Thermochimica Acta, 103 (1986) 97—106
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

STUDIES OF INTERFACIAL PROPERTIES IN POLYEPOXYDE / CARBON OR GLASS FIBER COMPOSITES BY MEANS OF MICROGRAVIMETRIC TECHNIQUES

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ABSTRACT

The microweighing techniques have been chosen to analyze the interface problem of composite materials with polyepoxyde matrix and fibrous reinforcement, particularly the surface interactions and the wetting of carbon and glass fibers with some reactive groups of the organic matrix. The experimental data deal with the nature and energy of interactions, the hydrophilic or hydrophobic behaviour of the surfaces, the wetting angle. The surface of the fibers is modified by various treatments : oxidation, laying of a coating agent. The results allow to make propositions on the role of these treatments during the making of the composite and they also allow to analyze the differences between carbon and glass behaviour.

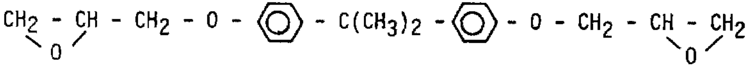
INTRODUCTION

The methods of thermal analysis have been used for a physicochemical study of the solid / solid interface in composite materials. We are concerned with epoxyde matrix reinforced by carbon and glass fibers. The making of these composites benefits from a satisfying "know how". Nevertheless the aging problems and the need for constant increasing of the mechanical qualities of the final product require a better understanding of the sticking mechanism of the matrix on the fiber and precise phenomena which develop on the whole of the binding layer between fiber and matrix (1 to 100 nm) (ref. 1 and 2).

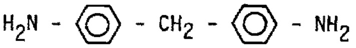
In the systems studied below :

- the interphase fiber / matrix can be largely modified either by surface chemical treatment or by coating layer. The influence of these treatments on the final properties of the composite is most important in industry.
- the polymer matrix is a constant phase. It is obtained by the heating of a stochiometric mixture 2/1 formed by :

. a diepoxyde prepolymer DGEBA (diglycidyl ether of bisphenol A)



. a primary diamine hardener D D M (4 4' diaminodiphenylmethane)



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The reaction mechanism between the epoxy cycles and the amine functions implies the opening of the cycles into secondary alcohol functions and the successive formations of secondary amine at first (polycondensation), then of tertiary amine (reticulation) (ref. 3 and 4). The matrix being insoluble and infusible, it is difficult to characterize the interactions with fibers by means of direct study techniques. This is why the methodology consists in a *modelization* of the matrix by a series of monofunctional compounds of low molecular weight acting as the active groups which are present in the course of the matrix making. We have chosen : epoxystyrene, aniline, glycerol, ethylene glycol. Water has been also retained for it is present in the environment and it is involved in the aging problems. These reactives can be used in vapor and liquid phase which allows to characterize their interactions with the fibers by means of classical adsorption and wetting methods.

FIBERS AND SURFACE TREATMENT

Carbon fibers

The carbon fibers are highly resistant fibers from Hercules Company distributed by Aerospatiale and S.E.P.. They are made from polyacrilonitrile by preoxidation in the air at about 250° C and by carbonisation in nitrogen between 1 000 - 1 500° C. They may then be modified superficially. Three fibers have been kept :

- . rough fibers from the threading machine : A U
- . oxidized fibers : A S
- . oxidized fibers with a "plastic" coating : A S G.

All the fibers are in the shape of wicks formed by 12 000 filaments ($\emptyset$ = 7 μm), density 1.8 g cm^{-3}, specific area 2 m^2 g^{-1} (the geometric surface being 0.5).

The characterization of the non coated fibers surface (A U and A S) has been obtained by X-ray photoelectron spectroscopy (ref. 5). Each element (C, N, O in this case) is characterized by a peak, the resolution of which indicates the different bindings possible. In this manner peak C shows four compounds : graphite, C = O, C - OH, $C\overset{O}{\leqslant}OH$. It is shown that the oxidation doubles the carbon fraction bound with oxygen, especially in the acid form.

The characterization of the coating of the fiber ASG is obtained by FTIR. After extraction, the transmission spectra show that the coating product present is of the DGEBA type. The ratio is 7.6 mg g^{-1} representing $44 \cdot 10^{-6}$ epoxy sites per gram.

