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PREPRINTS

DUAL CURING SYSTEMS BASED ON UV CURING AND ALKOXY-SILANE GROUPS CONDENSATION.

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INTRODUCTION

The use of dual curing systems was proposed in order to overcome some problems and unsatisfactory properties presented by UV curable coatings, mainly with respect to adhesion and mechanical properties.

In these systems two types of functional groups are present, one sensitive to the radical curing reaction induced by UV radiation (generally acrylic d.b.), the other suitable to react according to a different mechanism which is normally chosen among thermal curing processes at high or room temperature as well in the presence of epoxy or isocyanate groups(1,2).

The use of alkoxy-silane derivatives as coupling agents mainly for glass fibers(3,4) is well known; the condensation reaction between the silanolic groups of the organic network and the ones on the glass surface yields very strong siloxane bonds(5). Moreover the use of these compounds as adhesion promoters for metal substrates was reported in the literature(6). Therefore the study of a dual curing system based on UV curing and alkoxy-silane groups condensation seems to be interesting in order to achieve particular film properties (e.g. adhesion on glass substrates) or to modify the network structure.

EXPERIMENTAL

As a reference resin an epoxy-acrylic resin (BGEDA) was used containing bisphenol-A-diglycidil-ether-diacrylate and a reactive diluent (tri-propilene-glycol-diacrylate) in 75/25 weight ratio (UCB).

Methacryloil-oxypropyl-trimethoxy-silane (MEPTS), mercapto-propyl-trimethoxy-silane (MPTS) were pure grade products (Fluka) used as received. 2,2-Dimethoxy-2-phenyl-acetophenone (DMPA) was used as photoinitiator (Ciba-Geigy) and Sn-dibuthyl-diacetate as a condensation catalyst (Fluka).

The kinetics of the UV curing reaction was measured by means of FTIR analysis (Bruker IFS 45 Instr.) on thin films coated on KBr disks by measuring the decrease of the IR band at 1638 cm^{-1}, due to the acrylic d.b., under UV irradiation(7). On the same samples the methoxy-silane groups disappearance was followed through the IR band at 2841 cm^{-1}, due to the methoxy-silane groups, after thermal treatments.

The samples for adhesion measurements were obtained through a coating of borosilicate glass sheet with the mixture BGEDA/alkoxy-silane derivatives 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 20 cm. The curing was performed either in air or in N_2 atmosphere and after UV irradiation the samples were thermally cured under controlled humidity conditions. The

adhesion properties were evaluated by the cross-hatching test (DIN 53151) or by the pull-off test. The pull-off force was measured with a dinanometer (J. and J. Instr., T5K) by using aluminium cylinders glued on the coating surface by means of Araldite adhesive.

Wetting tension was measured by using formamide/ethyl cellosolve mixtures according ASTM D2578 procedure on the films cured in N_2.

FTIR-ATR measurements were performed on free films prepared by coating the mixture on a glass plate, irradiating under UV lamp, peeling the film from the glass and completing the curing process by irradiation (film thickness:50μm).

RESULTS AND DISCUSSION

The alkoxy-silane monomers (MPTS and MEPTS) used in order to introduce alkoxy-silane groups in the network formed in the UV curing process of BGEDA give rise to different structures.

MEPTS give a simple copolymerization reaction with the acrylic d.b. of BGEDA, whereas MPTS is bonded to the network through a chain-transfer reaction mechanism as previously reported(7).

Solubility experiments carried out on the mixtures of BGEDA containing 10 or 20 % w. of MEPTS or MPTS showed that, after UV curing, all the alkoxy-silane derivative was linked to the network.

The UV curing was performed until the maximum asymptotic value of the conversion of the double bonds was obtained, then the condensation of the methoxy-silane groups in different conditions was determined by FTIR analysis(8).

