Effects of Polymer-Filler Adhesion on the Properties of Polychloroprene Elastomers Filled with Surface-Treated Fillers

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Synopsis

A new analytical method has been employed to determine values for the surface-energy properties, such as the solid/vapor surface energy and the equilibrium work of adhesion, of several polychloroprene compositions filled with organosilane-treated wollastonite fillers. The equilibrium work of adhesion, which represents the amount of energy stored in the interface formed between polymer and filler, has been used as a key material parameter to correlate changes in the mechanical and rheological properties of wollastonite-filled polychloroprene compositions. Experimental results show that some properties such as tear strength, tensile modulus, shear viscosity, and compression set, which depend on polymer-filler adhesion to varying degrees, increase as the equilibrium work of adhesion increases. On the other hand, properties such as tensile strength and ultimate elongation, which largely depend on the degree of mixing of filler particles and such defect structures as microvoids, decrease with the increase of the equilibrium work of adhesion. A power-law relationship between the tensile modulus and the equilibrium work of adhesion has also been established. This relationship can be used for selecting organosilane-treated fillers in order to achieve optimum properties.

INTRODUCTION

Many mineral fillers are used in various polymer systems to enhance physical properties. There are two distinct mechanisms that can be used to describe the reinforcement effectiveness of these fillers in a polymer matrix. The first mechanism is due to polymer-filler adhesion, and the second one is due to hydrodynamic interaction.[1-3,13,14] A popular technique for enhancing the reinforcement effectiveness due to polymer-filler adhesion is the use of coupling agents to modify the filler surface. An example of such a filler system is wollastonite treated with organosilanes. In this filler system, the naturally occurring mineral containing calcium metasilicate as its major chemical constituent was treated with organosilanes of the structure, $R'Si(OR)_3$. The R' represents an organofunctional group and the OR represents a hydrolyzable alkoxy group attached to the silicon. In the surface treatment process, the alkoxy groups hydrolyze to form silanols which react with the OH groups on the surface of the wollastonite. When mixed with a polymer matrix, the R' group physically and/or chemically interacts with the polymer, thus forming a bridge between the polymer and the wollastonite. For enhancing the reinforcement effectiveness due to hydrodynamic interaction, the use of anisotropic filler is an effective method.

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Equation of state

$$\cos \theta = 1 + b \ln(\gamma_C/\gamma_{LV}) \tag{1a}$$

Solid/vapor surface energy

$$\gamma_{SV} = [b \exp(1/b - 1)]\gamma_C \tag{1b}$$

Liquid/solid surface energy

$$\begin{aligned}\gamma_{LS} = \gamma_{SV} + \gamma_{LV} - \gamma_{LV}\{1 + b \exp(1 - 1/b) \\ + b \exp(1 - 1/b)\ln[\gamma_{SV}/(b\gamma_{LV})]\}\end{aligned} \tag{1c}$$

Equilibrium work of adhesion

$$W_A = \gamma_{LV}[2 + b \ln(\gamma_C/\gamma_{LV})] \tag{1d}$$

Harkins' spreading coefficient

$$\lambda_{LS} = \gamma_{SV}b[\exp(1 - 1/b)]\{1 + \ln[\gamma_{SV}/(b\gamma_{LV})]\} - 1 \tag{1e}$$

Previous investigations[4,5] indicated that the use of surface-treated fillers can improve the properties of polymers. However, the selection of the proper surface treatment for a given polymer is still on a trial-and-error basis. Therefore, a significant research step is to understand the reinforcement mechanisms of surface-treated fillers in a polymer matrix. From the methodological viewpoint, it is important to determine the key adhesion variables so that the values of these variables can accurately characterize the reinforcement due to polymer-filler adhesion. Once the reinforcement due to polymer-filler adhesion is determined, we can then determine the reinforcement due to the hydrodynamic interaction.

