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Mechanical and thermal expansion properties of a particulate filled polymer

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The use of particulate filled polymer formulations over wide temperature ranges has resulted in a need to understand their mechanical behaviour better. In this investigation, a crosslinked epoxy-urethane polymer filled with Al_2O_3 particles was studied. Mechanical and thermal expansion properties were determined at ambient and liquid nitrogen temperatures and compared to theoretical predictions. Other parameters under consideration were volume fraction and adhesion between filler and matrix. The theoretical equations employed for predicting mechanical properties appear fairly reliable at ambient temperature but unreliable at liquid nitrogen temperatures. The degree of bonding between filler and matrix influences mechanical properties at ambient temperature but at liquid nitrogen temperature no difference in properties owing to matrix filler bonding was evident. This result is attributed to compressive stresses on the filler particles resulting from the lower thermal expansion of the filler.

List of symbols

α = coefficient of thermal expansion.
ν = Poisson's ratio.
Φ = volume fraction
σ^* = thermally induced tensile stress.
σ = tensile strength.
E = Young's modulus.
ϵ = elongation.
V = sedimentation volume.
S = stress concentration function.
ζ = adhesion parameter.
T = temperature.
c = composite.
m = matrix.
f = filler.
F = failure.

1. Introduction

For design purposes, it is desirable to have the capability of predicting mechanical and thermal expansion properties of filled systems at ambient and cryogenic temperatures. Thus, the objectives of this study are to (1) compare experimentally determined mechanical and thermal expansion properties obtained at ambient and liquid nitrogen temperatures to theoretical values with respect to adhesion versus non-adhesion in a composite system; (2) to determine whether composites displaying non-adhesion properties will exhibit greater elongation than composites possessing good adhesion at liquid nitrogen temperatures. Theory indicates this latter case is prevalent at ambient temperatures; however, comparisons have not been made at cryogenic temperatures.

Numerous past studies have been focused on the micromechanics of particulate filled composites [1-8]. Unfortunately, the discrepancies between theoretical predictions and experimental data continues to limit the understanding of these composite materials. For example, in the references cited above, difficulty has been encountered in separating such variables as interfacial adhesion, particle agglomeration, dispersion and particle shape, all of which affect mechanical behaviour. In this investigation care was taken to minimize the influence of these variables. Other parameters, such as polymerization-induced stresses

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and shear effects around filler particles, were neglected in this study for simplicity. The theories and equations employed in the following discussions were selected from those which Nielsen [8] considers to best approximate the experimental data available.

Here an attempt is made to ascertain the influence of adhesion on experimental and theoretically determined tensile and thermal expansion properties of a model formulation consisting of a crosslinked epoxy-urethane polymer filled with aluminium oxide particles (4 to 40 μm diameter). Tensile testing was conducted at ambient and liquid nitrogen temperatures while varying the volume fraction of filler and the bond strength between the polymeric matrix and filler particles.

2. Theory

2.1 Thermal expansion

In the absence of phase interaction, one may expect the coefficient of thermal expansion of a composite material to be derived from the simple rule of mixtures [9],

$$\alpha_{\text{composite}} = \alpha_f \Phi_f + \alpha_m \Phi_m \tag{1}$$

where α is the coefficient of expansion, Φ is the volume fraction and f and m refer to filler and matrix.

A cursory survey of experimental results [9-13] indicates that the coefficients of thermal expansion usually fall below the values predicted by the rule of mixtures. This is owing to positive ($\alpha_f > \alpha_m$) and negative ($\alpha_f < \alpha_m$) mismatches between filler and matrix. Generally, in polymeric systems, the filler has a much higher modulus, and a lower coefficient of expansion which creates a negative mismatch or induced stress at low temperatures. Resultant composite thermal expansions would then tend to fall below those values predicted by the rule of mixtures. Several theoretical equations have been derived for calculating coefficients of thermal expansion which take into account stress interactions between phases. A recent equation of this type is the Fahmy and Ragai equation [9] shown below:

$$\alpha_c = \alpha_m - \frac{3(\alpha_m - \alpha_f)(1 - \nu_m)\Phi_f}{2(1-2\nu_f)(\Phi_m)\dfrac{E_m}{E_f} + 2\Phi_f(1-2\nu_m) + (1+\nu_m)} \tag{2}$$

where α is the coefficient of expansion, ν is Poisson's ratio, Φ is volume fraction, E is Young's modulus and subscripts c, m and f refer to composite, matrix and filler, respectively.

