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Investigation of Surface and Interfacial Properties of Modified Epoxy Films Formed under Different Conditions

Ayzada Magsumova, Liliya Amirova, Makhmoud Ganiev*

Material Science Department, Tupolev Kazan State Technical University, Karl Marx 10, 420111 Kazan, Russia
E-mail: ajzamags@mail.ru

Summary: The surface free energies and their components of the modified amine-cured epoxy polymers were estimated using the geometric mean and acid-base approaches. The surface and interfacial properties of the modified epoxy films depend on the modifying agent percentage and on the conditions of the polymer formation.

Keywords: adhesion; interfaces; modification; resins; surfaces

Introduction

The epoxy resins are widely used as adhesives, surface coatings, polymer composite matrices, and encapsulators of electronic devices. In general the final adhesive properties of composite materials are determined by interfacial interaction on the epoxy/solid interface. Understanding, description and ultimate prediction of such interactions require, among other things, the knowledge of the energetic characteristics of the materials involved.

The analysis of numerous works shows, that experimental and theoretical methods of qualitative and quantitative estimation of the surface and interfacial properties are various enough. In papers[1-3] different semiempirical group contribution methods for an estimation of surface characteristics of epoxy-amine[1,2] and polyimide[3] polymers have been applied. Among the experimental methods inverse gas chromatography[4,5], flow microcalorimetry[6], atomic force microscopy[7,8], ellipsometry[9], NMR[9] and IR-spectroscopy[9,10] may be noted.

Among such variety of methods an indirect estimation of γ_S values, based on measurement of a contact angle of test liquids[11] is most applicable. The technique of a contact angle goniometry is one of the best according to the following reasons: ease of data collection and treatment, and it is an excellent indicator of relative changes occurring on a surface, including the results of modification. One of these methods, a geometric mean method (Fowkes approach) is based on

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the idea of the additive contribution of dispersion ($\gamma_S{}^d$) and polar ($\gamma_S{}^p$) components.[11,12] C.J. van Oss, R.J. Good and M.K. Chaudhury have offered other method to estimate γ_S[13] according to which polar components of a surface energy are brought about by short-range interactions which are donor-acceptor or acid-base by the nature (the vOGC approach or acid-base approach). However some features on interpretation of donor-acceptor components remain debatable.[14]

In order to improve some of important operating properties of epoxy resins (e.g. viscosity, wetting ability, shrinkage) the modifying agents active on the solid surface are added to the oligomer.

The purpose of this work was to study the surface and interfacial properties of oligomer and polymer systems of epoxy resin modified by triglycidyl phosphate.

Experimental Section

Aromatic epoxy oligomer consisting mainly of diglycidyl ether of bisphenol A was chosen as an epoxy compound. Glycidyl esters of phosphorus acids were used for modification of epoxy polymers with the purpose of imparting them some valuable operating properties (high strength and adhesion, low inflammability, adjustable optical properties).[15] In the present study the triglycidyl phosphate (TGP), which is a transparent colorless low viscous liquid was taken as an example from available series of glycidyl esters of phosphorus acids (GEPA). Presence of three epoxy groups in TGP molecule allows it to graft into a polymer network.

We also investigated the surface and interfacial properties of cured modified epoxy polymers. The amine compound, 4,4'-diaminodiphenyl methane, was selected as a hardener. After heating up to 60°C the two-step curing carried out as follows: first stage at 20°C for 6 h and postcuring at 150°C for 1 h. For obtained polymers the surface free energy and its components were estimated using contact angles of test liquids. The surface tension components of the test liquids are listed in table1.

Contact angles were measured using the sessile drop method using the microscope accompanied with eyepiece goniometer, in an atmosphere of saturated vapor of test liquids in the thermostatted chamber at 20°C. The test liquids were chosen according to criteria suggested in the paper.[16] All these liquids are inactive towards the surface of epoxy polymer.

The surface of used metal substrates was cleaned from contaminants using solvents and further staying under vacuum. The oxide films on the metal surface remained undestroyed.

Table 1. Surface tension and its components of test liquids

Test liquids	Surface tension and its components, mJ/m^2							
	According to [11,12]			According to [13]				
	γ	γ^d	γ^p	γ	γ^{LW}	γ^{SR}	γ^+	γ^-
Water	72.2	22.0	50.2	72.8	21.8	51.0	25.5	25.5
Glycerol	64.0	34.0	30.0	64.0	34.0	30.0	3.92	57.4
Formamide	58.3	32.3	26.0	58.0	39.0	19.0	2.28	39.6
Diiodmethane	50.8	48.5	2.3	50.8	50.8	0	0	0
Ethylene glycol	48.3	29.3	19.0	48.0	29.0	19.0	1.92	47.0

Results and Discussion

At the first stage influence of TGP on surface tension γ_{LV} of an epoxy oligomer has been investigated. Surface tension of the modified epoxy oligomers on the low energy surface (polytetrafluoroethylene, PTFE) was determined by the du Nouy's ring method and the sessile drop method. The most frequently used surfactants are known to adsorb on the liquid/vapor interface, thus reducing surface tension up to 1.5 times. It is evident from Figure 1 (rhombus) that used organophosphorus modifying agent does not reduce γ_{LV} magnitude, but even slightly rises it. Hence, triglycidyl phosphate is surface inactive on the liquid/vapor interface.

