

The Physical Chemistry of the Carbon Fiber/Epoxy Resin Interface

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Abstract. The surfaces of carbon HOPG, selated polymers, epoxy resins and various hardeners were characterized. The surface energy was described in terms of polar and dispersive surface energy components. Zisman's critical surface energy for wetting was predictable from the surface energy components. However, surface energy of curing resins can not be predicted from resin and hardener surface energies. The curing agent is the critical factor in dictating wetting of epoxies/curing agent systems.

The surface topography of PAN precursor carbon fibers does not significantly differ with increasing fiber modulus when observed with SEM at 10,000X or less. However, high magnification - 66,000X (TEM replicas) reveals that fiber surfaces get smoother with increasing modulus, and rougher with surface oxidation[1]. Additionally, the proportion of the fiber surface which is basal plane increases with fiber modulus. Consequently, wetting and adhesion by resins to surface of fiber will be expected to become poorer with increasing fiber modulus. The basal plane of HOPG was used to simulate the surfaces of HM carbon fibers. However, HOPG surface is not monoenergetic as it can consist of basal planes and edges, Fig. 1. Moreover, wetting of this type of surface depends on more than just the ratio of basal to edge sites, because the wetting characteristic. The aim of this paper is to describe the surface energy components of HOPG, epoxy resins, curing agents and a model from predicting their critical surface energy.

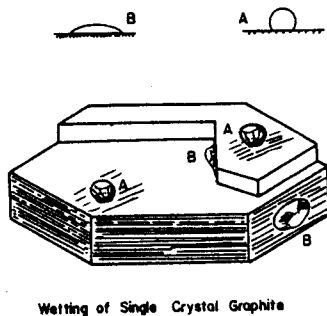


Fig. 1 Schematic of the basal plane and edges of HOPG.

The contact angle of water, formamide, methylene iodide, ethylene glycol and several other liquids of known surface energy were measured on the basal planes of HOPG, immediately after cleavage.

For comparison, similar measurements were carried out on polished surfaces ($0.05\mu\text{m Al}_2\text{O}_3$) of PTFE, polyethylene, polycarbonate, polystyrene, PMMA, to provide a set of calibrated solid surfaces.

The surface energy of various epoxy resins and hardeners were calculated from wetting studies on the calibrated surfaces. Finally, nadic methyl anhydride (NMA) and dodecenyl succinic anhydride (DDSA) were cured with diglycidyl ether of bisphenol A (Epon 828*), diglycidyl ether of Novolac (Epon 152*), cycloaliphatic resin (CY179**) and a tetraglycidyl derivative of methylene dianiline (Aradite MY 720**) with benzyldimethylamine (BDMA) as catalyst, to observe the role of the curing agent and the influence of epoxy hardener ratio on the physico-chemical properties of epoxies.

The polar and dispersive components of the polymers of the basal planes of HOPG were evaluated from the slope and intercept of the geometric mean model of Fowkes-Kaeble-Young-Depree relationship[2]:

$$\frac{\gamma_L(1+\cos\theta)}{2(\gamma_L^d)^{1/2}} = (\gamma_s^d)^{1/2} = \frac{(\gamma_L^p)^{1/2}}{\gamma_L^d} (\gamma_s^d)^{1/2}$$

where γ_L is the surface energy of the contacting liquid, γ_L^d , γ_L^p ; γ_s^d , γ_s^p and the dispersive and polar surface energy components of the liquid and solid respectively. The value of the surface energy of the basal surface of HOPG agree with those obtained by Drzal, for HMU carbon fibers[3], Table 1. The dispersive component of surface

* Shell Corp. TM; ** Ciba Geigy

Table 1. Surface Energy of Graphites and PTFE (20-25°C)

	$\gamma^d(\text{erg/cm}^2)$	$\gamma^p(\text{erg/cm}^2)$	$\gamma^t(\text{erg/cm}^2)$	Correlation Coefficient
HOPG (20-25°C)	34.5±3.2	12.9±4.3	47.4±4.3	0.9686
PTFE	20.8±0.01	0.05±0.01	20.8	0.9938
HMU*				
20°C V.T	33.0±1.2	8.1±3.0	41.1±3	---
300°C V.T	32.0±0.9	7.4±0.9	39.4±0.9	---
HMS*				
20°C V.T	28.2±0.3	20.4±4.0	48.9±4.0	---
300°C V.T	30.2±0.4	12.8±1.7	43.4±1.7	---

*Drzal, et al., Carbon, Vol 17, pp. 375-382 (1979)

energy for the basal region of HOPG is insensitive to surface treatments. The polar component can be modified readily. The surface energy components of epoxy resins and hardeners are presented in Table 2. For mixed epoxy resins and hardeners,

Table 2. The Surface Energy Components of Some Epoxy Resins and Their Curing Agent at 20-25°C.