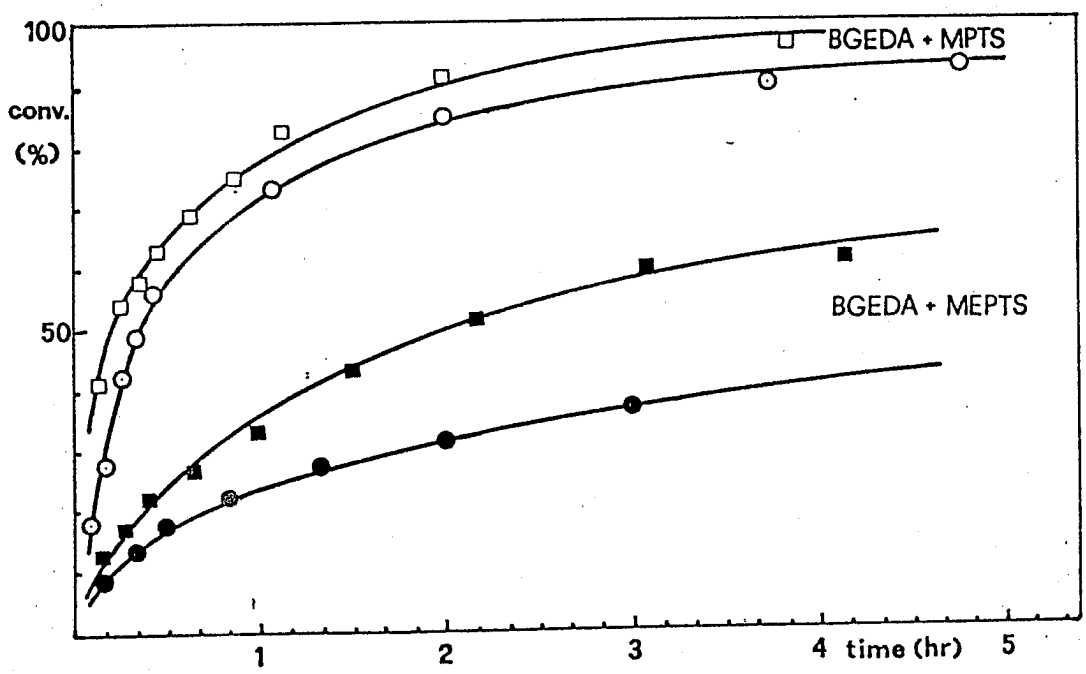


Fig. 1 Methoxy-silane groups conversion vs time at 100 °C
Water pressure (mm Hg): ● ■ 24
○ □ 93

Experimental conditions: 60/40 w. mixture of BGEDA resin and of the alkoxysilane compound; DMPA 5%,Sn-dibuthyl-diacetate 1% with respect to the BGEDA resin. UV irradiation time: 30 sec in air.
Sample with MPTS : 100% d.b. conversion
Sample with MEPTS: 45% d.b. conversion

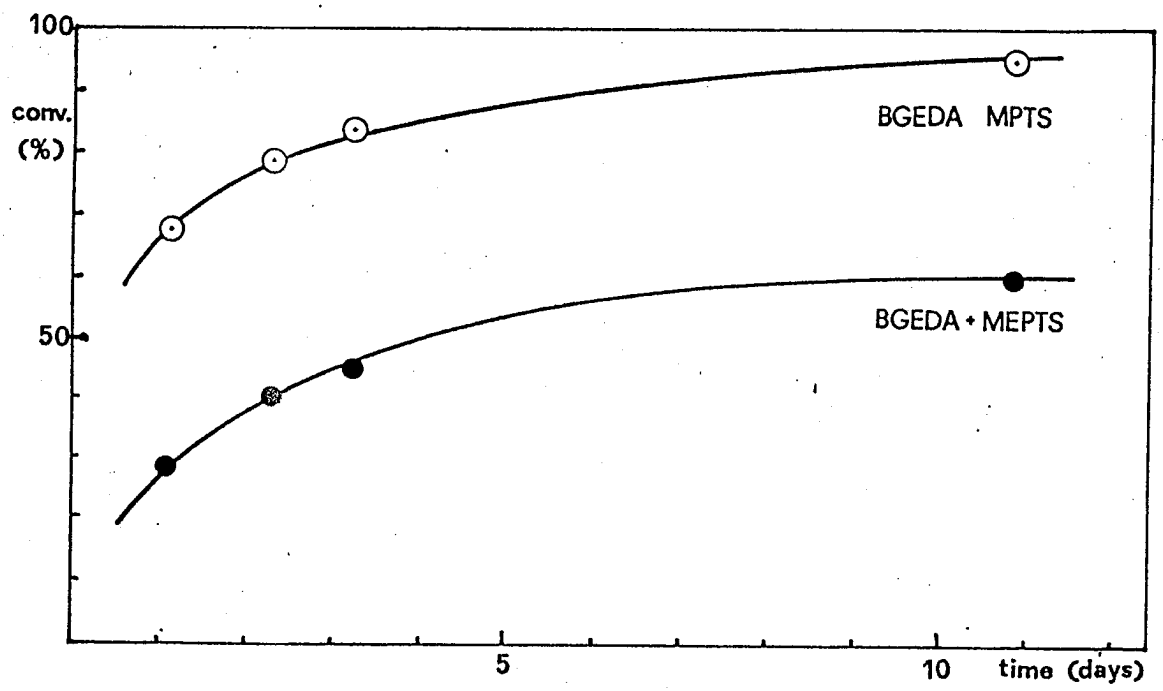


Fig.2 Methoxy-silane groups conversion vs time at 20 °C
Experimental conditions as in Fig.1

Table 1. Adhesion measurements on glass sheets of BGEDA resin with methoxy--silane additives (conc. 20% w.).