Recently, a new analytical method has been developed for determining the surface-energy properties of particulate fillers.[1] This method consists of: (1) a filler-column method[1,2,6,7] for measuring the contact angle data of the filler wetted by a series of solvents with known liquid/vapor surface energies, and (2) a unified theory of adhesion[1] for determining the surface-energy properties of the filler and the polymer. These properties are critical surface energy for wetting, γ_C, extent of interaction, b, and solid/vapor surface energy, γ_{SV}. The surface-energy properties of both the filler and the polymer were required to determine the values of equilibrium work of adhesion, W_A, and Harkins' spreading coefficient, λ_{LS}, of filled polymers. The equations derived from the unified theory of adhesion for calculating the above surface-energy properties are summarized in Table I. This unified theory also provided new criteria of spreading and failure that proved to be useful for characterizing polymer-filler and polymer/polymer systems. These criteria are illustrated in Figure 1. The above analytical method was successfully used in the determination of the surface-energy properties of several carbon black-reinforced polychloroprene elastomers.[2] Based on these surface-energy properties, optimized polychloroprene compositions with enhanced physical properties have been developed.[2,3]

In this work, we first used the above analytical method[1] to determine the surface-energy properties of wollastonite fillers treated with a series of organosilanes. We then determined the surface-energy properties of several polychloroprene compositions filled with the treated wollastonite. Finally,
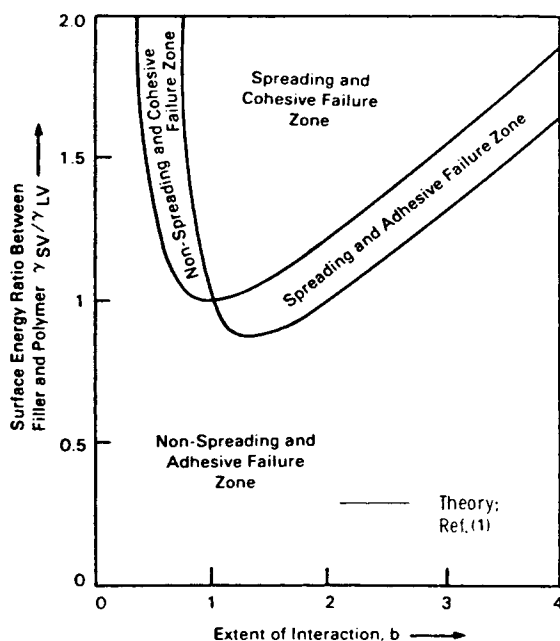
Fig. 1. Spreading and failure characteristics predicted from the unified theory for adhesion.[1]

based on the values of the surface-energy properties, we determined the effects of the two reinforcement mechanisms, namely, polymer-filler adhesion and hydrodynamic interaction, on mechanical and rheological properties of wollastonite filled polychloroprene compositions.

EXPERIMENTAL

Material

The fillers used in this work were a series of surface-treated wollastonite. The coupling agents used were organosilanes, which are designated as A1100, A174, and A151 (WOLLASTOKUP, NYCO) and have the chemical nomenclature and structure as shown in Table II. The average particle size of the

TABLE II
The Organosilane-Treated Wollastonite Fillers Investigated

Filler designation	Chemical nomenclature of the silane	Chemical structure of the silane	pH value in water slurry
A1100	gamma-aminopropyltri-methoxysilane	$(CH_3O)_3SiC_3H_6NH_2$	11.0
A174	gamma-methacryloxypro-pyltrimethoxysilane	$(CH_3O)_3SiC_3H_6O\overset{\text{C}}{\underset{O}{\overset{\parallel}{}}} - \overset{C=CH_2}{\underset{CH_3}{\overset{\mid}{}}}$	10.6
A151	vinyltriethoxysilane	$(C_2H_5O)_3SiCH=CH_2$	11.2

TABLE III
Values for the Viscosity and the Surface Energy of the Wetting Liquids[12]

Wetting liquids	Viscosity at 20°C (pa-sec)	Surface energy at 20°C (mPa-m)
Normal decane	9.2×10^{-3}	24.6
Benzyl alcohol	5.8×10^{-3}	39.0
Aniline	3.7×10^{-3}	43.1
Formamide	3.3×10^{-3}	58.4

TABLE IV
Compositions of Polychloroprene(CR) Filled with Organosilane-Treated Wollastonite

Ingredients	CR-1100 phr	CR-174 phr	CR-151 phr	CR-0 phr[a]
Neoprene	100.0	100.0	100.0	100.0
Stearic acid	0.5	0.5	0.5	0.5
ZnO	5.0	5.0	5.0	5.0
MgO	4.0	4.0	4.0	4.0
Ethylene thiourea	0.7	0.7	0.7	0.7
Sulfur	0.5	0.5	0.5	0.5
A1100 wollastonite	26.9	—	—	—
A174 wollastonite	—	26.9	—	—
A151 wollastonite	—	—	26.9	—

