Polymer–Filler Interaction in Polyurethane Kraft Lignin Polyblends

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SYNOPSIS

Kraft lignin fillers have been shown to enhance the mechanical characteristics of different types of polymeric-based sealants; however, the mechanism for reinforcement and the degree of interaction was not well understood. In this study, interactions between a polyurethane-based elastomer and various Kraft lignin fillers as well as kaolin and titanium dioxide filler combinations were investigated in an effort to determine the most useful elastomer–filler combination for use as a construction joint sealant. A relationship that describes and relates the characteristics of polymer–filler interaction requires that the surface-energy properties of both the polymer matrix and the filler be determined. Measurements using the sessile drop method are used to evaluate the critical surface energy of the polymer matrix, whereas the rate of rise of a liquid through a bed of filler provides the means to evaluate the surface energetics of the various fillers. Results obtained from this study show that the tensile modulus of the different elastomer formulations are proportional to the equilibrium work of adhesion, as described by the relationship derived by Lee that relates the degree of interaction of the formulation components and the mechanical properties of the blends. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The mechanical and, hence, the performance properties of filled elastomer formulations are a function of the degree of interaction between the filler and the polymeric-based elastomer matrix. Theories that relate the increase in mechanical properties of the elastomer to that of the filler are based on the assumption that the filler is perfectly adhered to the matrix. It has been shown that significant deviations from the proposed mechanical behavior occurs if the filler is not thoroughly bonded to the matrix or if debonding occurs as a result of stress concentrations at the interface between blend components.[1,2] It is evident that a method that is able to assess the interaction between blend components would be useful in determining the effectiveness of different modifiers.

Lee[3] derived an equation of state of adhesion that has been used to describe the surface-energy properties of various solids and to determine the adhesion properties for polymer–polymer and polymer–filler systems. The equation of state describes the relationships between the cosine of the contact angle of a wetting liquid on a given solid in terms of the liquid/vapor-surface energy of the liquid in the following manner[3]:

$$\cos \theta = 1 + b \ln\left(\frac{\gamma_c}{\gamma_{LV}}\right) \qquad (1)$$

where θ is the contact angle of a wetting liquid on the substrate; b, the extent of interaction; γ_c, the critical surface energy for wetting; and γ_{LV}, the liquid/vapor surface energy of the wetting liquid.

The equation implies that wetting a solid with various liquids will yield a linear relationship between $\cos \theta$ and $\ln(\gamma_{LV})$. The intercept of this linear relationship at $\cos \theta = 1$ defines the extent of interaction, b.

When investigating the adhesion characteristics of polymer–filler systems, the surface energy properties of both the polymer matrix and the filler are determined separately.[4,5] Hence, representative values for both the critical energy of wetting and the extent of interaction are obtained for either system component.

Based on these relationships, the mean interaction parameter, b, and the polymer–matrix bonding coefficient, Ω, can be determined based on the following equations[3-5] [eqs. (2) and (3), Ref. 5]:

$$b = (b_p \cdot b_t)^{0.5} \tag{2}$$

$$\Omega = \left[\frac{1}{b} \cdot \exp\left(1 - \frac{1}{b}\right) \right]^{0.5} \tag{3}$$

The subscripts p and f refer to the polymer and filler, respectively. These parameters are then used to assess the work of adhesion between polymer and filler, thus providing an indication of the degree of interaction between components.

Measurements using the sessile droop method are used to evaluate the critical surface energy of the polymer matrix, whereas the surface-energy properties of the fillers may be determined using a filler-column method. This latter technique, perfected by Crowl and Wooldrige,[6] relates the rate of capillary rise of a given liquid through a column of packed filler particles to that of the contact angle of the wetting liquid with the particles by the following relationship[4,6]:

$$\frac{l^2}{t} = k \frac{\gamma_{LV}}{2\eta} \cos \theta \tag{4}$$

where l is the distance of rise of a liquid through a column (cm); t, the time that liquid takes to rise a given distance (s); γ_{LV} the surface tension of wetting liquid (mPa-m); η, the viscosity of wetting liquid (Pa-s); θ, the contact angle of wetting liquid with the particles; and k, the column packing constant, dependent on the nature of the filler and the degree of compaction.

