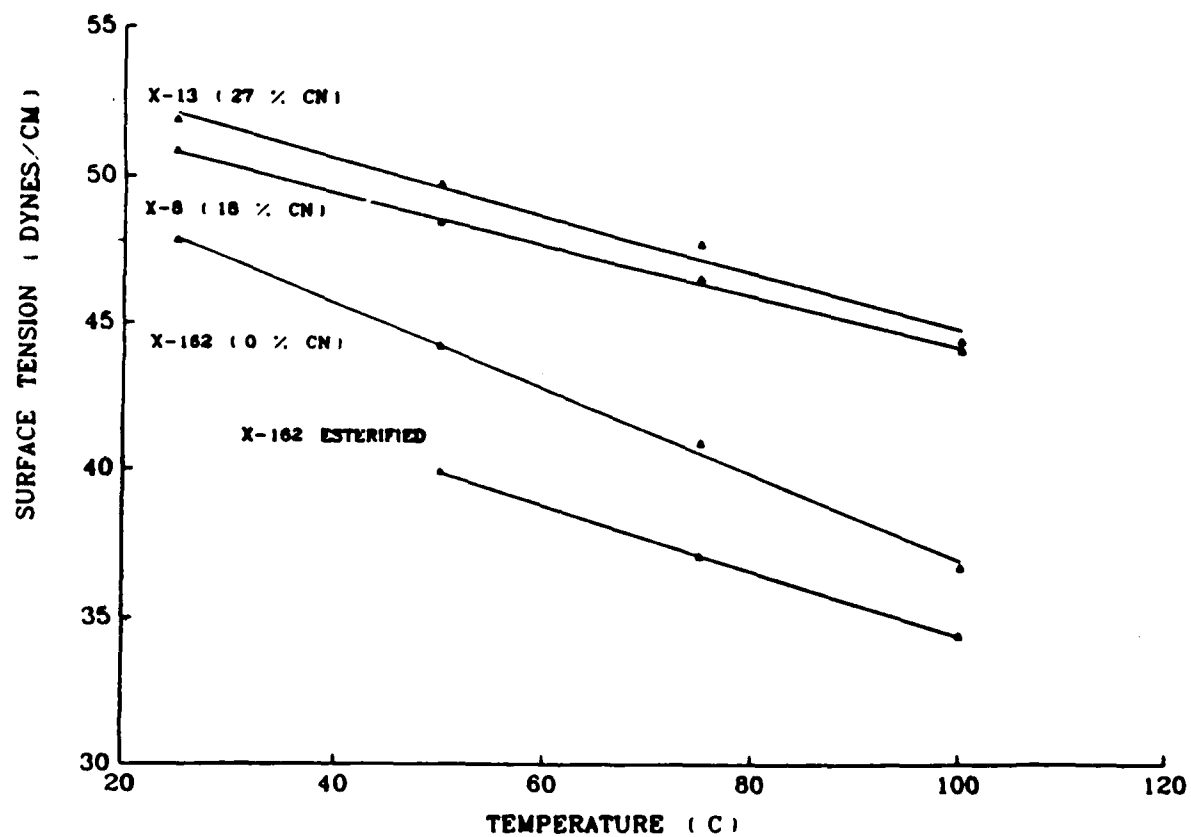**Figure 2.** Temperature dependence of the surface tension.