[a] phr = parts per hundred parts of rubber.

treated filler was 32 μms, and the aspect ratio was around 5 as determined by scanning electron microscopy. The weight concentration of each organosilane coupling agent used for the wollastonite was 1%. The pH value for each treated filler was measured at room temperature in an aqueous slurry and is also shown in Table II. The wetting liquids used in this work included normal decane, benzyl alcohol, aniline, and formamide. Values for the viscosity and the surface energy of each wetting liquid are summarized in Table III.[12] The elastomer used in this study was polychloroprene (CR) (Neoprene W, Du Pont). The compositions of the CR are shown in Table IV. The volume fraction for each filler used in the CR compositions was 10%.

SAMPLE PREPARATION

All the CR compositions were mixed using a 1.2 kg Banbury internal mixer. The polymer was first mixed for 1.5 mins. The filler was then added and mixed for 4 mins. Finally the curatives were added and mixed with the polymer and filler for 1.5 mins. The masterbatches were then sheeted out using a 152.4 × 304.8 (mm) two-roll mill. The cure characteristics of all the compositions were determined using the Monsanto Rheometer (R-100) at 172°C. The rheometer was used to measure the torque value required to oscillate a cone surrounded by the elastomer composition as a function of cure time at a given temperature. The cure time for each composition was then defined as the time interval at which 90% of its maximum torque was reached. ASTM slabs for each

composition were then molded using the corresponding cure conditions. Samples for tensile, compression set, and tear tests were prepared by die cutting.

TEST PROCEDURE

The contact angle measurements of all the fillers were conducted using a filler column method.[1,2,6,7] In this method, the flow of wetting liquids induced by capillary pressures as a function of time was measured for a vertical bed of filler at 20°C. The flow measurements at steady state were then analyzed by the modified Washburn's equation shown below.[1,6,7]

$$(l^2/t) = K(\gamma_{LV}/2\eta)\cos\theta \qquad (2)$$

where
    l = wetted column length of the filler bed
    t = flow time
    γ_{LV} = surface energy of wetting liquid at test temperature
    η = viscosity of testing liquid at test temperature
    K = system constant; its value being determined by the filler column method using a complete wetting liquid
$\cos\theta$ = cosine of the contact angle, θ

All the tensile tests were performed at 20°C using an Instron tensile machine at a crosshead speed of 508 mm/min (20 in./min) which corresponds to the rate of deformation of 0.33 (1/sec). The values of tensile strength, ultimate elongation, tensile modulus, and tear strength for all the elastomers were determined from the uniaxial stress–strain curve averaged using three samples. The compression set tests were conducted using a compressive strain of 25% at 150°C for 70 hs. The Monsanto Processibility Tester, which is a microprocessor-controlled capillary rheometer, was used to determine the steady-shear viscosity properties of all the materials. The rheometer test temperature was 80°C, and the shear-rate range was between 121 and 9980 sec^{-1}.

RESULTS AND DISCUSSION

Contact Angle Determination Using the Modified Washburn's Equation

The modified Washburn's Eq. (2) was used as the basis of the filler column method for determining the contact angle of many fillers.[1,6,7] This equation implies that there exists a constant slope for the plot of the square of the wetted length (l^2) versus flow time (t), when the flow process is at a steady state. Using Eq. (2), we show in Figure 2 a typical example for the system of the A151-treated wollastonite wetted by benzyl alcohol. In this plot, the slope at the steady state was determined to be 1.500×10^{-3} cm^2/sec. In order to obtain the value of $\cos\theta$ for the A151-treated wollastonite wetted by benzyl alcohol, we also needed to determine the system constant, K, as expressed in Eq. (2). The system constant, K, was determined using a low surface-energy wetting liquid which wets (or spreads) the wollastonite surface (i.e. $\cos\theta = 1$).
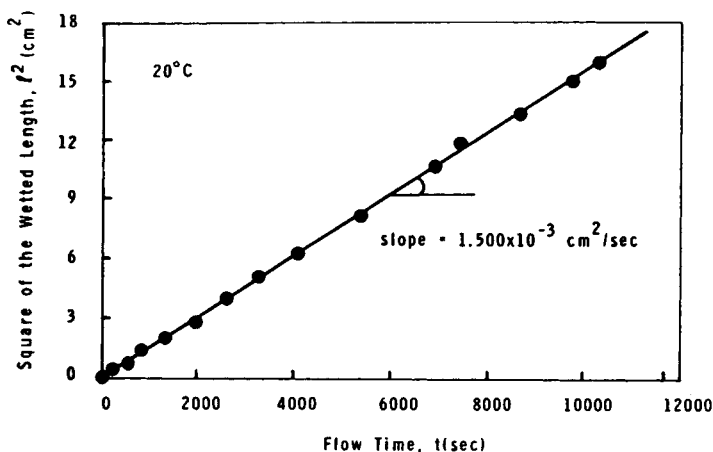
Fig. 2. The plot of square of the wetted length versus flow time of the A151 wollastonite/benzyl alcohol system.