EPOXY RESIN	Dispersive Components erg-cm^{-2}	Polar Component erg-cm^{-2}	Surface Energy erg-cm^{-2}
EPON-828	35.1	16.4	51.5
EPON-871	31.6	5.7	37.3
EPON-15.2	40.2	11.7	51.9
CY-179	24.4	19.3	43.7
MY-720	28.2	25.2	53.4
Curing Agents			
Diethylenetriamine			
DTA	27	14.6	41.6
Nadic Methyl Anhydride			
NMA	30.7	9.1	39.8
Dodecenyl Succinic Anhydride			
DDSA	29.8	9.4	39.2

the surface energies of the curing epoxies (Table 3) bear no relationship to the volume fraction of the surface energy, components of the resins and hardeners. The surface energy of the curing agent is the critical factor. For example, all DDSA epoxy systems have about the same value of polar and dispersive components irrespective of anhydride epoxy ratio. While this indicates the futility of attempting to use the volume averaged surface energies of resins and hardeners to estimate the wetting behavior, it does point out when adsorption is occurring. Considering that the polar groups on carbon fiber surfaces have been shown to be predominantly carboxyl and phenolic[4], it is not surprising that amine curing agents strongly interact with these groups.

Zisman[5] has shown for low surface energy systems the critical surface energy, γ_c , for wetting can be obtained by extrapolating the measured contact angle of various liquids to perfect wetting. For a predominantly dispersive type surface like PTFE and for homogeneous series

Table 3. Surface Energy Components of Anhydride Cured Epoxies.

SUBSTRATES	Dispersive Component	Polar Component	Total Surface Energy
DDSA. Cure			
CY-179 (85-100phr)	29.2±0.6	2.9±0.7	3.2±1.4
MY-720 (68-102phr)	26.2±1.2	3.5±1.4	29.8±2.6
Epon-828 (130-140phr)	30.1±0.6	2.5±0.7	32.6±1.4
Epon-152 (104-144phr)	27.1±1.2	2.3±1.5	29.4±2.7
NMA. Cure			
CY-179 (62-74phr)	34.3±1.2	10.2±1.4	44.4±2.6
MY-720 (52-66phr)	35.5±0.7	9.2±0.8	44.6±1.5
Epon-152 (77-89phr)	34.3±0.8	7.8±1.0	42.1±1.8

of liquids, the extrapolation produces unique values of critical surface energy. When a non-homogeneous series of liquid are used, the values of γ_c are not well defined. For a surface such as graphite, with local variations in edge and basal regions, γ_c exhibits even more scatter. Since wetting of fibers by resins is necessary for making good composites the relationship between wetting and γ_c is important. Energies of the various epoxy and non epoxide polymers were observed to be between the dispersive component and the total surface energy. Statistical analysis of these results indicate that γ_c can be expressed as a liner combination of the dispersive and polar components of surface energy, Fig. 2.

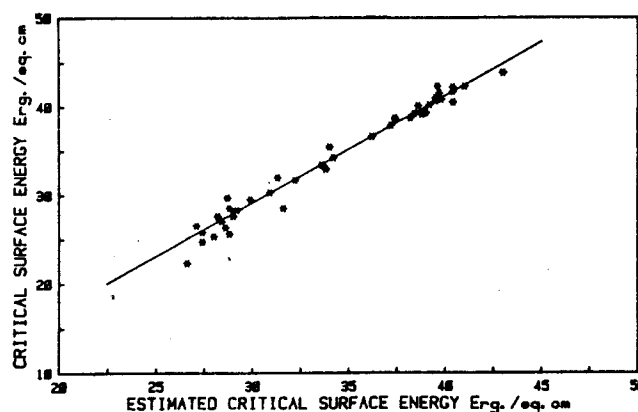


Fig. 2 Comparison of Zisman's Critical Surface Energy γ_c and estimated surface energy of various polymers.

This relation can be conveniently expressed as:

$$\gamma_c = \gamma_s^d + 1/2 \gamma_s^p$$

$$\text{Lim } \gamma_c \rightarrow \gamma^d$$

$$\gamma^p \rightarrow 0$$

he dispersive interaction will always be fully operable. However, for a randomly oriented

molecule with a constituent polar group, free rotation is severely restricted. Hence, polar-polar interaction with a contacting liquid will be considerably less. The screening effects and the inability of the molecules at the solid surface at low temperatures, to reorient themselves to the desired conformation in response to the contacting liquid may explain why only half the value of the non-dispersive components is required in the polymer surface energy.

References

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