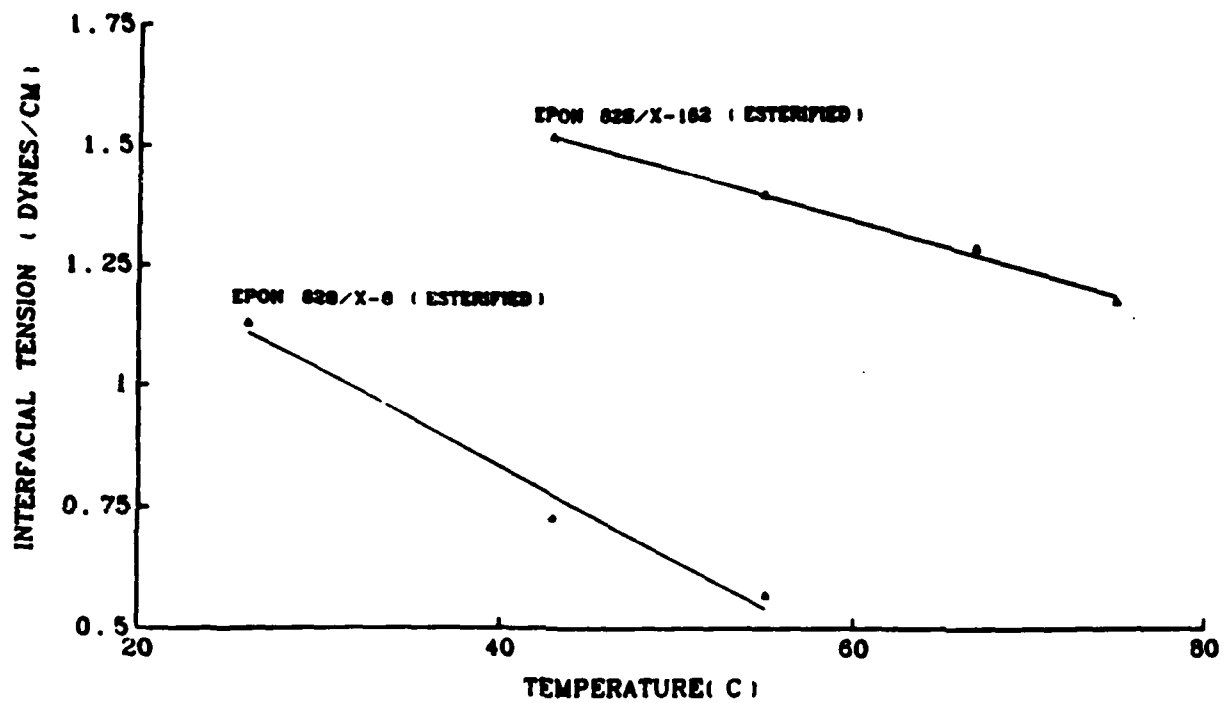Figure 3. Temperature dependence of the interfacial tension.

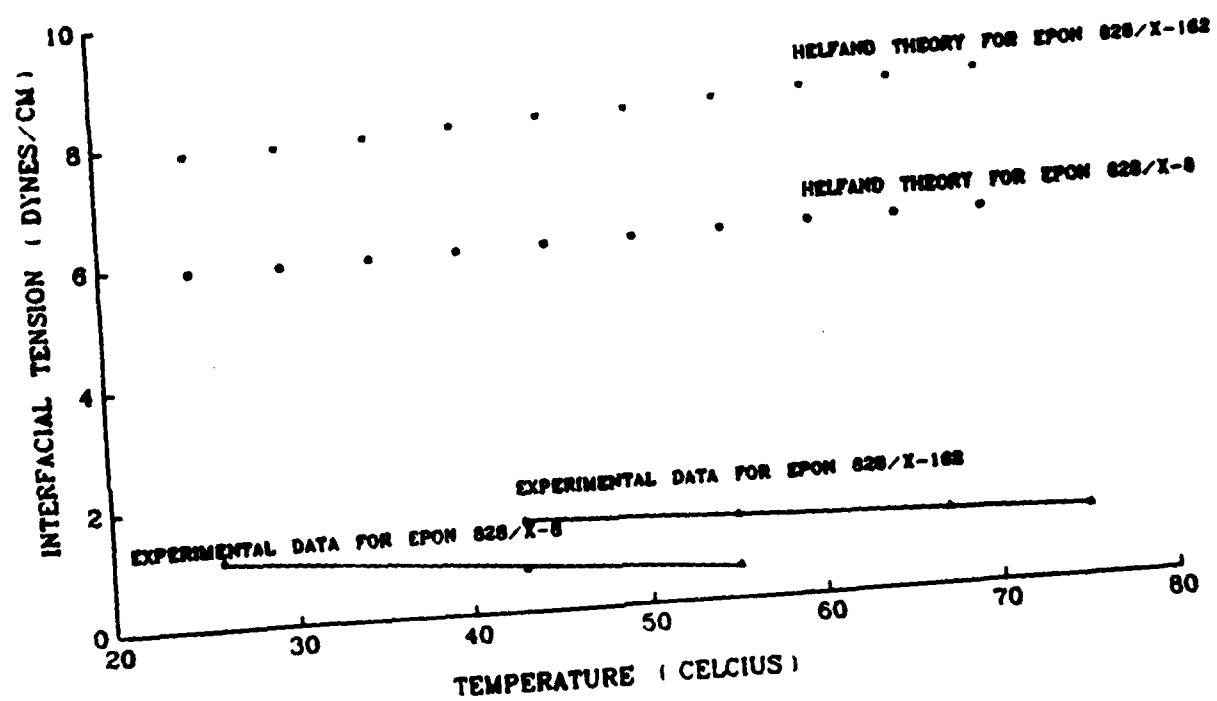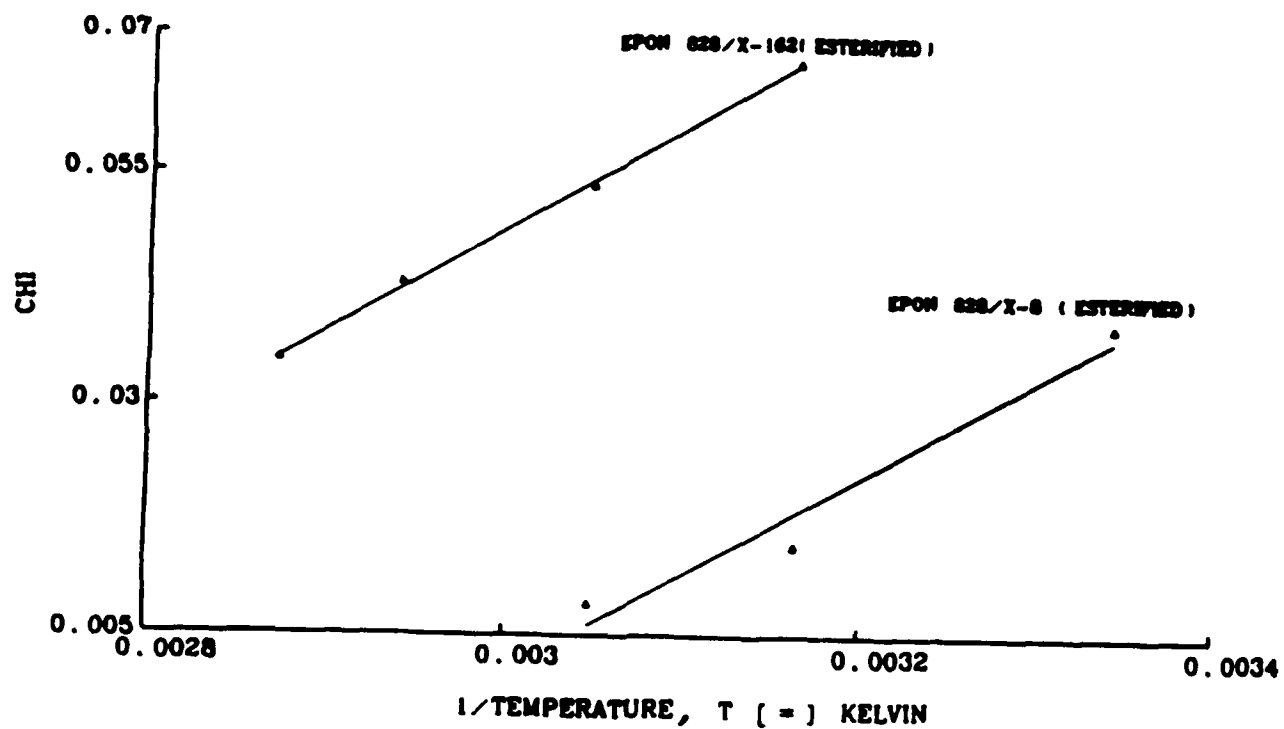**Figure 4.** Comparison of the theoretical and the experimental temperature dependence of the interfacial tension.

Figure 5. Apparent χ vs 1/T.

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