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Ultraviolet curable epoxy acrylic resins – network flexibilization in the presence of reactive diluents

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Different reactive diluents suitable for inducing network flexibilization of a typical ultraviolet curable epoxy resin based on bisphenol-A-diglycidyl-ether-diacrylate (BGEDA) were investigated. Firstly the influence of some monoacrylic reactive diluents, e.g. 2-ethylhexyl-acrylate (EHA) and 4-hydrocybutil-acrylate (HBA) and of a bis-acrylic diluent, polyethylene-glycol-diacrylate (PEGDA) was examined. Subsequently a systematic study was carried out on the properties of coatings resulting from mixtures of BGEDA and a poly(diethylene-glycol-carbonate) diacrylate (PGCDA) as reactive diluent. The main mechanical, dynamic-mechanical and technological properties of both free films and films coated on steel sheets, were evaluated. Interesting network flexibilization properties were observed when PGCDA was used as reactive diluent of BGEDA. The formulations investigated allowed us to obtain a broad range of flexibility for the resulting ultraviolet cured resins and to correlate the coating flexibility with other fundamental properties such as T_g, elastic modulus, abrasion resistance, hardness, adhesion, impact resistance, accelerated ageing and resistance to chemicals.

1. Introduction

Ultraviolet curable resins are receiving increasing interest due to their characteristics of high productivity, low energy consumption and low environmental pollution. Among the different types of ultraviolet curable resins, the epoxy acrylic resins take an important place with interesting possibilities of application in the field of coating of wood, plastics, metals, ink technology and printed circuits. The particular characteristics of this type of resin have been reported in recent reviews [1–3].

On the other hand, there are some problems when these products are used, related to their high viscosity and the low flexibility of the products obtained after ultraviolet curing. The use of particular reactive diluents may contribute to overcome both these problems. Some results on the use of reactive diluents in ultraviolet cured formulations are reported in the literature [1, 4].

Pursuing our previous investigations on structure–property relationships for radiation curable coatings [5], we have considered and compared the influence of different reactive diluents suitable to introduce flexible segments in the network of a typical epoxy acrylic resin. We have studied particularly a poly-diethyleneglycol carbonate diacrylate (PGCDA) with regard to the high flexibility and stability of the carbonate group [5].

Mixtures of the resin with different diluents were cured under constant conditions and the effect of the modification introduced on the

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TABLE I Some properties of the reactive diluents used

Reactive diluent	Unsaturation equivalent	Functionality	η, 25° C (cps)
2-ethyl-hexyl-acrylate, EHA	184	1	~ 10
4-hydroxy-butyl-acrylate, HBA	142	1	10
Poly-diethylene glycol-carbonate-diacrylate, PGCDA	290	2	870
Diethylene-glycol-diacrylate, DEGDA	107	2	13
Polyethylene-glycol(400)-diacrylate, PEGDA	254	2	46
PGCDA–DEGDA (60/40 by wt mixture)	217	2	60

physical and mechanical properties of free films and coatings on different substrates were investigated.

2. Experimental details

2.1. Materials

As starting material a typical epoxy-acrylic resin was used (BGEDA) prepared by acrylation of a commercial sample of bisphenol-A-diglycidyl-ether having an epoxide equivalent of 195, as previously reported [6]. Some reactive diluents (EHA, HBA, DEGDA, PEGDA) were commercial products used as-received. Some of their properties are given in Table I. Poly-diethylene-glycol-carbonate-diacrylate (PGCDA) was prepared as follows. Firstly poly-diethyleneglycol-carbonate bis-hydroxy-ended (PGC) was prepared by making a mixture of diethyleneglycol (5.5 mol) react with diethylcarbonate (3.1 mol) in the presence of C_2H_5ONa (0.5% by weight). The mixture was heated gradually by removing ethanol through a distillation column.