Glass fibers

The glass fibers (60 % SiO_2, 25 % $A\ell_2O_3$, 6 % CaO, 9 % MgO) are Vetrotex - St Gobain H.T. fibers, supplied in 4 models :

- . bare fiber (or water coated fiber) : R_0

. bare fiber + binding agent : R_p
. bare fiber + sticking agent : R_c
. bare fiber + mixture of binding and sticking agent : R_{cp}

The fibers are in the shape of wicks formed by filaments (Ø = 10 µm). The specific area is about 0.2 $m^2\ g^{-1}$ which corresponds to the geometric surface.

The characterization of coating agents is done by FTIR:

- The sticking agent is a DGEBA resin similar to that of carbon fibers AS G. It has no interaction with the glass and the chloroform extraction is almost complete (ref. 6) : 9 mg g^{-1} for R_c and 10 mg g^{-1} for R_{cp} which represent respectively 55 and 59 . 10^{-6} epoxyde sites per gram.
- The binding agent is a hydrolysed γaminopropyltriethoxysilane

$H_2N - CH_2 - CH_2 - CH_2 - Si(OH)_3$ (hydrolysed A 1100)

Its action is meant to interact with the surface OH and to form a polycondensate layer. The mechanism (ref. 6) is that of Ishida (ref. 7) represented in Fig. 1. The layer is formed by groups of three A 1100 moles ; the glass binding is made on only a fraction of the surface OH ; the H bonds between NH_2 and the last OH of A 1100 entails the "cyclisation" of the moles. The binding agent fixation cannot go over the ratio of 1.4 mg g^{-1} which corresponds to 10.10^{-6} A 1100 moles per gram.

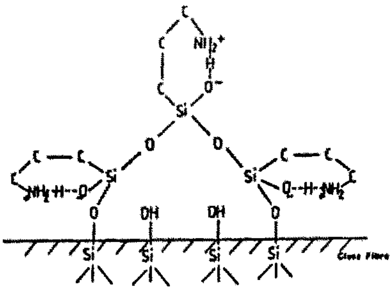

Fig. 1 - A 1100 fixation on glass surface

TECHNIQUES AND METHODS

Vapor phase studies : microbalance - microcalorimeter coupling

- Equipment (ref. 10) : a symetrical microbalance (SETARAM MTB 10-8) and an isotherm differential microcalorimeter (ELECTRONIQUE ARION BCP) are coupled in a classical adsorption device. The two 18.5° C thermostated samples can be kept under various partial pressures of the reactives (by means of regulating temperature of a central evaporator) or kept under saturated pressure by using two evaporators in the thermostated neighbourhood of the two samples. The weight uptakes and the thermal effects are simultaneously recorded on the two tracks of one recorder which allow the calculation of the interaction molar energy. In this case, the studies are only possible after a desorption of the equipment under high vacuum. This pretreatment ensures the separation of the inner hydrophobic surfaces of the wicks (cf. the vacuum dispersion of the hydrophobic pigments (ref. 8) and helps the diffusion of low vapor pressure at the very beginning (this can pose a problem if later on the reactive diffusion is no longer sufficient to maintain the initial concentration around the sample : there may be a spontaneous desorption and the final equilibrium is hidden).

- Sensitivity : Because of low fiber surface areas (water monolayers for example of 3 to 30 micromoles per gram) and of low coating ratios (10 to 60 microsites per gram) one must expect weight uptakes of a few dozen micromoles, in the order of mg, and thermal effects of the order of 1 J.

. in weight : the sensitivity is better than 0.01 mg. The equilibrium data, with 2 g samples, are always superior to 0.5 mg and empty holder corrections inferior to 0.1 mg.

. in heat : the sensitivity of the microcalorimeter thermoelectric module is 33 µV/mW, which gives, on the 100 µV full scale and with a paper winding speed of 1 mm per mn, thermograms of 1 300 mm^2/J. The thermal effects kept in this study are at least of 0.5 J with empty holder correction inferior to 0.1 J. The absolute precision on molar heat of interaction is less than 30 % but the relative precision is better than 15 %.