Under this condition, Eq. (2) reduced to the form shown below.

$$K = (l^2/t)/(\gamma_{LV}/2\eta) \qquad (3)$$

In this work, we identified normal decane as the spreading liquid for all the wollastonite fillers investigated. The value of K was then determined using Eq. (3).

Inserting the value of (l^2/t) for benzyl alcohol (1.500×10^{-3} cm^2/sec), in conjunction with the system constant, K, determined by using normal decane ($K = 9.874 \times 10^{-6}$ cm, in this system), the value of $\cos\theta$ for the system of

TABLE V
Values for the Slope of l^2/t, and the Cosine of Contact angle, $\cos\theta$, of the Wollastonite Fillers Wetted by the Wetting Liquids

Filler designations	Wetting liquids	l^2/t (cm^2/sec)	$\cos\theta$
A1100[a]	Normal decane	1.376×10^{-3}	1
	Benzyl alcohol	2.800×10^{-3}	0.814
	Aniline	4.185×10^{-3}	0.698
	Formamide	2.303×10^{-3}	0.224
A174[b]	Normal decane	2.120×10^{-3}	1
	Benzyl alcohol	3.256×10^{-3}	0.611
	Aniline	4.890×10^{-3}	0.529
	Formamide	2.185×10^{-3}	0.170
A151[c]	Normal decane	1.320×10^{-3}	1
	Benzyl alcohol	1.500×10^{-3}	0.452
	Aniline	1.580×10^{-3}	0.275
	Formamide	4.917×10^{-4}	0.056

[a] $K = 1.023 \times 10^{-5}$ cm.
[b] $K = 1.586 \times 10^{-5}$ cm.
[c] $K = 9.874 \times 10^{-6}$ cm.

A151-treated wollastonite wetted by benzyl alcohol was determined to be 0.452. Based on the procedure described in the above example, contact-angle data and the system constant, K, for all the fillers investigated were obtained and are shown in Table V. It is important to note that the contact-angle data obtained by employing the above procedure represent advancing contact-angle measurements. Physically, the advancing contact-angle measurements describe the lower limit of wettability for a given system.

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APPLYING THE NEW EQUATION OF STATE FOR DETERMINING SURFACE-ENERGY PROPERTIES OF WOLLASTONITE FILLERS

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The new equation of state for adhesion shown in Table I,[1] Eq. (1a), is the equation that can be used for analyzing contact-angle data of an arbitrary adhesion system.[1] Equation (1a) implies that a plot of $\cos \theta$ versus $\ln \gamma_{LV}$ will exhibit a linear relationship for a given wetting mechanism. The intercept at $\cos \theta = 1$ defines the critical surface energy for wetting, γ_C, and the value of the slope of the line determines the extent of interaction, b. The value of the extent of interaction, b, can be influenced by many independent factors,[1] such as surface roughness, dispersion and polar (including hydrogen bonding) interactions, electrostatic interactions, adsorption, diffusion, etc. The new equation of state was successfully employed in many different polymer-filler systems.[1-3] In this study, we also used Eq. (1a) to determine the values of γ_C and b of the wollastonite fillers.