Completion of the reaction was performed under vacuum (10 mm Hg) in order to remove the last quantities of ethanol, diethyl carbonate and diethylene glycol. The reaction product had $\bar{M}_n = 450$ and an –OH content = 7.5%. PGC was acrylated by reaction with acrylic acid in benzene solution in the presence of *p*-toluene-sulphonic acid as catalyst (1%) by using a Markusson head to remove water.

The reaction mixture was treated with K_2CO_3 in order to eliminate the excess acrylic acid, filtered and freed from the solvent by distillation. The final product had $\bar{M}_n = 580$, acid number = 2, $-$OH content $\leqslant$ 0.1%. It was used pure or diluted 60/40 by weight with DEGDA in order to decrease its viscosity.

2.2. Curing

The samples were irradiated in an air atmosphere using a IST-200 Labor Hildebrand Instrument equipped with a $80\,\mathrm{W\,cm^{-1}}$ medium pressure mercury lamp, at a distance of 11 cm. They were passed several times under the lamp with a belt speed of $24\,\mathrm{m\,min^{-1}}$. The irradiation time was about 0.5 sec per pass: after 20 passes the sample hardness reached in any case the maximum asymptotic value.

As photoinitiator, Darocur 1173 (Merck), i.e. 2-hydroxy-2-methyl-q-phenyl-propanone-1, as 5% by weight additive, was used.

Sheets of sanded steel were coated with K. Control Coater to obtain a thickness of about 30 μm and cured by passing under the ultraviolet lamp until the maximum asymptotic value of hardness was reached.

Free films of the samples were prepared by applying the curing mixture on a glass plate, passing it under the ultraviolet lamp, peeling the film from the glass plate and completing the curing process by irradiating both the sides of the film. Film thickness was 0.300 mm for mechanical property measurements, 0.200 mm for dynamic-mechanical measurements.

The kinetics of curing was followed by the measurement on thin films coated on NaCl discs, the decrease of the infrared band at $1633\,\mathrm{cm^{-1}}$ due to the acrylic double bonds present in the mixture. A 500 W medium pressure mercury lamp at a distance of 12 cm was used with exclusion of air and with an experimental device similar to that previously reported [7].

2.3. Testing methods

The mechanical and dynamic-mechanical properties were measured on free films with an Instron Tensile Tester at a $5\,\mathrm{mm\,min^{-1}}$ strain rate and with a Rheovibron Instrument DDV-II at 110 Hz respectively.

The shrinkage occurring during ultraviolet curing was determined by measuring the density of the products after and before curing [5].

TABLE II Properties of free films obtained from pure BGEDA and 20% by weight mixtures with reactive diluents

	Pure BGEDA	BGEDA–PEGDA (80/20)	BGEDA–EHA (80/20)	BGEDA–HBA (80/20)
Gel (%)	96.1	95.9	93.7	95.1
Shrinkage (%)	6.3	6.0	5.1	6.5
Tensile modulus, E (MPA)	2400	1200	800	–
Tensile strength (MPA)	61.0	42.5	37.5	–
Elongation at break (%)	3.4	4.5	5.5	–
T_g (°C)	122	106	100	100

König hardness, adhesion, impact resistance and impact flexibility were evaluated according to FN Unichim 91, DIN 53151, ASTM D 2794 and FTMS 141-6225 standards, respectively.

Weathering measurements were carried out with an Atlas Instrument equipped with a 6000 W Xenon lamp at 63° C and 50% relative humidity.

Chemical resistance was evaluated at room temperature by placing drops of different chemicals on the film, covering them with a watch glass and noting the effect after 24 h. Water absorption was determined by measuring the weight difference after 24 h immersion in distilled H_2O at 25° C.

The abrasion resistance was tested on coatings on polymethyl-methacrylate (PMMA) sheets, cured in air as previously reported, by using a Taber Abrader with CS-10F wheels and a total load of 1 kg. The Δ Haze values were recorded as a function of the number of cycles. The thickness of the sheets was 3 mm and of the coating 30 μm.