- Data analysis : The experimental data analyzed as function of the following terms :

. hydrophilic surface : the reactives form a mono then multilayer film, structured by the solid surface. The interaction molar heat is superior or equal to the liquefaction energy and it is specific of the binding.

. hydrophobic surface with more or less dispersed active sites : The adsorption on these sites is energetically low, highly entropic and tends to develop around the first sites rather than cover the whole surface (clustering mechanism) (ref. 9). The interaction molar heat is inferior to the liquefaction value.

. coating layer : the reactives may show either an interaction or a mixing with the organic phase according to active sites or compatibility aptitude.

. heterogeneous substract (fiber + coating layer) : if the coating forms a simple sheath around the fiber, the fiber surface and the coating act separately and both effects can be seen. If the coating is bound to the surface, the reaction to be seen is different and specific to the binding.

. hydrophilic or hydrophobic behaviour can be confirmed,near the saturated pressure, from heat data. In the first case, there is a condensation or dissolution of the reactives with $E \cong E_L$. In the second case, one can observe the diffusion of the reactives in the wicks with very low interaction energy.

Wetting studies : tensiometric method or "Wilhemy balance"

A Cahn electronic balance allows to measure the weight P of the liquid lifted by a monofilament (perimeter a). This weight depends on the surface tension of the liquid γ_{LV} and on the contact angle θ :

$$P = a\ \gamma_{LV}\ \cos\theta$$

P can be measured in different points of the monofilament during wetting as well as unwetting by means of a cycle device which gives to the liquid a vertical alternate motion followed by a floater linked to an induction sensor. A table XY records the weight as function of the motion. The maximum sensitivity used is 250 µg full scale (ref. 11).

EXPERIMENTAL RESULTS AND ANALYSIS

Adsorption studies ; reactives : water, aniline, epoxystyrene

Figure 2 represents some isotherms obtained at 18.5° C.