To further digress, as a material is cooled from the fabrication temperature (T_0) to liquid nitrogen temperature (T), stresses develop in the polymer near the filler surface owing to the difference in the coefficients of thermal expansion of the two components. At the interface, the radial stresses are compressive and equal the tangential stresses in the matrix which are tensile, thus making chemical bonding unnecessary for load transfer; this assumes $\alpha_m > \alpha_f$. Thus, the tangential tensile stresses occurring at the polymer/filler interface (at low concentration where there is no interaction between particles) can be determined by Equation 3 [4-6],

$$\sigma^* = E_m(\alpha_m - \alpha_f)(T_0 - T)K \tag{3}$$

where α^* is the thermally induced tensile stress at the interface, E_m is Young's modulus of the matrix in the unstressed state (assuming $E_m \ll E_f$) and T_0 indicates the temperature at which thermally induced stresses are relieved. The factor K depends upon the shape of the particles and upon the properties of the constituents of the composite. For a plane, K is unity and for a single sphere embedded in an infinite matrix K is expressed by Equation 4 [7],

$$K = \frac{1}{2\left[\dfrac{1+\nu_m}{2} + \dfrac{1-2\nu_f}{E_f/E_m}\right]} \tag{4}$$

where ν is Poisson's ratio and E_f is Young's modulus of the filler.

2.2. Mechanical properties

The mechanical properties under consideration are elongation, Young's modulus and tensile strength; each property will be discussed in terms of adhesion versus non-adhesion. The equations employed are predicated on spherical filler particles and a large difference in modulus between filler and matrix.

First, let us consider tensile strength or ultimate strength, which will be defined as the strength at failure. Assuming a material exhibits a linear (Hookean) stress/strain relationship, then tensile strength can be obtained from Equation 5 by substituting elongation values obtained from Equation 7 [1] and modulus values obtained from Equation 8,

$$\sigma_F = E\epsilon_F \tag{5}$$

where σ_F is tensile strength at failure and ϵ_F is elongation at failure (subscript F denotes failure). The values predicted by this equation are generally in poor agreement with experimental results because the composite system exhibits non-linear elastic or plastic deformation at ambient test temperatures. However, Equation 5 was utilized with satisfactory results at liquid nitrogen test temperatures where plastic deformation is not prevalent. Thus, to obtain a strength measurement at ambient conditions, Equation 5 was related to yield strength, σ_Y, which was derived as 0.5% offset yield strength. Employing this method, predicted data agreed quite well with those found experimentally. The above described technique was applied to composite systems featuring good adhesion between filler and matrix.

For composite systems displaying non-adhesion between filler and matrix, the tensile strength can be obtained by the following relationship [1]:

$$\sigma_{\text{composite}}/\sigma_{\text{matrix}} = (1 - \Phi_f^{2/3})S \qquad (6)$$

where Φ_f is the volume fraction of filler and S is the stress concentration function. In the case of non-adhesion, the filler particles do not carry any of the load; all the load is carried by the matrix. Consequently, it might be assumed that the tensile strength of the composite is equal to the product of the matrix tensile strength and volume fraction of the polymer. This is not the case since the filler particles perturb the stress field. Thus, the above equation accounts for a decrease in cross-sectional area of the polymer as filler is added, but it does not enable one to calculate the additional stress concentration around the particles. Thus, tensile strength values calculated by this equation are considered maximum values; stress concentrators will lower these values by an undetermined amount.