3. Results and discussion

3.1. Properties of free films

Firstly the tensile and dynamic-mechanical properties of free films obtained from different mixtures after ultraviolet curing were measured. The presence of different flexibilizing agents determines a modification of the properties of the film which can be summarized as follows:

1. a decrease in the elastic modulus and tensile strength, which are an index of the material cohesion;
2. an increase in the elongation at break which can be related to the flexibility behaviour;
3. a decrease in the glass transition temperature, T_g, of the material.

As reactive diluents more suitable as flexibilizing agents of BGEDA, some monofunctional acrylates (EHA, HBA) or bifunctional acrylates (PEGDA, PGCDA) were taken into account. The last product was obtained by acrylation of poly-diethylene-glycol-carbonate having $\bar{M}_n$ = 450 (see Section 2). The product was used also as a 60/40 by weight mixture with DEGDA in order to obtain a viscosity value similar to PEGDA. In Fig. 1 the influence of the different reactive diluents on the viscosity of mixtures with BGEDA is reported. It can be seen that the effect of decreasing viscosity increases in the order:

$$\text{HEA} > \text{HBA} > \text{PEGDA} \simeq$$

$$\text{PGCDA–DEGDA (60/40)} > \text{PGCDA}.$$

We can divide the reactive diluents into two groups containing the commercial products (HEA, HBA, PEGDA) and the products PGCDA or PGCDA–DEGDA 60/40 respectively. Fig. 2 shows the stress–strain curves for free films obtained from pure BGEDA resin and its mixtures with 20% HEA or PEGDA. The values of the parameters characterizing the mechanical properties of the samples are given in Table II. It can be seen that the modulus and tensile strength decrease in the order BGEDA > PEGDA > EHA, while the elongation follows an opposite trend.

The mechanical behaviour of the samples can be better understood through the dynamic-mechanical analysis results shown in Figs. 3 and 4. The values of storage modulus, E', at low temperature, shows a tendency to coalesce, while at high temperature they depend on the crosslink density of the network [6]. The transition from glass state to rubber state occurs at lower temperatures in the presence of the reactive diluents. From the maximum peak of a plot of tan δ