Using Eq. (1a) to analyze the contact-angle data of all wollastonite fillers from the filler-column method, we obtained linear relationships in the plots of $\cos \theta$ versus $\ln \gamma_{LV}$. As an example, plots of $\cos \theta$ versus $\ln \gamma_{LV}$ for the A151-treated wollastonite are shown in Figure 3. The values of γ_C and b for all the fillers were determined from the plots and are summarized in Table VI. Performing contact-angle measurements on flat substrate, Lee[9, 10] determined the wettability of polysiloxane films polymerized from the corresponding oily monomeric organosilane. Comparisons of the results for the critical surface
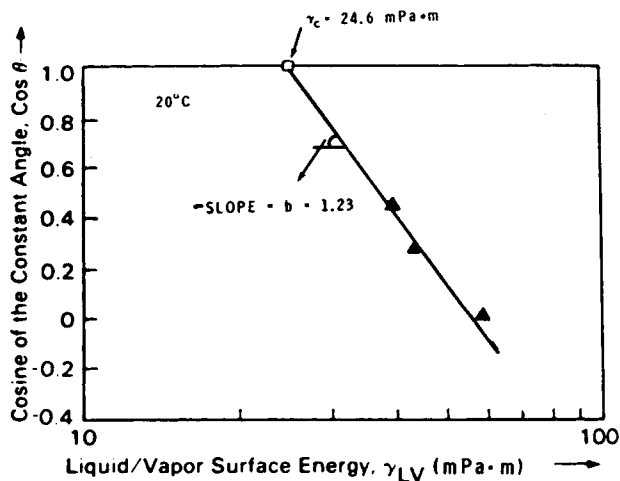

Fig. 3. The plot of $\cos \theta$ versus $\ln \gamma_{LV}$ for A151-treated wollastonite: (▲) A151.

TABLE VI
Surface Energy Properties of Wollastonite Fillers and Polychloroprene(CR) at 20°C

Surface-energy properties	Treated wollastonite fillers			Polychloro-prene(CR)
	A1100	A174	A151	
Critical surface energy (γ_C), (mPa · m)	35.0	28.4	24.6	31.3
Extent of interaction, (b)	1.52	1.18	1.23	0.72
Solid/vapor surface energy, (γ_{SV}), (mPa · m)	37.8	28.8	25.1	33.2

TABLE VII
Values for the Critical Surface Energy of the Organosilane-Treated
Wollastonites and the Polysiloxane Films[9] at 20°C

Coupling agents[a]	Critical surface energy(γ_c) (mPa · m) of	
	Treated filler	Polysiloxane film
A1100	35.0	35.0
A174	28.4	28.0
A151	24.6	25.0

[a] The silane structures are shown in Table II.

energy, γ_C, measured by Lee[9,10] and measured in this work are summarized in Table VII. Excellent agreement between the two sets of results for γ_C was obtained. These findings not only verify the validity of the method used in this work for determining the surface-energy properties of fillers, but also suggest that each wollastonite filler investigated was completely covered by the organosilane coupling agent. Another important surface-energy property, namely, the solid/vapor surface energy, γ_{SV}, can also be determined by using the values of γ_C, and b. The mathematical form for determining γ_{SV} of the filler is also shown in Table I. The values of γ_{SV} for each of the wollastonite fillers determined using Eq. (1b) are also shown in Table VI.

The results shown in Table VI clearly indicate that treating the filler with different organosilane coupling agents leads to different surface-energy properties (γ_C, b, and γ_{SV}) of the wollastonite filler. It is also important to note that the values of γ_C, b, and γ_{SV} for the wollastonite treated by gamma-methacryloxypropyltrimethoxysilane (A174) and vinyltriethoxysilane (A151) are very close and considerably lower than those for the wollastonite treated by gamma-aminopropyltrimethoxysilane (A1100). The above phenomena can be attributed to the formation of certain specific surface chemical structures by the reaction of different organosilanes and filler surfaces of wollastonite.[11] For example, the values of γ_{SV} for the wollastonite treated with A174 and A151 shown in Table VI are close to those for the polymers of paraffin and polyethylene (γ_{SV} = 24 to 28 mPa · m).[1] These results imply that the dominant surface chemical structures for the above two silane systems are nonpolar groups. This implication is obvious for the system of A151 in which the vinyl

group sticks out of the filler surfaces. It is, however, not obvious for the system of A174 in which the hydrocarbon group, instead of the carbonyl group, is the dominant surface structure as indicated by the values of γ_{SV} shown in Table VI. Certainly, more analytical work is needed for characterizing the surface structures of the organosilane-treated wollastonite fillers.