The column packing constant, k, is first determined for a liquid that will completely wet the particles, i.e., one for which $\cos \theta = 1$, such that k is given by the equation

$$k = \frac{l^2}{t} \cdot \frac{2\eta}{\gamma_{LV}} \tag{5}$$

Hence, the contact angle given for various liquids wetting the particles may readily be determined, and by using eq. (1), the critical surface energy for wetting, γ_c, and the extent of interaction, b_f, for the fillers may also be evaluated.

Kraft lignin fillers have been shown to enhance the mechanical characteristics of different types of polymeric-based sealants[7-10]; however, the mechanism for reinforcement and the degree of interaction has not been established. In this study, interactions between a polyurethane-based elastomer and various Kraft lignin fillers as well as clay and titanium dioxide filler combinations were investigated in an effort to determine the most useful elastomer–filler combination for use as a construction joint sealant. The relationship between the degree of interaction and the mechanical properties of the filled elastomers are analyzed in terms of the tensile modulus and the equilibrium work of adhesion according to the method adopted by Lee.[4] Both these terms represent an amount of stored energy: mechanical energy stored per unit volume in the case of the tensile modulus and interfacial energy per unit area between the filler and polymer in the case of the work of adhesion. By establishing a relationship between these terms, it is possible to assess the effectiveness of the various polymer–filler combinations in providing useful sealant products.

EXPERIMENTAL

Materials

The polyurethane (PU) elastomer is based on a two-component chemically cured system formulated with appropriate additives to ensure the cure and flexibility of the final product. The formulation components are given in Table I. A toluene diisocyanate (TDI)-based difunctional isocyanate prepolymer was formulated in stoichiometric amounts with a polyether prepolymer polyol to form the basic elastomer matrix.[11-13] PU components were blended in a 250 mL glass beaker with a plasticizer, molecular sieve, antioxidant, solvent, and catalyst at room temperature and under nitrogen atmosphere. The resulting blend was stirred manually for 3 min and then poured into cylindrical silicone elastomer molds (12.7 mm height; 32 mm diameter) and allowed to cure for 24 h. Samples were then placed in a glass dessicator to cure for another 30 days prior to use in surface analysis testing.

Table I Polyurethane Formulation Components

Component	Name	Description	Density (20°C) g/cc	Other Information
Catalyst[b]	Lead 24%	Lead octoate	1.1–1.2	NIL
	Calcium 5%	Calcium octoate	0.9–0.92	NIL
Plasticizers	Mesamoll[c]	Alkyl sulfonic ester of phenol	1.03	Vis.[a]: 95–125 mPa-s
	Santicizer[d]	Butylbenzyl phthalate	1.115	Vis.: 2.12 mPa-s
Molecular sieve[c]	Baylith paste	Zeolite in 50% (wt) castor oil	1.25	Water absorption capacity 10% (wt)
Antioxidant[c]	Vulcanox BKF	2,2'-Methylenebis(4-methyl-6-tert-butylphenol)	1.04	NIL
Solvent[e]	Solvesso 100	Naphtalene		NIL

[a] Vis: Absolute viscosity.
[b] Product of Hüls Canada.
[c] Product of Bayer Canada.
[d] Product of Monsanto Canada.
[e] Product of Esso Canada.

The physical characteristics of the particulate matter are given in Table II. Average particle size for the various fillers was obtained, where possible, by sedimentation analysis an verified by optical microscopy.

Surface Analysis of Elastomer Matrix

A sessile drop method was used to obtain the critical energy of wetting of neat polymer blends. The apparatus used to record contact angles of various liq-

Table II Physical Properties of Inorganic and Organic Particulate Fillers

			Inorganic			
Name	Type	S. G.	Specific Surface Area (m²/g)	Average Particle Size (μm)	Oil Absorption	$\phi_m{}^a$
SIL-CO-SIL #400	Ground silica	2.65	0.6	7.4	33	0.52
Sillitin Z86	Silica/Kaolin	2.60	12	1.35	45–55	0.42
Titanox 2101	Titanium dioxide	4.00	10	0.3	25	0.48