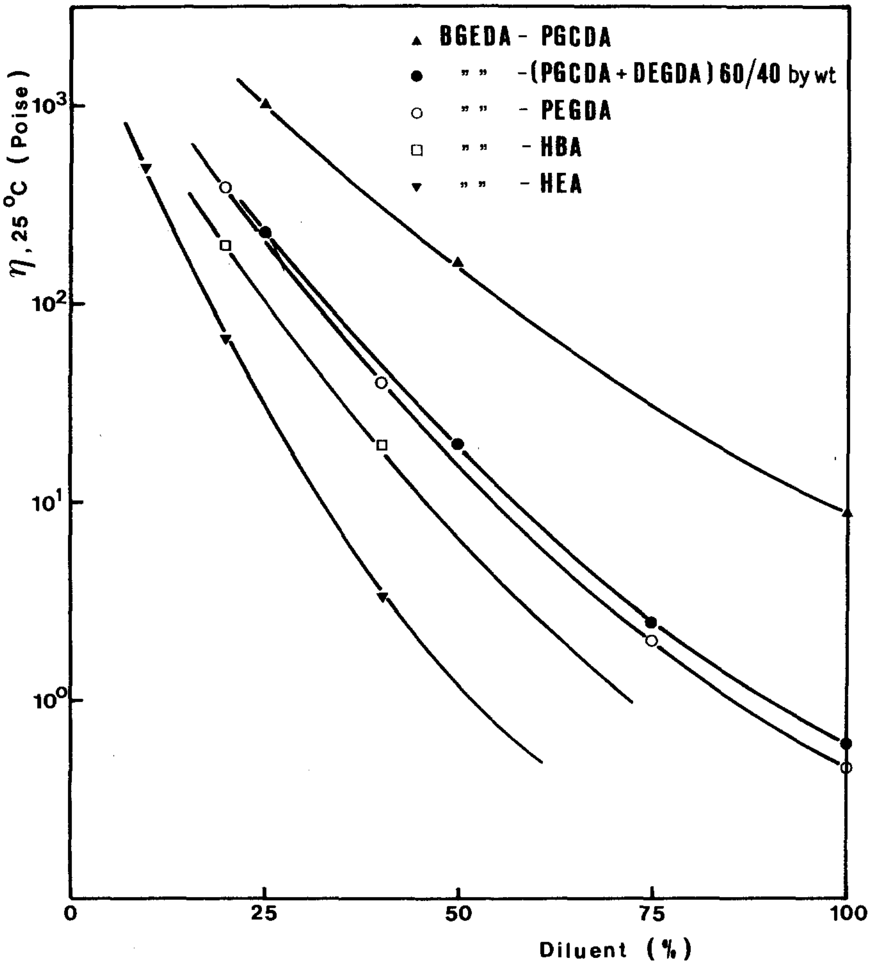

Figure 1 Viscosity as a function of diluent concentration for BGEDA based mixtures.

against T, the value of T_g can be evaluated. The values of T_g are reported in Table II; they show a decrease in the order BGEDA > PEGDA > HBA $\simeq$ EHA. In the same table the shrinkage values during the ultraviolet curing of the different films are reported. These values can be important in determining the adhesion of the coating on metallic substrate as reported previously [1, 4]. The ranking of the data is between 5 and 6.5% and they can only in part be foreseen on the basis of the value of the unsaturation equivalent of the different samples. In fact the disappearance of the unsaturations is probably incomplete and it can reach different levels in the samples examined, as will be discussed subsequently.

All the determinations were repeated on mixtures of BGEDA and PGCDA or the mixture PGCDA–DEGDA (60/40 by weight). The obtained stress–strain curves are given in Figs. 5 and 6. Values of the parameters characterizing the curves are reported in Table III. It can be seen that, at equal concentration of diluent, higher values of modulus and tensile strength and similar elongation values are obtained using PGCDA and PGCDA–DEGDA mixture compared to the other diluents. In the same figures the properties of the films obtained from pure PGCDA and PGCDA–DEGDA mixture are reported. They are rubbery products with low mechanical properties. By plotting the tensile modulus values of the films as a function of the concentration of the reactive diluent (PGCDA–DEGDA 60/40 mixture) a linear relationship is obtained as shown in Fig. 7. The ultimate property values, tensile strength and elongation, of the same products show a rather different behaviour (Fig. 8): low concentration

