

Adhesion of UV-curable resins containing alkoxy silane monomers on glass surfaces

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UV-curable systems containing different alkoxy silane monomers coated on glass surfaces were studied with the aim of deepening the knowledge of the factors influencing the adhesion properties between the two phases. Two monomers containing alkoxy silane groups (methacryloyloxypropyltrimethoxysilane, MEPTS, and 3-(trimethoxysilyl)propanethiol, TSPT) were introduced into a typical epoxy-acrylic resin network by an UV-curing technique and linked to the network through copolymerization (MEPTS) or chain transfer (TSPT) reaction. The formation of adhesion bonds between the polymer network and the glass surface was investigated. Higher adhesion values and faster bonding formation were obtained by using the TSPT monomer. XPS analyses on the polymer films indicated differences in the atomic content on the two sides of the films. The different adhesion results obtained are attributed to the network structures and cross-linking densities.

Key words: polymer glass adhesion; coupling agents; alkoxy silanes; epoxy-acrylic resin; UV curing; XPS analysis

The adhesion between a polymeric matrix and glass surfaces is extremely important in order to achieve high mechanical properties in glass fibre-reinforced polymer composites. It is often the critical point in the use of the composite materials.

Much work has been carried out on the use of alkoxy silane compounds as coupling agents for glass fibre surface treatment to improve the adhesion of the fibres to the polymer matrix^{1,2}.

A previous paper³ has reported an investigation of dual curing systems based on UV curing of acrylic double bonds and alkoxy silane group condensation. By using FTIR analysis both these curing reactions were studied in the bulk.

The work reported here takes into account the interactions of these polymeric films with a glass surface. The presence of alkoxy silane groups in the polymer network allows condensation reactions to be obtained with the silanolic groups present on the glass surface; this can originate the formation of strong adhesion bonds⁴. The formation of this bonding and some factors which influence the adhesion properties between the two phases, have been studied.

Experimental

An epoxy-acrylic resin (BGEDA) containing bis-phenol-A-diglycidyletherdiacrylate and a reactive diluent (tripropylene glycol diacrylate) in 75/25 weight ratio³ was used as a reference resin.

Two alkoxy silane monomers: methacryloyloxypropyltrimethoxysilane (MEPTS), $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3$, and 3-(trimethoxysilyl)propanethiol (TSPT), $\text{HS}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3$ were used.

The monomers were mixed in different amounts with the BGEDA resin; 2,2-dimethoxy-2-phenyl-acetophenone, $\text{C}_6\text{H}_5-\text{CO}-\text{C}(\text{OCH}_3)_2-\text{C}_6\text{H}_5$, was added as a photoinitiator (5 wt%) and dibutyltindiacetate as a condensation catalyst (1 wt%).

The samples for adhesion measurements were obtained by coating a borosilicate glass sheet with the mixture BGEDA + alkoxy silane derivative to obtain a thickness of about 50 μm . The resulting films were irradiated with a 500 W medium pressure mercury lamp at a distance of 200 mm. The UV curing was performed either in air or in a nitrogen atmosphere until the maximum asymptotic value of hardness was

obtained. After the UV irradiation the samples were thermally cured to obtain condensation of the alkoxy silane groups.

The gel content was determined, immediately after UV curing, by measuring the weight loss of the sample after extraction with CHCl_3 for 24 h at room temperature.

The adhesion properties were evaluated by the cross-hatching test (DIN 53151) making the cross-cut incision followed by tape treatment (tape adhesion). Moreover, the pull-off test was performed by measuring the pull-off force with a dynamometer (J. and J. Instrument, TSK), with a crosshead speed of 5 mm min^{-1} : aluminium cylinders (diameter, 20 mm) were used, glued on the coating surface by means of a liquid epoxy-resin (Araldite type) cured with an amine hardener for 24 h at room temperature.

Wetting tension was measured on the films cured in N_2 by using formamide-ethylcellosolve mixtures according to ASTM D2578 procedure.

Humidity resistance tests were performed in a humidity cabinet, $T = 40^\circ\text{C}$, $\text{RH} = 95\%$, with 100 h treatment.