SURFACE-ENERGY PROPERTIES OF WOLLASTONITE-FILLED CR

The contact-angle data for polychloroprene was well studied by Wu[8] and others.[1,3,9,10] Employing the unified theory for adhesion, we determined values for the solid/vapor surface energy, γ_{SV}, and the extent of interaction, b, for the polychloroprene[1,3] at 20°C. The results are also shown in Table VI.

Based on the data shown in Table VI, in conjunction with the unified theory for adhesion summarized in Table I,[1] the key surface-energy properties for all the CR compositions were determined and are listed in Table VIII. These properties include extent of interaction, b, surface-energy ratio between the filler and the polymer, $(\gamma_{SV}/\gamma_{LV})$, equilibrium work of adhesion, W_A, ratio between work of adhesion and surface energy of the polymer, and Harkins' spreading coefficient, λ_{LS}.

As discussed previously, based on the new adhesion theory, criteria for predicting the adhesion characteristics of multicomponent polymer systems were also established.[1] As illustrated in Figure 1, four regimes—spreading and cohesive failure, spreading and adhesive failure, nonspreading and cohesive failure, and nonspreading and adhesive failure—can be defined using the plot of $(\gamma_{SV}/\gamma_{LV})$ versus b. For wollastonite-filled CR compositions, the plots of $(\gamma_{SV}/\gamma_{LV})$ versus b are shown in Figure 4. The results show that the CR-1100 system is in the spreading and cohesive failure zone, while the CR-174 and CR-151 systems are in the nonspreading and adhesive failure zone.

In the next section, we will use the above adhesion properties to explain and to correlate other physical properties of the polychloroprene compositions investigated.

TABLE VIII
Surface-Energy Properties of the Wollastonite-Filled
Polychloroprene(CR) Compositions at 20°C

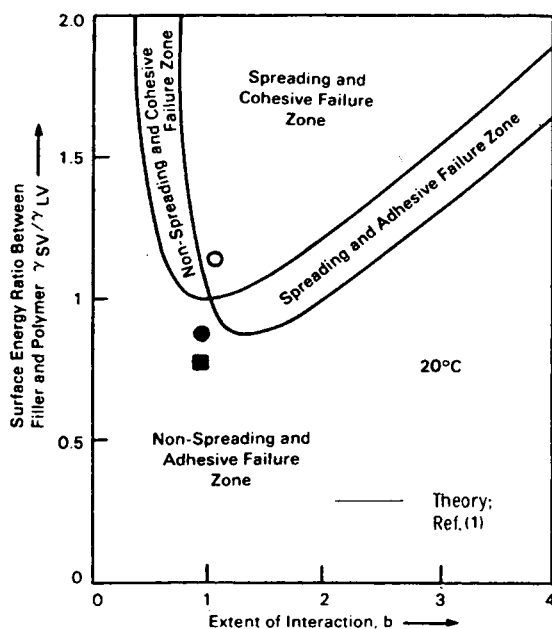| Properties	CR-1100	CR-174	CR-151
Extent of interaction, (b)	1.04	0.92	0.94
Surface-energy ratio between filler and polymer, (γ_{SV}/γ_{LV})	1.14	0.87	0.76
Equilibrium work of adhesion, (W_A), (mPa · m)	70.80	61.88	57.58
Ratio between W_A and γ_{LV}, (W_A/γ_{LV})	2.14	1.87	1.74
Harkins' spreading coefficient, (λ_{LS}), (mPa · m)	6.09	−6.85	−10.28

Fig. 4. Spreading and failure characteristics of the wollastonite-filled polychloroprene compositions: (O) CR-1100; (●) CR-174; (■) CR-151.

PROPERTIES OF WOLLASTONITE-FILLED CR

The values of tensile, compression set, and rheological properties for all the wollastonite-filled CR systems were determined. The effects of polymer-filler interaction on these properties can be systematically divided into two categories: (1) properties improved with the increase of the ratio, (W_A/γ_{LV}), and (2) properties worsened with the increase of the ratio, (W_A/γ_{LV}). Properties in the first category are tear strength, compression set, tensile modulus, logarithmic steady-shear viscosity at 1 sec^{-1}, and power-law index of shear viscosity. These properties are listed in Table IX. Mechanistically, all these properties depend on the polymer-filler adhesion to varying degrees. Therefore, proper-