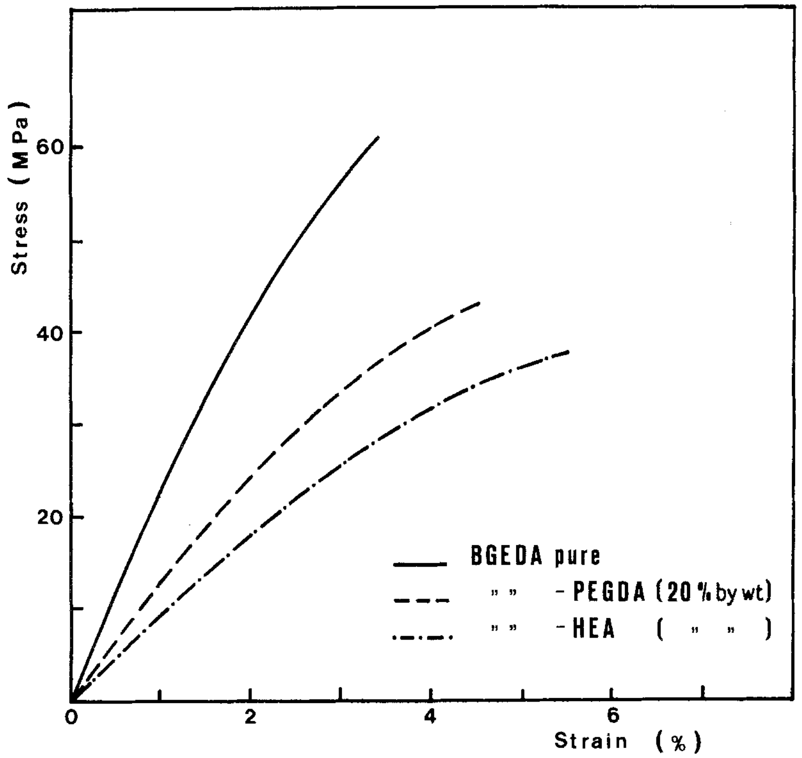

Figure 2 Stress–strain curves for mixtures of BGEDA with different diluents.

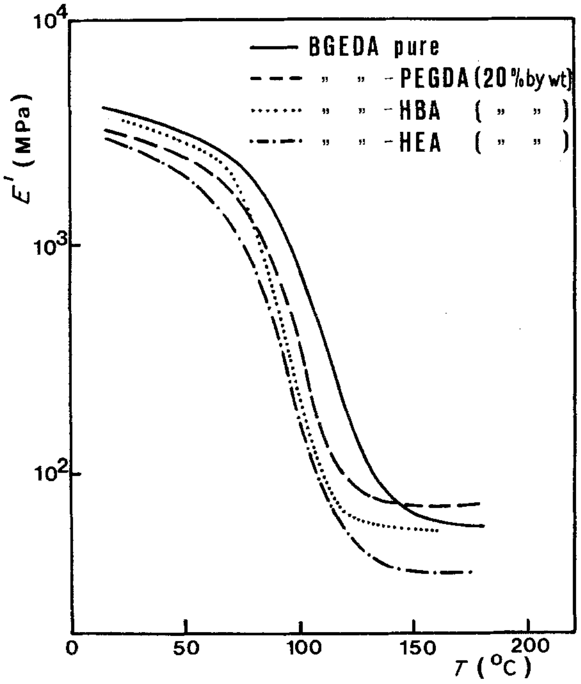

Figure 3 Dynamic moduli plotted against temperature for films from mixtures of BGEDA with different diluents.

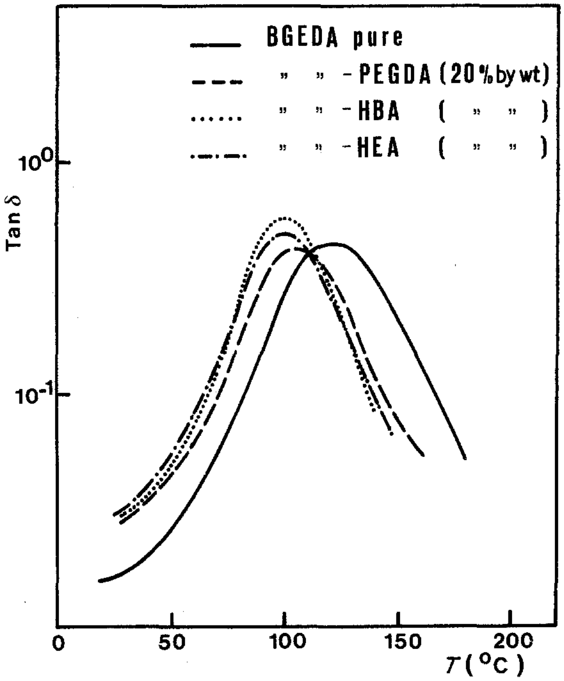

Figure 4 Tan δ as a function of temperature for films from mixtures of BGEDA with different diluents.

of the diluent has little influence on the property, but higher concentrations drastically change the values of these parameters.

Figs. 9 and 10 show the dynamic-mechanical spectra of BGEDA and BGEDA–PGCDA mixtures at 25 and 50% concentrations. T_g values of 97 and 85° C are obtained for the two mixtures, respectively, in agreement with a better flexibilization capacity of this diluent in comparison with the previously reported products. These results are confirmed in Figs. 11 and 12 by using as a diluent of BGEDA a mixture PGCDA–DEGDA (60/40). It can be seen that the viscoelastic region of the material shifts at low temperature values and T_g attains values near room temperature (Table III).