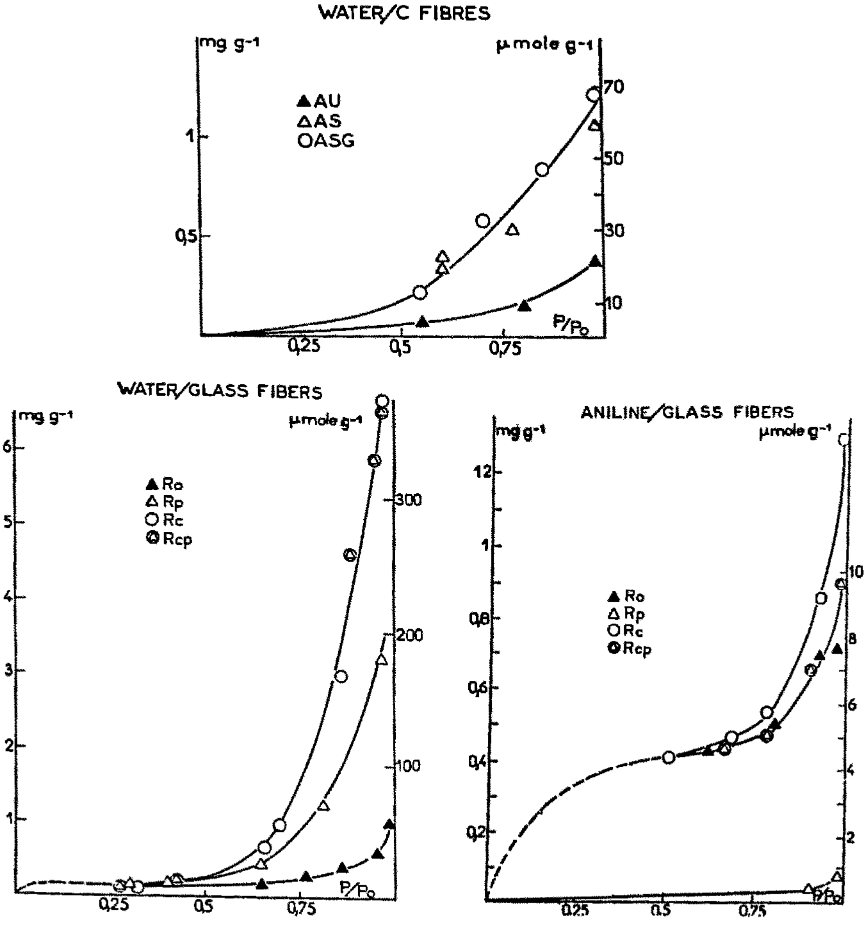

TABLE I

		WATER E_L = 44 kJ mole^{-1}							ANILINE E_L = 48 kJ mole^{-1}					EPOXYSTYRENE E_L = 52 kJ mole^{-1}		
HR %		40	60	70	80	90	98	100	70	80	90	98	100	70	98	100
AU	a		< 6		9		22					1			1	4*
	E															
AS	a		21		33		58	130*				2,5			2	8*
	E		15		18,9		16	5				24				20
ASG	a		13		34		69	172*	7,5			13	35*		8	45*
	E		24		22		17	4	28			23	7		48	38
R_o	a	10		12	15	22	35	65*	5	5	7,5	8	10*	1	>2	
	E	65		74	73	63	50	40	150	140	125	125	104		200	
R_p	a	12		27		72	182	400*			<0,5	< 1		0	0	
	E	60		46		39	28	20								
R_c	a	15		37		167	300	700*	5,5	6	8		75*	<1	3	
	E	60		20		21	20	25	150	160	140		50		200	
R_{cp}	a	14		55		264	385	550*	4,5	5	7	10	55*	< 1	2	
	E	68		35		29	29	20	150	160	170	150	45			

Table 1 gives the weight uptakes at different relative pressures (a in mole g^{-1}) and the average molar energy all over this weight uptake (E in kJ $mole^{-1}$). In this table, the data with symbol *, for saturated pressures, are not the equilibrium values.

The analysis of the data brings the following observations for the different systems studied :

- Water / carbon fibers. The interactions are low with an energy inferior to 25 kJ $mole^{-1}$ that is to say half the liquefaction energy. The active site concentration is trebled by oxidation which suggests that the sites concerned are carbonyl, acid, hydroxyl sites. For AS, the effective area would then be at best 30 % of the total value with a monolayer of 10 water micromoles per gram. As for ASG, the reactive site concentration is not modified by the coating which does not intervene and behaves therefore as a superficial sheath. At saturated pressure, for the 3 fibers, the texture of the wicks and the hydrophobicity of the surfaces favor the diffusion of the water with a very low interaction energy.
- Aniline / carbon fibers. Similar to what happens with water, the aniline interactions are low. For the two bare fibers, the number of reactive sites is trebled by oxidation. On the other hands, one notices that the DGEBA coating interacts with aniline (25 % of epoxyde sites concerned). At saturated pressure, all the fibers have an hydrophobic behaviour.
- Epoxystyrene / carbon fibers. The main difference with the two previous cases, is that the interaction heat is nearer the liquefaction value in presence of coating : the interaction between epoxystyrene and the DGEBA coating would be of the mixing type favourable to wetting (see under).
- Water / glass fibers. The interaction energy is in all cases higher than 60 kJ $mole^{-1}$ for at least 15 micromoles of water per gram. This energy corresponds exactly to the physisorption energy of one water mole bound on two surface OH of mineral oxides highly desorbed (ref. 12). Given a concentration of 5 to 10 OH per 100 $Å^2$, a simple calculation shows that the glass fiber surface is in fact ∿ 10 times bigger than that measured using nitrogen. The coating agents don't modify much the water accessible OH number : therefore the sticking agent behaves as a sheath and the binding agent leaves a large fraction of the hydroxyls accessible to water. On the other hand the coating agents favor the manifestation of water diffusion in the wicks with a low interaction energy.
- Aniline / glass fibers. One notices on the rough fiber R_0 the possibility of very strong interactions between OH and NH_2. The energy shows a chemisorption mechanism. The formation of an amine salt of the SiO^- HNH_2R^+ type can be envisaged. The binding agent, when alone (fiber R_p) cancels any aniline reaction. On the contrary the sticking agent (R_c) or the mixture of the binding / sticking

agents (R_{cp}) do not modify the aniline interaction (except at the saturated pressure where they favor the hydrophobic behaviour) :one can think, for the R_{cp} fiber, that in the presence of DGEBA moles the cyclisation of the A 1100 moles (Fig. 1) is impeded and consequently a certain amount of hydroxyl sites remain present at the interface.