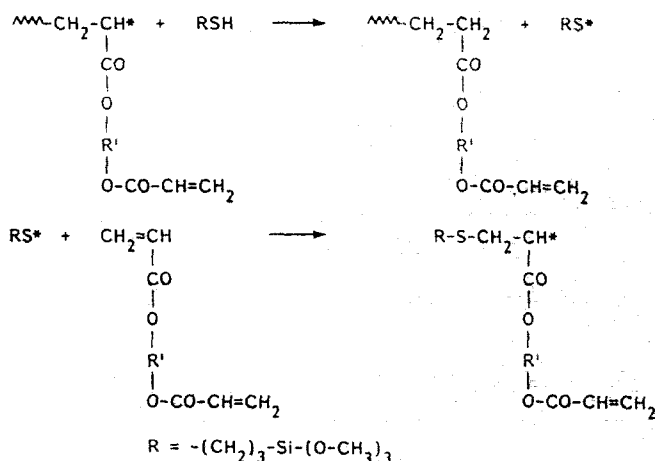
XPS analysis was performed on a Leyboldt Heraeus system connected to a Hewlett-Packard HP 1000 computer system for data collection and handling. Mg K α radiation at 1253.6 eV was used for exciting the specimens.

Results and discussion

Two alkoxy silane monomers (TSPT and MEPTS) were used to introduce alkoxy silane groups in the network formed during the UV curing process. MEPTS gives a simple copolymerization reaction with the acrylic double bond of BGEDA, whereas TSPT was bonded to the network through a chain transfer reaction⁵ according to the mechanism reported in Scheme 1.

Solubility experiments carried out on the samples immediately after UV curing showed that all the alkoxy silane derivatives were linked to the network. In fact, all the samples listed in Table 1 gave a gel content value higher than 97%

The kinetics of the alkoxy silane group condensation



Reaction Scheme 1

in the bulk for the systems containing TSPT or MEPTS have been investigated previously³ by means of FTIR analysis. A higher reaction rate was observed in the system containing TSPT than with the systems containing MEPTS.

The interactions of the two systems with a glass surface were then considered. The presence, in the polymer network, of the alkoxy silane groups could originate condensation reactions with the silanolic groups present at the glass surface giving rise to strong adhesion by chemical bond formation⁴. Therefore, the adhesion properties of the two systems on glass surfaces were measured after thermal treatment so that the condensation reaction had been performed.

Some results of these measurements are reported in Table 1 related to the systems containing the same molar content of TSPT or MEPTS and to the pure BGEDA resin. Some preliminary data has been reported previously³.

It is evident from the data of Table 1 that the adhesion properties of the system containing TSPT are higher with respect to the MEPTS system and pure BGEDA resin.

In Table 2 the results of humidity cabinet tests performed on coatings from pure BGEDA resin and its mixtures with TSPT and MEPTS on glass sheets are reported. It can be seen that there is no influence of

Table 1. Adhesion measurements on glass sheets of BGEDA resin containing methoxy silane additives

Additive*	Curing conditions		Cross-hatching (%)	Tape adhesion (%)	Pull-off test [†] (MPa)
	T(°C)	Time (h)			
TSPT	100	1	100	80	> 5
TSPT	100	2	100	80	> 5
TSPT	25	24	80	0	3.2
TSPT	25	96	90	0	3.4
MEPTS	100	2	100	30	1.8
MEPTS	100	4	100	0	1.2
MEPTS	25	24	40	0	1.5
MEPTS	25	96	50	0	1.8
—‡	100	1	80	0	1.3
—‡	25	24	90	0	1.4

*The concentration of the additive was 6.8 m moles/10 g of BGEDA resin. In all samples 1 wt% of dibutyltin diacetate was added

[†]Mean of three determinations, deviation range $\pm 10\%$

[‡]Pure BGEDA resin

Table 2. Results of humidity resistance tests of coatings from BGEDA resin and its mixtures with TSPT and MEPTS on glass sheets

Type	Additive Concentration (mmol/10g)	Curing conditions		Cross-hatching (%)		Tape adhesion (%)		Pull-off test† (MPa)	
		Time (min)	T (°C)	(a)	(b)	(a)	(b)	(a)	(b)
—	—	60	100	80	40	0	0	1.3	0.8
TSPT	3.3	30	100	100	100	70	40	> 5	> 5
TSPT	6.6	30	100	100	100	80	70	> 5	> 5
MEPTS	6.6	90	100	100	100	30	20	2.0	1.7

(a) before humidity treatment

(b) after humidity treatment

†as in Table 1

Table 3. Quantitative analysis via XPS of UV cured films containing MEPTS or TSPT

Element	Sample with MEPTS				Sample with TSPT			
	'air-side'	'glass-side'	bulk	calc*	'air-side'	'glass-side'	bulk	calc*
O	23.5	22.5	23	24.9	23	22.5	22.5	24.5
C	73.5	76.5	76	74.3	72	74.5	75.5	73.8
Si	3	1	1	0.8	3.5	1.5	1	0.8
S	—	—	—	—	1.5	1.5	1	0.8

*All concentrations in atomic % (average of 2 experiments) calculated on the basis of the composition of the mixture

this treatment on the adhesion properties, particularly for the films containing TSPT. These results indicate that strong, humidity-resistant adhesion bonds are formed mainly in the presence of TSPT.