			Organic			
Name	Type	S. G.	Specific Surface Area (m²/g)	Average Particle Size (μm)	pH	Oil Absorption (g/100 g)	$\phi_m{}^b$
Eukalin[c]	Kraft lignin— Eucalyptus wood	1.379	—	10.5[a]	9–10	40	0.63
Indulin AT[d]	Kraft lignin–softwood	1.238	1.5	8	6.5	85	0.47
Tomlinite[e]	Kraft lignin–hardwood	1.295	0.7	16	6	74	0.49

[a] Estimated visually from photomicrographs of EU particles.
[b] Maximum packing fraction.
[c] Empresa Nacional de Celulosas, S. Q., Madrid, Spain.
[d] Westvaco, Chemical Division, Charleston, SC.
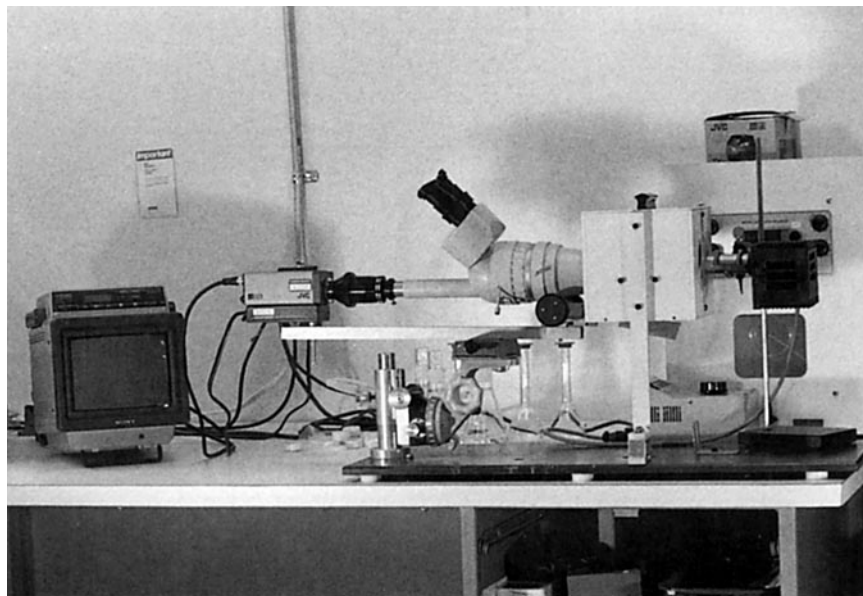[e] Domtar Corporation, Cornwall, Ontario.

Figure 1 Surface analysis of elastomer matrix using the sessile drop technique showing video camera setup.

uids on the surface of the polymer is shown in Figure 1. It consists of essentially three parts: an environmental chamber, a microscope, and a recording device.

The chamber comprises an inner transparent glass box used to accommodate the specimen and a small quantity of test liquid, such that the test is conducted in an atmosphere saturated with the test liquid. The glass box is positioned at the center of the larger enclosure and along the optical axis of the microscope. The outer enclosure serves to minimize thermal fluctuations as well to provide appropriate conditions for capturing video images.

An Olympus ZX stereomicroscope with 4× magnification was used to observe the specimens and the formation of sessile drops on the specimens. A backlight was used to achieve a picture having sufficient contrast from which data could be extracted. The microscope was fitted onto a two-axis sliding carriage and a double-acting pivoting head such that its horizontal and vertical positions could be adjusted as well as the angle of inclination and rotation with respect to the longitudinal viewing axis.

A video camera (JVC C40) was used to record a continuous set of events from the moment the drop was deposited onto the substrate until the time equilibrium was reached. The use of such a device for measuring contact angles enables the subsequent digitization of specific images using appropriate computer software.

The tests were conducted at room temperature (25°C) using a series of wetting liquids whose relevant characteristics are given in Table III. The surface tension (γ_{LV}) of the liquids was established using this maximum bubble pressure method[14] in which a gas is blown into the liquid in question by means of a tube having a capillary orifice that projects below the surface of the liquid. The surface tensions of liquids can readily be evaluated using this method since the pressure required to produce a bubble is proportional to the surface tension of the liquid being evaluated. The apparatus was calibrated by determining the characteristic pressure head obtained for triple distilled water ($\gamma_{LV} = 72.8$

Table III   Characteristics of Wetting Liquids (25°C) Used in Surface-Energy Evaluations