At the same time, the addition of TGP to the epoxy oligomer led to essential decrease of contact angles on solid surfaces (Figure 1, triangles, squares, circles). The greatest effect of TGP addition is observed at its content up to 10 mass-% that can be explained by adsorption of TGP on the solid substrate. It is well known that the interactions at the interface of solid (S), liquid (L) and vapor (V) may be expressed using Young's equation:

$$\gamma_{SV} = \gamma_{LV}\cdot\cos\theta + \gamma_{SL} \qquad (1)$$

When the same substrate is used (γ_{SV} = const) addition of the modifying agent results in an increase of $\gamma_{LV}\cdot\cos\theta$. Accordingly this lowers the interfacial tension γ_{SL}. Such influence of the modifying agent on the values of γ_{LV} and γ_{SL} gives an evidence of modifying agent (TGP) adsorption on the solid/liquid interface.

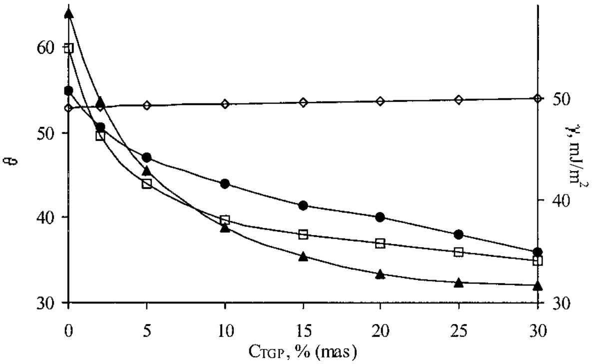


Figure 1. Dependence of contact angle θ on the interface metal/epoxy oligomer and surface tension γ_{SV} of the epoxy oligomer (◊) as a function of TGP concentration; ● = steel (USt 37-2); □ = titanium (TiAl6V4); ▲ = aluminum (AlCuMg2).

According to[11,12] the relationship between components of a surface free energy and equilibrium contact angle for solid and liquid phases is determined by Owens-Wendt equation:

$$(\cos\theta + 1)\,\gamma_L = 2(\gamma_S^d\,\gamma_L^d)^{1/2} + 2(\gamma_S^p\,\gamma_L^p)^{1/2}, \tag{2}$$

where γ_L is the surface tension on the liquid/vapor interface; γ_S^d and γ_L^d are dispersion components of the surface free energy of a solid and liquid; γ_S^p and γ_L^p are the polar components of the surface free energy of a solid and liquid.

The total surface free energy γ_S can be expressed by the sum:

$$\gamma_S = \gamma_S^d + \gamma_S^p \tag{3}$$

The estimation of acid γ_S^+, base γ_S^- and specific, polar or acid-base γ_S^{AB} components of the surface free energy of cured polymers were carried out with the consideration of values of non-polar Lifshitz-van der Waals component γ^{LW} which is practically identical to dispersion component γ^d as is offered in paper.[13] According to this approach the surface energy polar component γ^{SR} is determined by donor-acceptor (acid-base) interaction and can be estimated by the equation

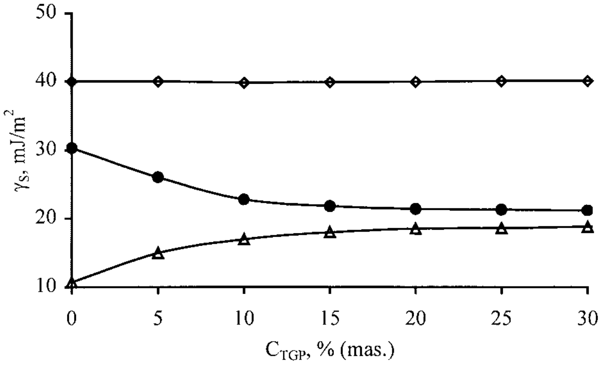
$$\gamma^{AB} = 2\,(\gamma^-\gamma^+)^{S}, \tag{4}$$

where γ^- and γ^+ are donor (base) and acceptor (acid) component of a surface free energy, respectively.

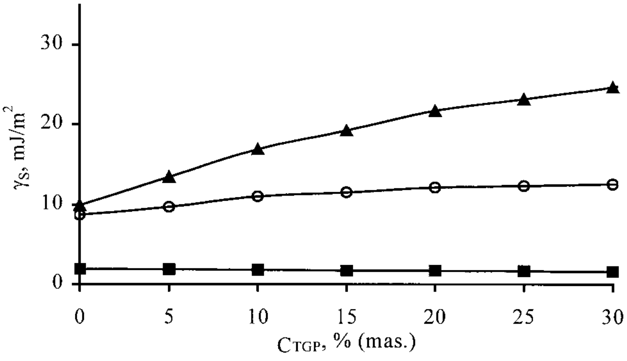
The basic equation connecting acid-base and non-polar interactions with value of a contact angle θ, looks as follows:

$$(\cos\theta + 1)\,\gamma_L = 2\,[(\gamma_S^{LW}\,\gamma_L^{LW})^{1/2} + (\gamma_S^{+}\,\gamma_L^{-})^{1/2} + (\gamma_S^{-}\,\gamma_L^{+})^{1/2}] \qquad (5)$$