The different behaviour of the systems containing TSPT and MEPTS could be attributed either to a higher surface concentration of the alkoxy silane groups or to a higher reactivity of the groups present in the system containing TSPT. To clarify these possibilities and to obtain information about the surface composition of the systems containing TSPT or MEPTS, some surface composition measurements (*ie* XPS measurements) were performed on the films containing the two additives. Films having the same molar content of the silane monomers were coated on glass sheets, UV cured under N₂, then detached from the substrates and maintained for 2 h at 100°C.

In Table 3 the results of the XPS analysis performed on both the sides and on the bulk of the films are reported. 'Air-side' refers to the side of the film in contact with air or nitrogen atmosphere; 'glass-side' refers to the side of the film in contact with the glass surface during UV curing.

The data of Table 3 indicate that the composition of the same sides of the films containing MEPTS or TSPT is practically the same. Some interesting features can be noted by considering the composition of the different surfaces of the films:

- on the 'air-side' of both the films there is an increase in the silicon content with respect to the bulk (it is about three times higher than the Si content in the bulk);
- on the 'glass-side' of both films the silicon content is practically the same as the bulk content; and

- the sulphur content on the air-side of the TSPT film is lower than the content of silicon.

The presence of an excess of the silane compound at the air surface is in agreement with the thermodynamic prediction that in a mixture there is a surface excess of the compound which decreases the surface tension of the liquid. On the opposite side, at contact with glass, which is a solid with high surface energy, this effect is not observed because the liquid has the tendency to increase its surface energy in order to decrease the total interfacial energy of the system⁶.

It can be concluded that the UV curing reaction appears to 'freeze' the situation existing in the liquid system when the curing reaction occurs.

In Table 4 some results of the wetting tension measurements performed on films containing different amounts of the two monomers and obtained under different conditions are presented. They are in agreement with the XPS results. It can be observed that:

- on the 'air-side' the wetting tension decreases by increasing the concentration of the alkoxy silane derivative; on the same side, the thermal treatment causes very small change of the wetting tension;
- on the 'glass-side' of the film the wetting tension is slightly higher than on the 'air-side', in agreement with the XPS data; and
- the wetting tension of the samples having the same content of the alkoxy silane derivative is very similar.

Conclusions

The results of the surface analyses performed on the systems containing TSPT or MEPTS show that similar

Table 4. Wetting tension measurements on films from mixtures of BGEDA resin with MEPTS or TSPT

Type	Additive	Curing conditions		Wetting tension (mN/m)	
	Concentration (wt%)	Time (h)	T (°C)	'air-side'	'glass-side'
—	—	—	—	> 58	> 58
MEPTS	2.5	—	—	44	—
MEPTS	2.5	1	100	45	—
MEPTS	2.5	3	100	45	—
MEPTS	10	—	—	43	46
MEPTS	10	1	100	45	46
MEPTS	10	3	100	45	—
MEPTS	20	—	—	39	—
MEPTS	20	1	100	37	—
MEPTS	20	3	100	37	—
TSPTS	10	—	—	39	42
TSPT	10	1	100	41	43
TSPT	10	3	100	41	—

surface concentration of silicon is present in the two systems. Therefore, a higher reactivity of the alkoxy silane groups present in the system containing TSPT with respect to the MEPTS system has to be assumed. This higher reactivity can be attributed to the following two factors: the low cross-linking density of the network; and the different structure of the silane group linked to the network.

The reaction scheme for the insertion of TSPT in the network is reported in the previous paragraph. It is evident that each introduction of the alkoxy silane group in the network causes a chain breaking event, hence a lower cross-linking density is obtained. Moreover, in this system the silanolic unit is always at the end of a chain segment, thus having a higher mobility with respect to the same unit inserted in a polymer chain. Both these considerations can explain the higher reactivity of the system containing TSPT with respect to the system containing MEPTS either in the bulk reactions³ or at the interface with glass surfaces.

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