Wetting Liquid	Surface Energy γ_{LV} (mPa-m)	Viscosity η (Pa-s)
Acetic acid : water		
0 : 100	72.8	1.002
5 : 95	62.3	1.11
10 : 90	56.3	1.22
20 : 80	49.3	1.51
30 : 70	44.9	1.69
70 : 30	38.4	2.65
Hexane	18.4	0.326
Cyclohexane	25.2	0.980

mPa-m at 25°C). Values of surface tension for the various wetting liquids were obtained by measuring the respective heads required to produce bubbles in the liquid. The results shown in Table III are an average of 15 observations. Viscosity measurements were extrapolated from known data.[15]

Cylindrical samples of the neat PU elastomer (12.7 mm height; 32 mm diameter) were first cleaned using tap water and detergent followed by repeated rinsing with singly distilled water. The specimens were then wicked dry with absorbent paper, after which they were placed in an oven at 90°C for 10 min. The cleaned samples were stored in a desiccator prior to use.

A digital micropipette was used to produce 5 μL sessile drops on the substrate. Up to four drops could be placed on any given substrate and at least 24 measurements were taken for each liquid.

The formation of the drop was recorded on videotape and an image was reproduced from the digitized data representing the form of the drop 10 s after it was deposited on the surface of the substrate.

Surface Analysis of Particulate Fillers

The flow of specific wetting liquids was measured under capillary pressures generated by a packed particle bed contained within a vertical glass column. This technique is similar to that used by Lee[4] and by Cheever and Ulicny,[16] and was developed by Crowl and Wooldrige[6] based on the work of Washburn.[17]

The apparatus used for measuring the capillary flow of liquids through a packed tube is shown in Figure 2. It consists of a 10 mm (i.d.) × 120 mm glass tube filled with the filler to be evaluated and stoppered at either end with filter paper and surgical cotton plugs. To facilitate the even flow of liquid through the tube, the glass columns were prerinsed in the appropriate wetting liquid, dried in a forced air oven, and finally stored in a desiccator.

It was determined that reliable values for the column constant k were dependent on the uniformity of packed columns. Hence, to ensure useful results, a known mass of particulate matter was placed in a column and packed using a consolidation device. The device consists of a circular plate capable of moving in a vertical direction by means of a wheel and cam mechanism. A column containing the sample was placed on top of the plate and the repeated up and down movements of the platen cause to particles to consolidate themselves into a uniformly packed bed.

The tube was then placed in contact with a wetting liquid. A millimetric card, placed adjacent to
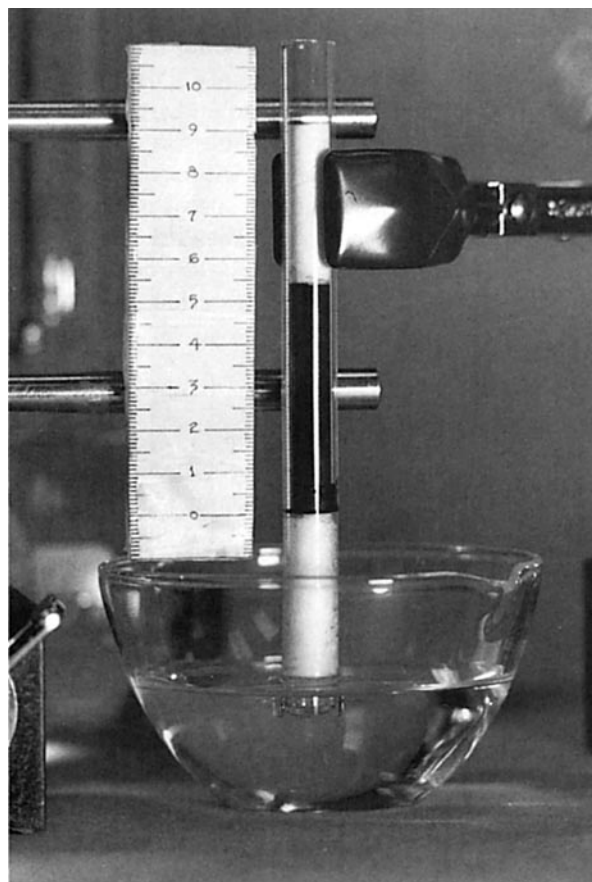

Figure 2 Apparatus for evaluating the capillary flow rate of various wetting liquids through a column of packed particulate matter.

the tube, was used to determine the rate of rise of the liquid front through the packed bed. The value of the system constant, k, was determined by using a liquid that completely wets the particles. Hexane and cyclohexane were used to determine these values. Values for cos θ for each liquid type and particulate combination were determined from flow-rate measurements.