TABLE IX
Values for Tensile Modulus, Tear Strength, and Rheological Properties
of Wollastonite-Filled Polychloroprenes(CR)

Properties	CR-1100	CR-174	CR-151
Tensile modulus (E), (MPa)[a]	1.83	1.56	1.35
Tear Strength, (Te), (KN/m)	5.25	5.16	4.04
Logarithmic steady-shear viscosity at 1 sec^{-1}, (ln K), (KPa · s)	5.82	5.06	4.06
Power-law index[b]	−0.93	−0.83	−0.75
Compression set (%)	69.7	77.6	83.0

[a] For CR gum, E(gum) = 1.31 MPa.
[b] Power-law index defined as the slope of the double logarithmic plot between steady-shear viscosity and steady-shear-rate.

TABLE X
Values for Tensile Strength and Ultimate Elongation of
Wollastonite-Filled Polychloroprenes(CR)

Properties	CR-1100	CR-174	CR-151
Tensile strength, (σ_b), (MPa)	12.3	13.1	13.3
Ultimate elongation, (ϵ_b), (%)	641	656	703

ties (in the first category) of filled polymers having a strong polymer-filler adhesion (indicated by being within the spreading and cohesive failure zone as shown in Figure 4) are better than those of filled polymers having a weak polymer-filler adhesion (indicated by being within the nonspreading and adhesive failure zone).

Properties in the second category, which consist of tensile strength and ultimate elongation, are shown in Table X. These properties are fracture properties of filled elastomers and do not necessarily depend on the polymer-filler adhesion. In contrast, these properties largely depend on different processing conditions which can lead to carying degrees of mixing of the filler and microvoid concentrations in the polymer matrix.[2,3] It has been shown[2,3] that tensile strength and ultimate elongation of filled polymers having poor degrees of mixing are inferior to those having good degrees of mixing which are shown morphologically by having uniform dispersions of the filler particles and few microvoids. It has also been concluded[1-3] that carbon black-filled CR systems with the characteristics of spreading and cohesive failure have poor degrees of mixing. Based on these reasons, the inferior tensile properties of the CR-1100 system, which is the only system inside the spreading and cohesive failure zone as shown in Figure 4, would indicate that the degree of mixing for the CR-1100 system is poorer than that of either the CR-151 system or the CR-174 system.

RELATIONSHIP BETWEEN TENSILE MODULUS AND EQUILIBRIUM WORK OF ADHESION FOR FILLED CR

Tensile modulus, E, is one of the most important properties of elastomers for automotive applications.[2,3] Physically, tensile modulus represents the amount of mechanical energy stored per unit volume of elastomer. Equilibrium work of adhesion, W_A, represents the amount of energy stored in a unit interface formed between polymer and filler. Since both tensile modulus and equilibrium work of adhesion describe the amount of energy stored in the system, it will be valuable to establish a correlation between the two properties. Assume that there exists a power-law relationship between tensile modulus and equilibrium work of adhesion. Mathematically, the above relationship can be expressed as shown below.

$$E = a(W_A)^m \tag{4}$$

or
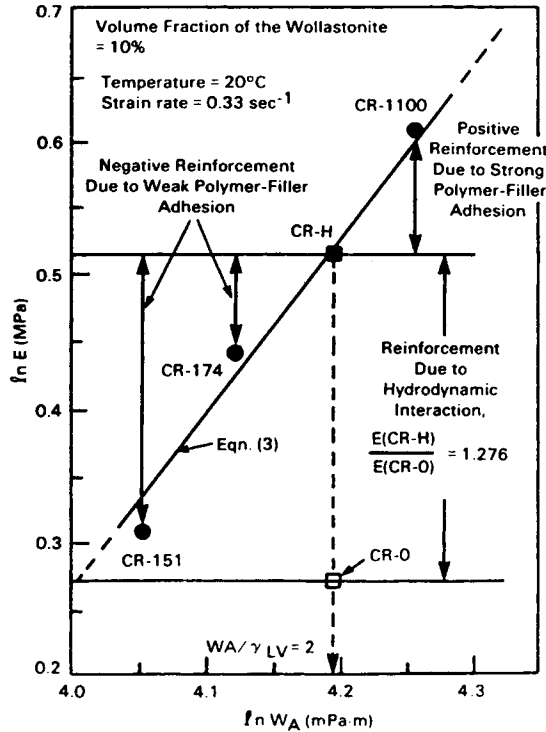
$$\ln(E) = \ln(a) + m\ln(W_A) \tag{5}$$

Fig. 5. The relationship between tensile modulus(E) and equilibrium work of adhesion(W$_A$) and the reinforcement mechanisms of the wollastonite-filled polychloroprene compositions.