Concerning elongation, assuming that a polymer fails at the same elongation in a filled system as the bulk unfilled polymer, the elongation to failure in the case of good adhesion can be determined by the following equation [1]:

$$\epsilon_{F(\text{composite})}/\epsilon_{F(\text{matrix})} = 1 - \Phi_f^{1/3} \qquad (7)$$

where Φ_f is the volume fraction of filler. As stated, this equation assumes good adhesion between the two phases while neglecting shear effects around the filler, triaxial stresses in the matrix and effects due to Poisson's ratio. Elongation in non-adhesion situations were obtained by simply substituting tensile strength values (obtained from Equation 6) and modulus values (obtained from Equation 9) into Equation 5 [1].

The Eilers-Van Dijck equation [2], shown below, was used for calculating Young's modulus in composite systems possessing good adhesion. In this

$$E_{\text{composite}}/E_{\text{matrix}} = \{1 + [1.25\Phi_f/(1 - V\Phi_f)]\}^2 \qquad (8)$$

relationship, V is sedimentation volume (volume of filler/true filler volume). For this work, the value of V was experimentally found to be 2. Filler particle size and shape will tend to influence the value of V. Thus, when $V = 2$ and the volume fraction equals 0.5, the modulus will go to infinity. Hence, in these experiments, Equation 8 would be void at volume fractions exceeding or approaching 0.5.

The more frequently used Hashin-Shtrikman equations [14, 15] were also considered for calculating Young's modulus. However, owing to the large difference in elastic moduli of the constituents, the bounds calculated were too far apart, thus producing little advantage over the simpler Eilers approach.

The theoretical equation of Sato and Furukawa [3] was employed in obtaining Young's modulus for composite systems exhibiting non-adhesion.

$$\begin{aligned} E_{\text{composite}}/E_{\text{matrix}} &= \{1 + [\Phi_f^{2/3}/2\,(1 - \Phi_f^{1/3})]\}\,(1 - \psi\zeta) \quad \text{volume effect} \\ &+ K\frac{\Phi_f\,(1 - \Phi_f^{1/3}/2)}{(1 - \Phi_f^{1/3})^2}\,(1 - \psi\zeta) \quad \text{surface effect} \qquad (9) \\ &- \frac{I_f^{2/3}\,\psi\zeta}{(1 - \Phi^{1/3})\,\Phi_f} \quad \text{cavitation effect.} \end{aligned}$$

In this equation, $\psi = (\Phi_f/3)\,(1 + \Phi_f^{1/3} - \Phi_f^{2/3})/(1 - \Phi_f^{1/3} + \Phi_f^{2/3})$, $K = K_0\,(1 - \zeta)$, $K_0 = g_f^{(m)}/g_r d$, where $g_f^{(m)}$ is surface density and $g_r d$ is volume density. ζ is an adhesion parameter, $\zeta = 0$ for good adhesion and $\zeta = 1$ for non-adhesion. For purposes of this paper, only the latter adhesion parameter was instituted, because when $\zeta = 1$, the surface effect portion of the equation drops out, eliminating some complexity in the relationship. This equation could also be used to obtain modulus in the case of perfect adhesion except the surface effect is quantitatively difficult to obtain [3]. In essence, the Sato-

Furukawa equation assumes the unbonded filler particles act as holes (vacuoles) and, therefore, predicts a decrease in modulus with increasing filler content.

3. Experimental

The polymer matrix consists of 50 parts polyurethane (adiprene L-100, Du Pont), 35 parts epoxy (Epon 828, Shell Chemical Company), 15 parts epoxy (Epon 871, Shell Chemical Company) and is cured with 24 parts MOCA (4,4′-methylene-bis-2-chloroaniline). This matrix has a glass transition temperature at + 51° C and a suborder transition temperature at − 140° C [16]. The Al_2O_3 powder used is essentially spherical in shape and has a particle size distribution ranging from 4 to 40 μm, with 15 μm determined as the median size.