In Figure 2(a) (rhombus, circles, triangles) represent the dependence of the surface free energy values of epoxy polymers, formed on the polymer/vapor interface, obtained according to eqs (2) and (3) with the different content of the modifying agent.



a



b

Figure 2. Dependence of a surface energy and its components as a function of TGP contents in amine-cured epoxy polymer: a - ◊ = surface energy, γ_S; ● = dispersion component, γ_S^D; Δ = polar component, γ_S^P; b - ○ = polar (acid-base) component, γ_S^{AB}; ■ = acid component, γ_s^+; ▲ = base component, γ_s^-.

It is seen that γ_S does not practically depend on TGP concentration up to 30 % (mas.). At the same time in the 0-10 % (mas.) range of the modifying agent the considerable reduction of the dispersion component γ_S^d and increase of the polar component γ_S^p are observed.

It is known, that the surface of the amine-cured epoxy polymers is practically monopolar and has basic character.[17,18] According to our data calculated using the vOGC approach (Figure 2b) addition of TGP to epoxy polymer composition does not change the nature of a surface, but strengthens its basicity. The last can be apparently explained by the increase of quantity of oxygen atoms in the base polymer network due to the rise of number of ester bonds and appearance of phosphoryl groups from TGP.

To study the influence of the substrate energetic properties on surface characteristics of the polymers formed on this substrate interface, two solid surfaces were used - polytetrafluoro ethylene (PTFE) and aluminum (AlCuMg2). It is seen from Figure 3 that the surface free energy of polymer formed on the PTFE and aluminum interfaces have different dependence on TGP concentration.

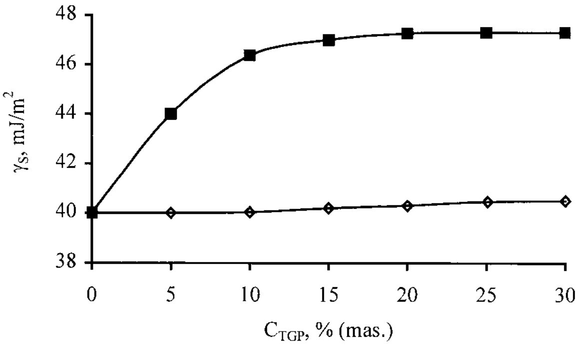


Figure 3. Change of surface energy of the modified epoxy polymer, formed on the PTFE (◊) and aluminum – AlCuMg2 (■) interface as a function of TGP concentration.

When the polymer is formed on the PTFE interface (Figure 3, rhombus), dependence analogous to behavior of polymer on the air interface (Figure 2a, rhombus) is observed. This means that the surface of polymer cured on the PTFE interface as well as on the air interface is formed predominantly by the non-polar groups. Samples formed on the high-energy surface aluminum interface (Figure 3, squares) have higher γ_{SV} values. The Figure 3 shows that addition of the modifying agent up to 10 % (mas.) is already sufficient for formation of polymer with high γ_{SV} value Further, at the greater concentrations of the modifying agent the curve (Figure 3, squares) reveals saturation (plateau).

Thus, the results obtained reveal that increase of the substrate surface energy results in adsorption of triglycidyl phosphate on the solid substrate.

The study of adhesion properties of glues prepared from epoxy oligomer modified by TGP, shows, that addition of the modifying agent up to 10 % (mas.) considerably increases the adhesion strength of bonds (Figure 4). Apparently, it is also related with preferential adsorption of triglycidyl phosphate on a high-energetic solid surface.

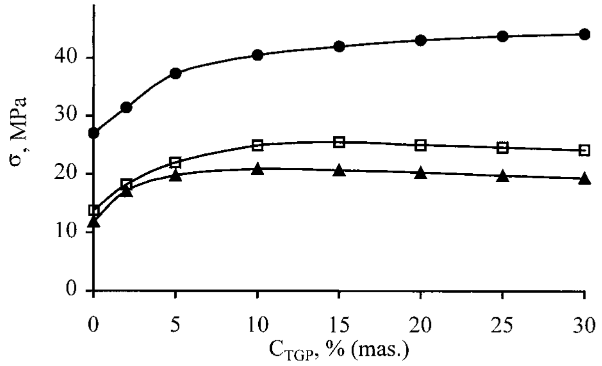


Figure 4. Strength at steady separation σ of the metal/(modified adhesive)/metal adhesion bonds as a function of the TGP content: ● = steel (USt 37-2); □ = titanium (TiAl6V4); ▲ = aluminum (AlCuMg2).

Conclusions

Triglycidyl phosphate shows activity on the high-energy solid/oligomer interface. Such distribution of the modifying agent allows increasing the wetting ability of oligomer to the solid substrate and adhesion of forming polymer to the substrate.

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