Equation (5) implies that there is a linear relationship between $\ln(E)$ and $\ln(W_A)$. The slope of the line determines the value of m. Using the results shown in Table IX, we plotted the data of $\ln(E)$ versus $\ln(W_A)$, and the results are shown in Figure 5. A linear regressional analysis of the data leads to the following equation:

$$\ln E(\text{MPa}) = -4.80 + 1.267 \ln W_A(\text{mPa} \cdot \text{m}) \qquad (6)$$

The correlation coefficient of the regressional analysis is 0.962.

MECHANISMS FOR ENHANCING THE MODULUS PROPERTIES OF FILLED POLYMERS

As described previously, two mechanisms are involved in the reinforcement effectiveness for the tensile modulus properties of filled polymers. The first is polymer-filler adhesion, and the second is hydrodynamic interaction. Einstein[13] analyzed the reinforcement effectiveness due to hydrodynamic interaction for spherical-filler-filled systems. His results in terms of the relative modulus, E^{rel}, and the volume fraction of the filler, ϕ, have the following mathematical form:[13,14]

$$E^{\text{rel}} = (E/E_1) = 1 + 2.5\phi \qquad (7)$$

where E and E_1 are the tensile moduli of the filled and the unfilled elastomers, respectively.

Based on the analysis of the results described by Eqs. (6) and (7), we now can make a distinction between the two mechanisms. Assume that there is a polychloroprene composition (designated as CR-H), which is filled with the wollastonite filler treated with a coupling agent H, such that the work of adhesion of the CR-H system equals the work of cohesion of the polychloroprene gum (designated as CR-0). This means that the only difference between the CR-H system and the CR-0 system is that the CR-H system contains a wollastonite concentration of 10% by volume. In other words, any reinforcement effectiveness for the tensile modulus of the CR-H system should be totally attributed to hydrodynamic interaction. The value of tensile modulus of the CR-H system was calculated using Eq. (6) and has the value of 1.674 MPa. Since the tensile modulus of the CR-0 system was measured and equals 1.309 MPa, we accordingly determined the relative modulus of the CR-H system, which has the value of 1.276. The results are also illustrated in Figure 5. Using Eq. (7), we also calculated the value for the relative modulus of the CR-H system, which equals 1.250 for a wollastonite concentration of 10% by volume. Comparing the two values, 1.276 and 1.250, we conclude that the reinforcement effectiveness for the tensile modulus property of the CR-H system indeed results from hydrodynamic interaction. The slight deviation between values of the relative tensile modulus (1.276 vs. 1.250) is attributable to the anisotropic shape of the wollastonite particles.

It can be further concluded that the organosilane, A1100, has a positive contribution to the total reinforcement effectiveness for the tensile modulus of the wollastonite filled CR as shown in Figure 5. This is because the polymer-filler adhesion in the CR-1100 system is very strong as indicated by the ratio, (W_A/γ_{LV}) being greater than 2 (see Table VIII). In contrast, the organosilanes, A174 and A151, have negative effect on the total reinforcement effectiveness due to weak polymer-filler adhesion. As shown in Table VIII, values for the ratio, (W_A/γ_{LV}), of both the CR-174 and the CR-151 systems are less than 2.

CONCLUDING REMARKS

An effective method for determining the optimum polymer-filler compositions has been developed. The usefulness of this method can be illustrated by the following: (1) For applications in which fracture properties are the important requirements, one should choose a polymer-filler system so that this system is in the nonspreading and adhesive failure zone. For example, the wollastonite filler treated with vinyltriethoxysilane, A151, is recommended for polychloroprene elastomers in order to obtain better fracture properties. (2) For applications in which tensile modulus and tear strength are the major concerns, one should choose a polymer-filler system so that this system is in the spreading and cohesive failure zone. For example, the wollastonite treated with gamma-aminopropyltrimethoxysilane, A1100, is the optimum choice for polychloroprene elastomers in order to obtain better tensile modulus and tear strength.

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