For the sample involving good adhesion, the resins are pre-heated to 200° F, after which they are thoroughly mixed and placed in a vacuum chamber at a pressure of 0.5 mm Hg for about 5 min in order to remove adsorbed air and volatiles. A pre-determined amount of Al_2O_3 powder, which was also pre-heated to 200° F is thoroughly mixed into the resin system after which the mixture is placed in the vacuum chamber for de-aeration. The mixture is then reheated to 200° F; the MOCA curing agent (at 250°F) is then added and mixed. The composite material is again de-aerated in the vacuum chamber at a pressure of 0.5 mm Hg. A sheet of the composite is then formed by pouring the material into an aluminium mould coated with a fluorocarbon release agent (RAM-225), followed by curing at 285°F for 10 h.

The Al_2O_3 particles are sufficiently small and the matrix gel time sufficiently rapid so that settling is minimized. The degree of settling was determined by measuring the hardness of both sides of the composite sheet with a Shore Durometer Type D.

Tensile strength (ASTM-D01708) and thermal expansion specimens of the pure matrix and composites were machined to desired dimensions. The stress/strain measurements were carried out with an Instron testing machine (Model TTD) with an initial strain-rate of 0.05 min^{-1} which is then increased to 1.0 min^{-1} after deformation at ambient temperature. A strain-rate of 0.02 min^{-1} was employed at liquid nitrogen temperature. The thermal expansion measurements were carried out via quartz dilatometer.

The composites having no adhesion between the polymer matrix and filler were prepared in the same manner with the exception that the Al_2O_3 powder was first treated with a 1% solution of stearic acid in benzene. The stearic acid forms a submicron layer around the surface of the Al_2O_3 particle; the excess stearic acid was then washed off several times with benzene. Owing to the non-polar nature of the stearic acid's long aliphatic tail, the degree of bonding between the filler particles and polymer matrix should be significantly reduced. The fracture surfaces of the tensile specimens having both good and poor adhesion between filler and matrix were studied under a scanning electron microscope in order to verify the degree of bonding.

4. Results and discussions

4.1. Thermal expansion

The coefficients of thermal expansion of the various filled composites were experimentally determined and compared to values predicted by the rule of mixtures and the Fahmy and Ragai equation, see Table I. The data in Table I have also been illustrated graphically in Figs. 1 and 2.

The experimentally determined coefficients of expansion are in fair agreement with the rule of mixtures at low volume fraction but in better agreement with values predicted by Fahmy and

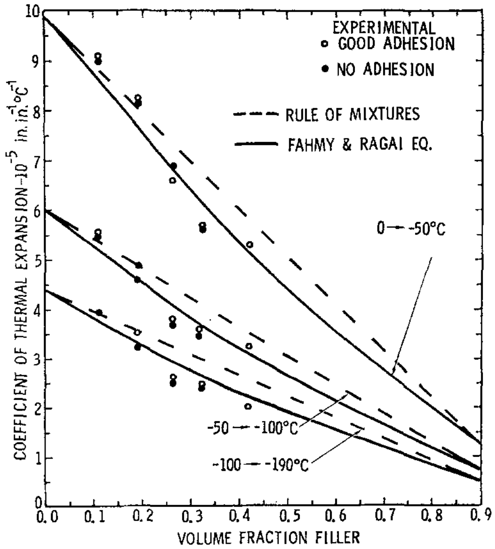

Figure 1 Average coefficient of thermal expansion versus volume fraction filler for composites with good adhesion and no adhesion.

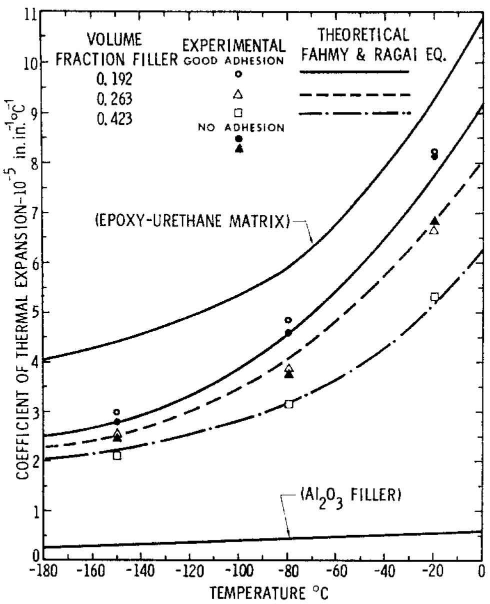

Figure 2 Average coefficient of thermal expansion versus temperature for composites with good adhesion and no adhesion.