Additive	Curing Time	Temp °C	Cross-hatching (%)	Tape adhesion (%)	Pull-off (N/cm^2)(**)
MPTS	30 min	100	100	80	> 500
MPTS	90 min	100	100	40	> 500
MPTS	60 hrs	25	100	40	> 500
MEPTS	30 min	100	100	0	215
MEPTS	90 min	100	100	0	420
MEPTS	60 hrs	25	50	0	170
- (*)	-	-	90	0	140
- (*)	60 min	100	70	0	120

(*) Pure BGEDA resin
(**)Mean of 4 determinations

In Fig. 1 some conversion vs. time curves of the methoxy-silane groups at 100 °C are reported at two different water vapor pressure values. The condensation rate is always higher in the system containing MPTS with respect to the MEPTS system.

In Fig. 2 the same curves obtained at 20 °C are reported which confirm the data of Fig. 1.

Table 1 collects some adhesion measurements data on glass sheets obtained by using mixtures of BGEDA with 20 % w. of MPTS or MEPTS at 100 °C or at room temperature. Some comparative experiments with pure BGEDA resins are also reported. The better adhesion results obtained with the MPTS system with respect to the MEPTS system and the pure BGEDA resin are evident.

The different behaviour of the two methoxy-silane derivatives is particularly interesting. In order to clarify this different behaviour, several surface measurement on the film obtained in the presence of the two derivatives were performed , namely wetting tension measurements and ATR-FTIR analysis.

Table 2 collects the values of the wetting tension measurements performed on films containing different amounts of MPTS and MEPTS and otained in different conditions. It can be observed that:

- the wetting tension decreases by increasing the concentration of the alkoxy derivative;
- after the thermal treatment very small change of the wetting tension is observed;
- the wetting tension of the films having the same MEPTS and MPTS concentration are very similar;
- ATR-FTIR spectra, reported in Fig. 3, show a similar pattern for the films based on the two methoxy-silane derivatives in agreement with the wetting tension measurements.

Table 2. Wetting tension measurements on films from mixtures of BGEDA resin with MEPTS or MPTS additives.

Additive		Curing conditions		Wetting tension
Type	Conc.(w.%)	Time(hrs)	Temp(°C)	(dynes/cm)
-	-	-	-	>58
MEPTS	2.5	-	-	44
MEPTS	2.5	1	100	45
MEPTS	2.5	3	100	45
MEPTS	10	-	-	43
MEPTS	10	1	100	45
MEPTS	10	3	100	45
MEPTS	20	-	-	39
MEPTS	20	1	100	37
MEPTS	20	3	100	37
MPTS	10	-	-	39
MPTS	10	1	100	41
MPTS	10	3	100	41

In conclusion the obtained data do not show any clear difference in the concentration of the alkoxy-silane groups at the surface of the systems containing MPTS or MEPTS and therefore we think that the different adhesion properties of the two systems is due to the different structures of the two silane derivatives when introduced in the network.

Fig. 4 shows a scheme of the structures obtained in the presence of MPTS (structure A) and MEPTS (structure B) on the basis of the different mechanism of polymerization(7). It is evident that in the case of structure A the silanolic unit is always at the end of a chain segment thus having an higher mobility with respect to the same unit inserted in the structure B.

Moreover in the structure A, each introduction of alkoxy-silane group in the network causes a rupture of the polymer chain, hence a lower crosslinking density is obtained.

Both this considerations can explain the higher reactivity of the alkoxy-silane groups in the system containing MPTS with respect to the system containing MEPTS.