Tensile Tests

Tensile tests were conducted on filled elastomer specimens according to ASTM D412.[18] Dumbbell specimens, cut from a 3.2 mm-thick cast specimen slab with die "D," were marked with a standard gauge length of 25 mm. The cross-sectional area of the specimens was determined with a micrometer dial gauge accurate to 0.0254 mm, by measuring the depth and width of the specimens at three equidistant points along the gauge length. Stress was calculated based on the original cross-sectional area.

Tests were conducted using an Instron universal testing machine on at least nine but in most cases on 12 specimens at room temperature using a crosshead speed of 50 mm/min. Load and crosshead displacement data were recorded on the testing machine's chart recorder. Changes in gauge length were recorded using a video camera such that specimen strain could be related to crosshead displacement. Using this technique, the stress–strain properties and, hence, the modulus of the various elastomers could be determined.

RESULTS

Surface Properties of the Elastomer Matrix

The contact angle of a drop of wetting liquid on the surface of the unfilled PU elastomer was measured from the digitized video image. An example of such an image is shown in Figure 3, which depicts the profile of a drop of water magnified 100 times, 10 s

after being deposited on the surface of the elastomeric matrix.

The straight line that runs parallel to the edge of the image represents the interface between the sessile drop and the surface of the elastomer matrix. The contact angle is the angle between a line perpendicular to the profile of the drop at the liquid matrix interface and the line representing the interface.

A continuous recording of the event was found to be quite useful from the point of view of being able to extract information of a given event at prescribed times or time intervals. The events can also be recorded using photographic techniques; however, the task is logistically more complicated by virtue of the number of operations required at the beginning of a test sequence. It was also found that consistent results were more easily obtained using a video camera technique.

Results from tests on the PU elastomer formulation are given in Table IV. The data, reduced from readings extracted off of profiles of at least 24 drops,
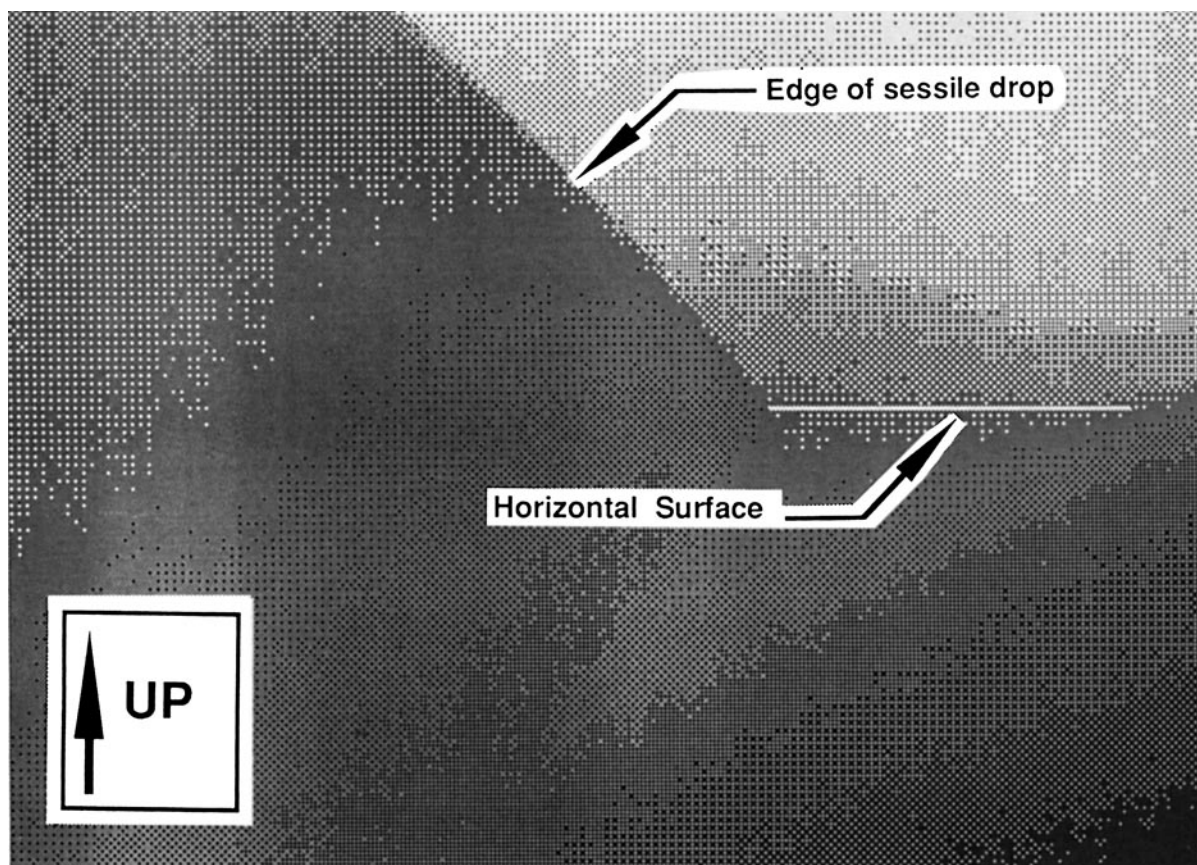