Ragai equation, especially at higher volume fractions. This is probably due to the high elastic modulus of the Al_2O_3 filler and resultant negative mismatch ($\alpha_f < \alpha_m$) which tends to make experimental values fall below the values predicted by the rule of mixtures. The degree of bonding between filler and matrix does not appear to have an effect on thermal expansion from ambient to liquid nitrogen temperatures. Again, this is probably owing to the thermal expansion coefficient of the matrix being greater than that of the filler. As the temperature is decreased, the filler particle is subjected to radial compressive stresses; therefore, creating a mechanical bond or stress field between the matrix and filler.

4.2. Mechanical properties

Mechanical properties were experimentally determined at ambient (Figs. 3 to 6) and liquid nitrogen temperatures (Figs. 7 to 9) and then compared to theoretical predictions.

At ambient temperature with good adhesion between filler and polymer, the experimental values (yield strength, elongation, Young's modulus) agree fairly well with theoretical values. When poor adhesion is prevalent between filler and polymer at ambient temperature, the experimental results are in poor agreement with the theoretical data; the exception being ultimate tensile strength which shows fair agreement. With respect to elongation (Fig. 5), the ideal case of non-adhesion apparently has not been fully realized; however, this effect was partially achieved as evidenced by the experimental data which fell between the theoretical curves for adhesion and non-adhesion. Again, with respect to non-adhesion at ambient temperature, Young's modulus, as predicted by the equation of Sata and Furukawa (Equation 9), was in poor agreement with experimental values (Fig. 6).

TABLE I Coefficients of thermal expansion of Al_2O_3 filled epoxy-urethane composite

	Average α; (10^{-5} in. in.$^{-1}$ °C^{-1})						
Volume fraction filler	0	0.108	0.192	0.263	0.323	0.423	1.0
Good adhesion – exp							
(0 to −50°C)	9.90	9.05	8.25	6.60	5.70	5.30	0.57
Temp. (−50 to −100°C)	6.00	5.55	4.99	3.70	3.45	3.24	0.42
(−100 to −190°C)	4.35	3.85	3.52	2.55	2.35	1.97	0.30
Non-adhesion – exp							
(0 to −50°C)		9.00	8.20	6.90	5.65		
Temp. (−50 to −100°C)		5.54	4.60	3.65	3.40		
(−100 to −190°C)		3.92	3.17	2.50	2.35		
Rule of mixtures							
(0 to −50°C)		8.90	8.10	7.44	6.62	5.87	
Temp. (−50 to −100°C)		5.40	4.92	4.51	4.15	3.55	
(−100 to −190°C)		3.85	3.56	3.27	3.02	2.55	
Fahmy and Ragai equation							
(0 to −50°C)		8.65	7.75	6.87	6.17	5.15	
Temp. (−50 to −100°C)		5.20	4.60	4.10	3.75	3.15	
(−100 to −190°C)		3.77	3.35	3.00	2.70	2.25	

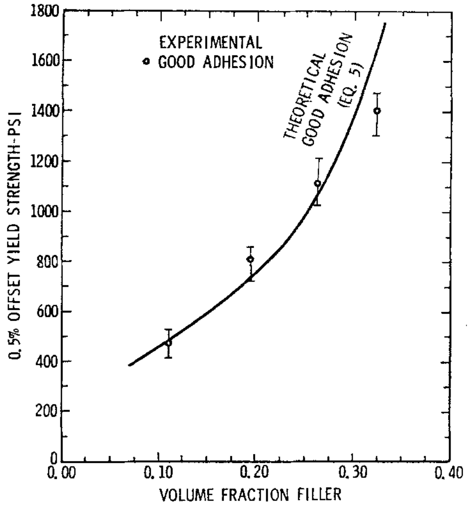

Figure 3 Tensile yield strength (0.5 % offset) versus volume fraction filler for composites with good adhesion at ambient temperature.