- Epoxystyrene / glass fibers. Similar to the previous case, one notices the possibility of very strong interactions with the various fibers except with fiber R_p. The retention under high and long vacuum is ∿ 60 % of the weight uptakes. Regarding quantity epoxystyrene does not interact directly with the sticking agent of R_c fibers contrary to the case of carbon ASG fibers.

Wetting studies ; reactives : epoxystyrene, glycerol, ethyleneglycol

The cos θ values obtained with the 3 carbon fibers, when using the wick extracted monofilaments, are indicated on figure 3 (the hatched areas correspond to uncertainty).

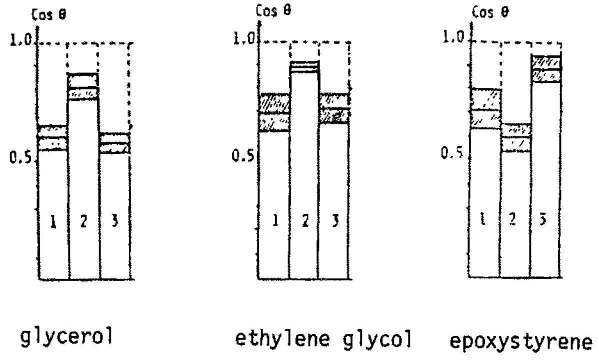

Fig. 3 - Cosine of wetting angle on AU (1), AS (2), ASG (3)

For the glass fibers the measuring has been experimented on monofilaments treated directly by the agents. The similarity of all the results shows that the coating does not take place in these conditions. A new way of measuring is being experimented on wick extracted monofilaments.

The analysis of figure 3 brings the following information :

- Apolar epoxystyrene / carbon fibers : the ASG fiber stands out clearly of the others by a smaller wetting angle.
- Polar alcohols / carbon fibers : for the two alcohols dealt with, it is clear that the wettability of the oxidized AS fiber is strongly improved compared with the two others.

Moreover in taking a polar and an apolar liquid and in applying the OWENS theory one has been able to measure the surface tension of the fibers γ and to calculate the polar component γ_p and the dispersion component γ_d. For AU and ASG the surface tension is near 45 dynes cm^{-1} with a polar component inferior to 10 %. For the AS oxidized fiber, the surface tension is 50 dynes cm^{-1} with a polar component superior to 30 %.

CONCLUSIONS

Concerning the carbon fibers

- On bare fibers, there is an evident relation between the surface oxygen ratio and the possibilities of interactions with the composite matrix functions. More precisely the wetting of the oxidized fiber by polar reactives implies that the oxidation process is a very favourable factor for a good final adherence between carbon fiber and reticulated polyepoxyde matrix rich in hydroxyl functions.
- On DGEBA coated fibers, the interactions and the wetting by an epoxyde reactive are better than on bare fibers implies to say that the impregnation of ASG by the DGEBA - DDM mixture before heating is favoured.

Consequently the ASG fiber unites both the best outlook for impregnation and final adherence. This conclusion has been clearly confirmed by a survey of the mechanical properties of the composites made with these various carbon fibers (ref. 13, 14).

Concerning the glass fibers

The bare fiber completely desorbed is reactive and "hydrophilic", to the functions of the composite matrix. Both sticking and binding agents do not intervene directly in the interactions, a fact which implies that their active sites are concentrated (or bound) onto the glass surface : one can say that coatings should not improve the impregnation of fibers by the DGEBA - DDM components of the matrix. As far as the final adhesion is concerned one can say, for the time being, that the binding agent when alone impedes the surface OH interaction possibilities whereas the sticking agent or the binding / sticking mixture maintains favourable conditions at the interface.

Concerning carbon - glass differences

These differences seem to be essentially linked to the presence of hydroxyls, the action of which is clearly shown on the highly desorbed fibers. No doubt that, in the surrounding environment, the glass behaviour can be quite different because of the action of the pollutants and of the air humidity level. At the beginning of this study, one could have thought that the binding agent could act as a stabiliser and a protector but the efficiency of the A 1100 film, vis a vis humidity in any case, does not seem evident.

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