The behaviour of the mixture PGCDA–DEGDA 60/40 by weight is very similar in relation to the pure PGCDA, but the viscosity values are clearly lower.

Fig. 12 also shows the presence in the BGEDA curve at low temperatures of a second tan δ peak due to a secondary transition [6]. The shrinkage during ultraviolet curing of these mixtures (Table III) is very similar to the values obtained with the other diluents.

3.2. Properties of the films coated on different substrates

In this section the properties of the ultraviolet cured films coated on different substrates were examined and compared with the properties of

TABLE III Properties of free films from pure BGEDA and its mixtures with PGCDA

		PGCDA (pure)			PGCDA–DEGDA (40% mixture)			
BGEDA (%)	100	75	50	0	75	50	25	0
Reactive diluent (%)	0	25	50	100	25	50	75	100
Gel	96.1	96.2	97.4	96.8	96.5	96.0	97.0	97.5
Shrinkage (%)	6.3	6.1	–	–	6.9	–	–	–
Tensile modulus, E (MPa)	2400	1600	600	25	1700	1250	300	40
Tensile strength (MPa)	61	46.9	23.9	1.9	56.9	35.8	15.3	6.8
Elongation at break(%)	3.4	5	14	6.7	5.0	8.4	15.2	15.4
T_g (°C)	122	97	85	34	98	84	65	48

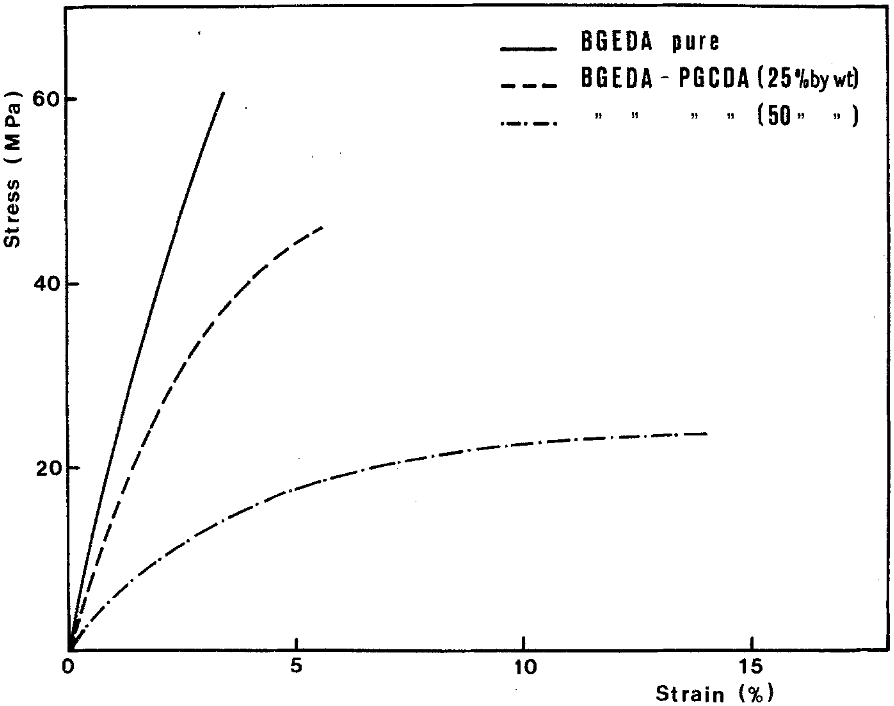

Figure 5 Stress–strain curves for mixtures of BGEDA with PGCDA.