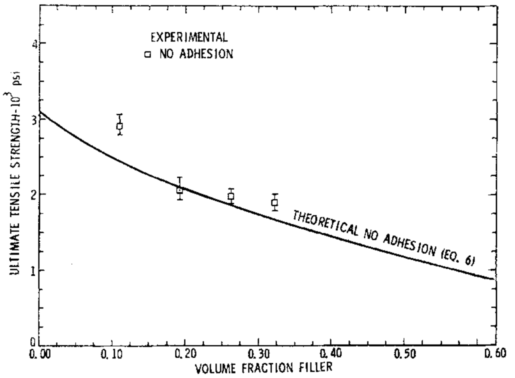

Figure 4 Ultimate tensile strength versus volume fraction filler for composites with no adhesion at ambient temperature.

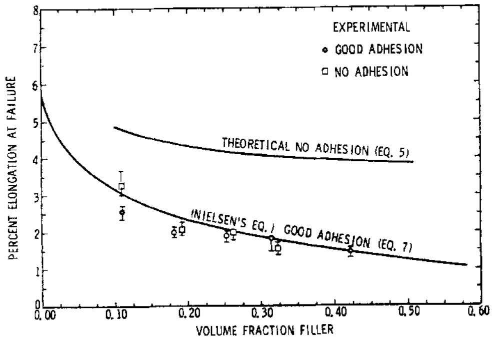

Figure 5 Elongation at failure versus volume fraction filler for composites with good adhesion and no adhesion at ambient temperature.

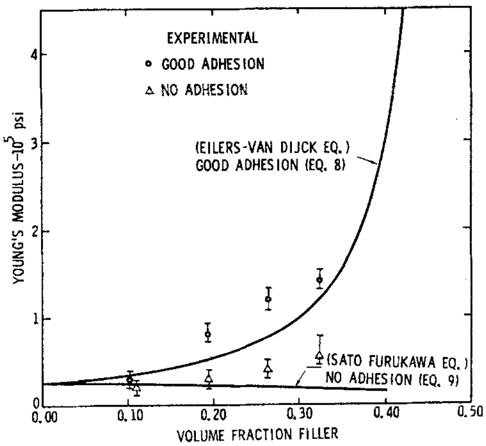

Figure 6 Young's modulus versus volume fraction filler for composites with good and no adhesion at ambient temperature.

This equation assumes a decrease in modulus as the volume fraction of filler increases. If this is true, then one must argue that the unbonded filler particles act as holes (vacuoles) in which case the modulus would decrease with increasing filler content. However, the unbonded particles do not act entirely as holes, but restrain the matrix from collapsing. In this case, the modulus should increase with increasing filler content, which was observed.

At liquid nitrogen test temperatures, fair agreement was obtained in the case of good adhesion with respect to elongation (Fig. 8);

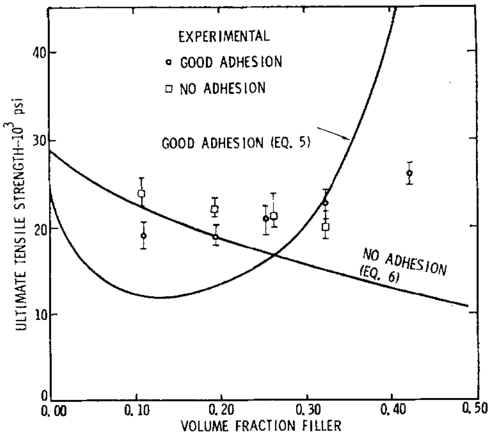

Figure 7 Ultimate tensile strength versus volume fraction filler for composites with good adhesion and no adhesion at liquid nitrogen temperature.

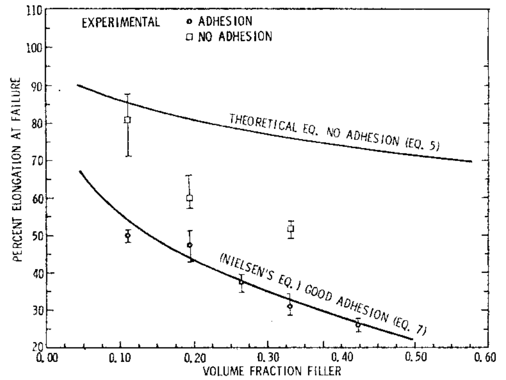

Figure 8 Elongation at failure versus volume fraction filler for composites with good adhesion and no adhesion at liquid nitrogen temperature.