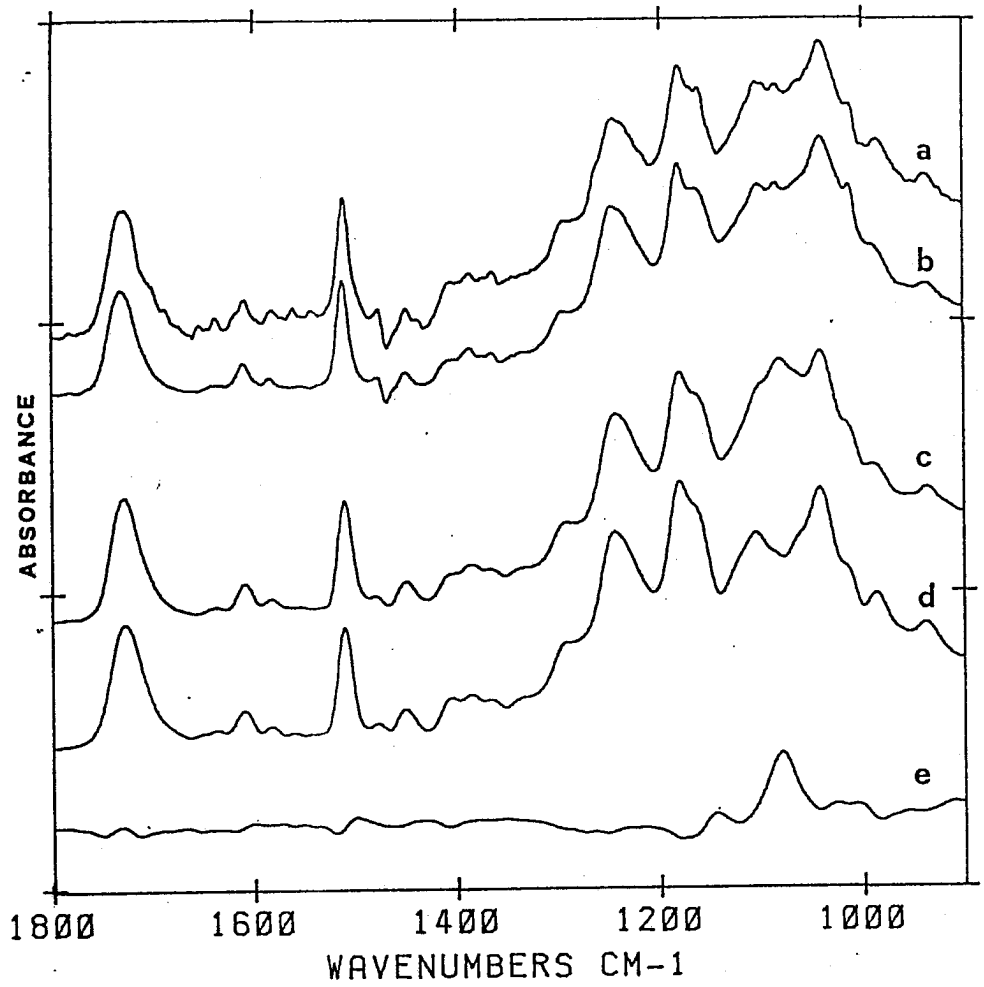
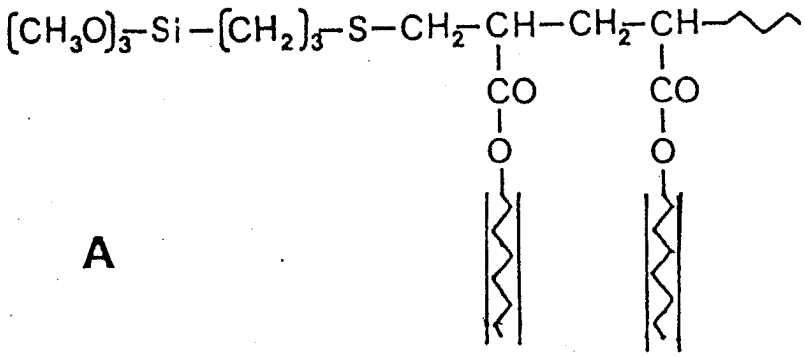


Fig.3 ATR-FTIR spectra of films from mixtures of BGEDA resin with MEPTS or MPTS additives.
(a) BGEDA with MEPTS (10% w.) after UV and thermal curing.
(b) BGEDA with MPTS (10% w.) after UV and thermal curing
(c) BGEDA with MPTS (10% w.) after UV curing
(d) BGEDA resin after UV curing
(e) spectrum resulting from difference (c)-(d)



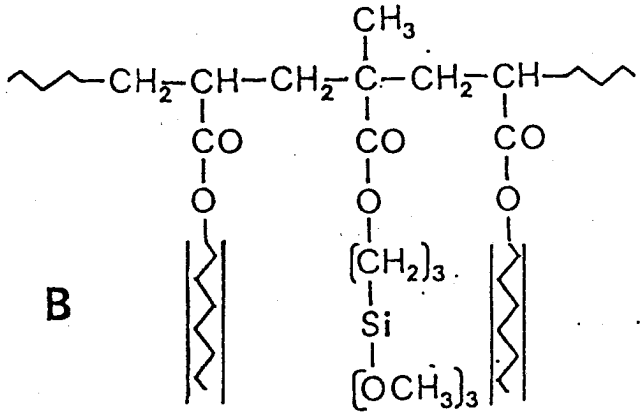


Fig. 4 Scheme of the different structures of the alkoxy silane groups present in the systems containing MPTS (structure A) and MEPTS (structure B)

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