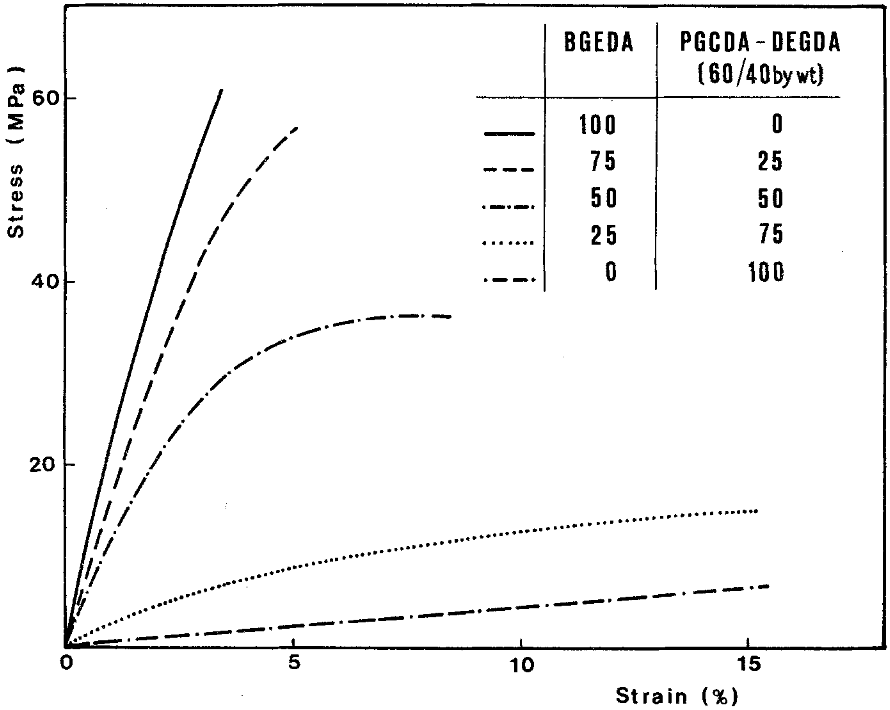

Figure 6 Stress–strain curves for mixtures of BGEDA with PGCDA–DEGDA (60/40).

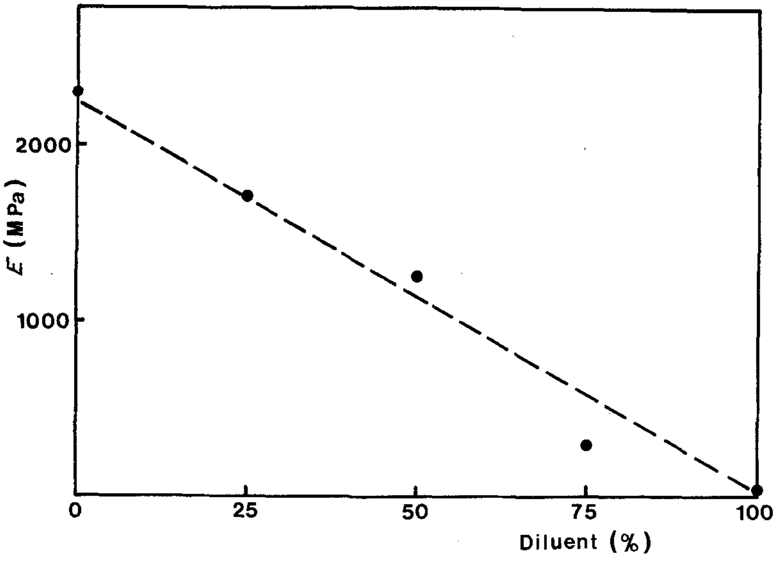

Figure 7 Tensile modulus plotted against diluent concentration for BGEDA–PGCDA mixtures.

the free films. Firstly, the influence of the presence of flexibilizing agents on the kinetics of the unsaturation disappearance was studied, and then the properties of films coated on steel and PMMA sheets were evaluated.