Figure 3   Digitized image (100×) of a sessile drop of water on the surface of a PU elastomer 10 s after contact with the surface.

Table IV Results from Contact-angle Measurements on PU Elastomers Using the Sessile Drop Technique

Wetting Liquid	Surface Energy of Liquid γ_{LV} (mPa-m)	Average Contact Angle
Acetic Acid : Water		
0 : 100	72.8	86.2
5 : 95	62.3	79.3
10 : 90	56.3	73.1
20 : 80	49.3	64.8
30 : 70	44.9	56.4
70 : 30	38.4	43.5

are plotted according to eq. (1) on Figure 4. The figure shows the cosine of the contact angle as a function of the logarithm of the liquid–vapor surface energy of the wetting liquid.

The values for the critical surfaces energy of the polymer, $\gamma_{c(p)}$ and the interaction parameter, b_p, were determined graphically from the plot in Figure 4. The value of $\gamma_{c(p)}$ was evaluated by determination of the intercept on the x-axis at cos θ equal to 1. The interaction parameter, b_p, is simply the slope of the straight line drawn through the data points.

The solid–vapor surface energy, $\gamma_{SV(p)}$, is determined from the following equation[5]:

$$\gamma_{SV(p)} = \left\{ b_p \cdot \exp\left[\frac{1}{b_p} - 1\right] \right\} \gamma_{c(p)} \qquad (6)$$

Table V Results from Analysis of Contact-angle Data from PU Elastomers

Critical Surface Energy for Wetting, $\gamma_{c(p)}$ (mPa-m)	Extent of Interaction b_p	Solid/Vapor Surface Energy $\gamma_{SV(p)}$ (mPa-m)
29.1	1.048	29.1

where $\gamma_{SV(p)}$ is the solid/vapor surface energy of the elastomer (mPa-m); b_p, the extent of interaction between the wetting liquid and the elastomer; and $\gamma_{c(p)}$, the critical surface energy for the wetting elastomer (mPa-m). Values obtained for $\gamma_{c(p)}$, b_p, and $\gamma_{SV(p)}$ are given in Table V.

Surface Properties of Particulate Fillers

The Crowl–Wooldrige method[6] was used to assess the surface properties of the various particulate fillers being investigated. Use of this method enables the rate of rise of a known liquid through a bed of packed particles to be determined such that the contact angle can be evaluated based on the Washburn equation [17].