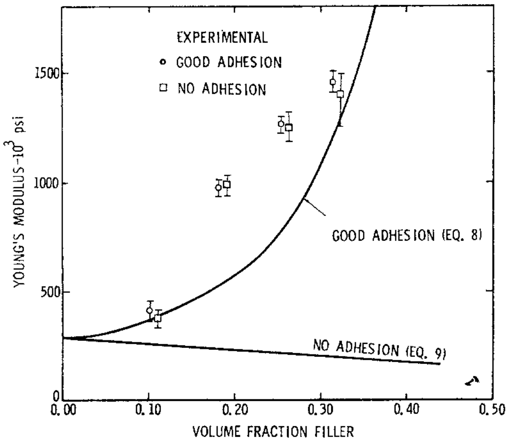

Figure 9 Young's modulus versus volume fraction filler for composites with good adhesion and no adhesion at liquid nitrogen temperature.

otherwise, generally poor agreement existed between experimentally determined mechanical properties and theoretical values. Besides correlating experimental and theoretical values, an attempt was made to increase elongation at liquid nitrogen temperature by employing poor adhesion between filler and matrix. At ambient temperature, this technique increased elongation values from both a theoretical and experimental standpoint. However, the degree of adhesion between filler and matrix does not appear to have any effect on the elongation or other mechanical properties obtained at liquid nitrogen temperature.

In many composite systems, stresses develop at the filler/matrix interface as the material is cooled from the fabrication temperature. These stresses are caused by differences in thermal expansion coefficients of the respective constituents. By employing Equations 3 and 4 (using data in Tables I and II), model calculations were made to contrast the thermally induced stresses resulting from a temperature cycle of +140 to −196°C. Upon cooling from a +140°C fabrication temperature to ambient, a stress at the interface of approximately 1000 psi* was calculated; continued cooling to liquid nitrogen temperature yields a value of about 2300 psi which is more than twice the stress found at ambient temperature. This suggests that the thermally induced stresses incurred during cool down must contribute largely to the formation of an effective mechanical bond between the filler and matrix which could conceivably offset any other bonding effects. This explanation would account for similar mechanical and thermal expansion properties being observed with the two degrees of bonding at this low temperature. This rationale does not deny that other effects could contribute to the above observations.

TABLE II Mechanical properties of the composite constituents

	Epoxy-urethane matrix	Al_2O_3 filler
Young's modulus (psi)	0.3×10^5	3.9×10^7
Poisson's ratio	0.36	0.23
Tensile strength (psi)	3120	
% Elongation to failure	105	

5. Conclusions

Coefficients of thermal expansion can be estimated by the rule of mixtures at low volume fractions of filler and with greater confidence by the Fahmy-Ragai equation at higher volume fractions. The degree of chemical bonding between filler particles and polymer matrix appears to have little effect on thermal expansion from ambient down to liquid nitrogen temperatures. This is owing to the negative mismatch between filler and matrix ($\alpha_f < \alpha_m$) which is reflected as a mechanical bond resulting from thermally induced stresses.

The theoretical equations used for predicting

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*1000 psi = 9.81 N mm^{-2}.

mechanical properties of these formulations appear fairly reliable at ambient temperature and unreliable at liquid nitrogen temperatures. Generally, the formulations possessing good adhesion exhibit better agreement with theoretical values than those which exhibited non-adhesion at ambient temperature. The latter phenomenon was due to the fact that total non-adhesion was not fully achieved. Similar to the observations on thermal expansion, the degree of chemical bonding between filler and matrix does not appear to have an effect on mechanical properties at liquid nitrogen temperatures. Again, this is probably owing to mechanical bonding resulting from thermally induced stresses.

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