A plot of the reduced data for lignin fillers is shown in Figure 5, in which the cosine of the contact angle, calculated using eq. (1), is given in relation to the logarithm of the energy of the wetting liquid. At least 12 trials were used for each determination. Values for the clay and titanium dioxide filler were
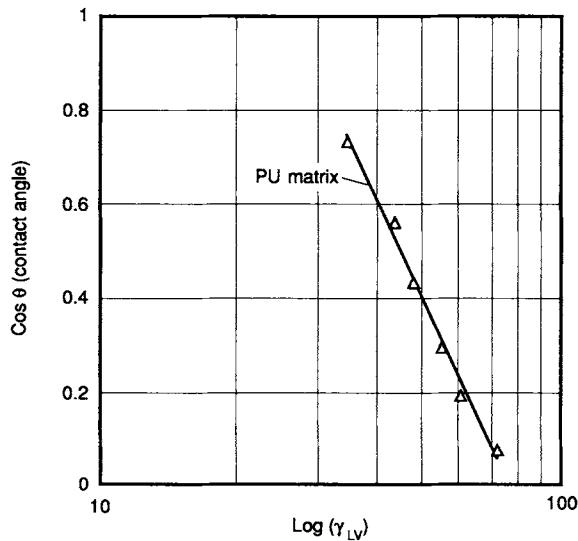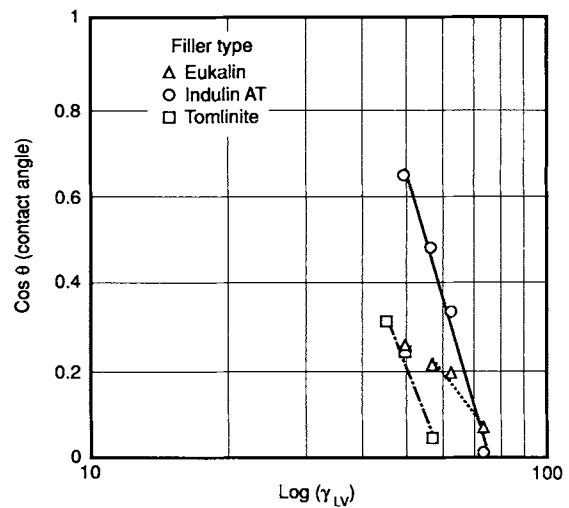

Figure 4 Contact angle of wetting liquids on the surface of a PU-based elastomer substrate as a function of the surface tension of the wetting liquid.

Figure 5 Contact-angle analysis of lignin fillers. Cosine of the contact angle as a function of the surface energy of the wetting liquid.
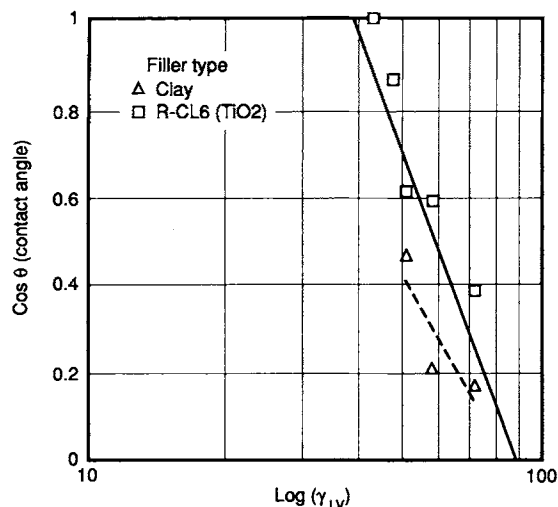
Figure 6 Dependency-angle analysis of selected fillers. Cosine of the contact angle as a function of the surface energy of the wetting liquid.[16]

taken from Cheever and Ulciny,[16] whose results are shown in Figure 6. The data represent contact-angle data obtained using the same technique described above. The results obtained for the clay/TiO₂ filler combination are a combined result that reflects the weight proportion (22 : 7) in which these fillers were used in the formulation.

Both Figures 5 and 6 were analyzed graphically to extract the values of $\gamma_{c(f)}$ and the interaction parameter, b_f, from which the solid–vapor surface energy of the filler, $\gamma_{SV(f)}$, was calculated according to eq. (6). The results are given in Table VI.

Based on these data, an analysis was performed to determine the work of adhesion, W_A, and the work of cohesion, W_C, using the following equations,[3] results of which are presented in Table VII:

$$W_A = 2 \cdot \Omega \sqrt{\gamma_{SV(f)} \cdot \gamma_{SV(p)}} \qquad (7)$$

$$W_C = 2 \cdot \gamma_{SV(p)} \qquad (8)$$

Table VI   Results from Analysis of Contact Angle of Particulate Fillers

Filler	Interaction Parameter b_f	Critical Surface Energy $\gamma_{c(f)}$	Solid–Vapor Surface Energy $\gamma_{SV(f)}$
Eukalin	0.844	14.1	17.5
Indulin AT	1.70	40	25.9
Clay/TiO₂	1.56	40	44.2
Tomlinite	1.53	25.2	39.4

The degree of interaction between filler and polymer may be assessed from the relative values of the work of adhesion and the corresponding values of the work of cohesion for the various polymer–filler combinations. Fillers that have a value for the work of cohesion, W_C, are not considered to interact strongly with the polymer and, consequently, are more likely to undergo interfacial failure when being stressed. Furthermore, these fillers do not contribute as significantly to the reinforcement of the matrix as fillers having values of W_A equal to or exceeding those of W_C.

Polymer–Filler Interaction and Mechanical Properties

In an effort to demonstrate relationship between the degree of interaction and the mechanical properties of the filled elastomers, the results are analyzed in terms of the tensile modulus E and the equilibrium work of adhesion, W_A, according to the amount of stored energy. Lee[4] assumed that there exists a power-law relationship between both terms such that a logarithmic plot of the data should yield a straight line. Figure 7 shows a series of log–log plots of the modulus E, as a function of the work adhesion at different volumetric loadings. The results indicate
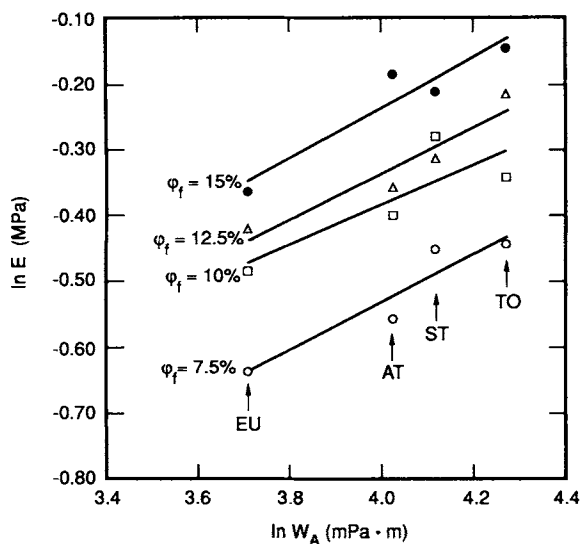
Table VII   Analysis of Contact-angle Data for Particulate Fillers

F	b_p (Table IV)	b_f (Table V)	b Eq (4)	Ω Eq (5)	$\gamma_{SV(p)}$ (Table IV)	$\gamma_{SV(f)}$ (Table V)	W_A Eq. (7)	W_C Eq. (8)
EU	1.048	0.844	0.940	0.999	29.1	14.3	40.8	58.2
AT	1.048	1.70	1.335	0.981	29.1	33.2	61.0	58.2
ST	1.048	1.56	1.279	0.986	29.1	43.4	70.1	58.2
TO	1.048	1.53	1.270	0.987	29.1	45	71.4	58.2

F: filler type; EU: Euklain; AT: Indulin AT; ST: Clay/TiO₂; TO: Tomlinite.

Figure 7 Dependency of the work of adhesion, W_A, on the tensile moduls at different volumetric filler loadings.

that values of the modulus are proportional to the work of adhesion. The scatter of the tensile modulus data for a given filler volume fraction may easily be attributed to filler agglomeration, geometry, or measurement error. The moduli used in calculation were the initial ones.

CONCLUSION

The surface analysis was most useful for assessing the relative contributions to the work of adhesion of the various fillers. Hence, for lignin fillers having essentially the same average particle size, the relative performance is dependent on the respective surface properties. At a given particle size, fillers having values of the work of cohesion are more likely to contribute to the reinforcing effect in the filled polyurethane elastomer. Thus, the order of decreasing interaction potential was found to be Tomlinite > clay/TiO_2 > Indulin AT > Eucalin filler. In the case of the clay/TiO_2 combination, however, particle

size plays a more significant role in determining the final mechanical properties.

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