3.2.1. Kinetics of unsaturation disappearance

Fig. 13 shows the kinetics of the unsaturation disappearance under ultraviolet irradiation of films coated on an NaCl disc obtained from pure BGEDA and mixtures with 20% of different reactive diluents. Each reactive diluent increases the rate of the unsaturation disappearance in the following order: HBA > HEA > PEGDA. These results can be interpreted by considering that the reactive diluents flexibilize the polymeric matrix and allow us to obtain a higher mobility of the reactive species. Therefore, a higher rate of conversion of the unsaturated

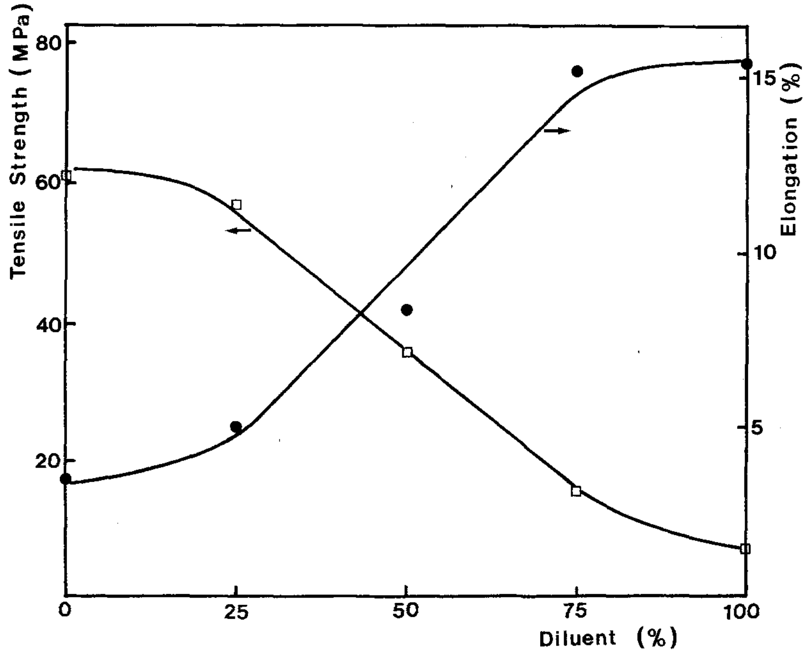

Figure 8 Tensile strength and elongation at break as a function of diluent concentration for BGEDA–PGCDA mixtures.

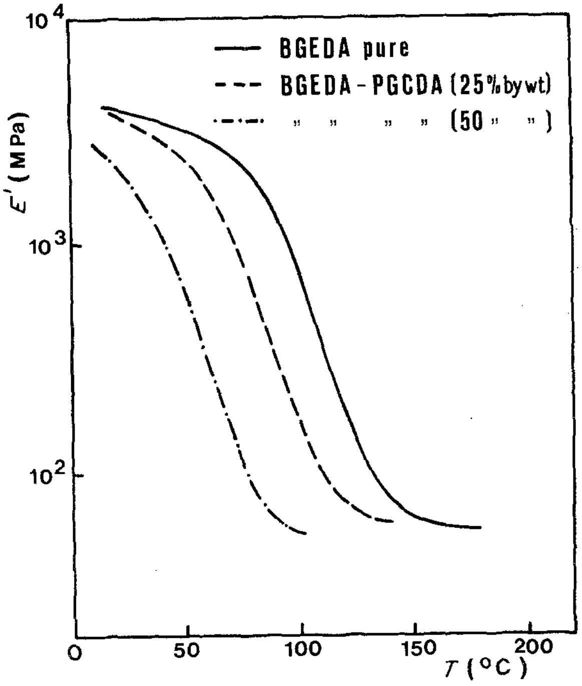

Figure 9 Dynamic moduli plotted against temperature for films from mixtures BGEDA–PGCDA.

portions in the mixture is obtained. The fact that different conversions of the unsaturations are obtained for the different systems cured under the same conditions, makes interpretation of the properties of the films more complex. As a matter of fact, it was impossible to accurately determine the final conversion of the unsaturations and the samples were ultraviolet cured until the maximum asymptotic value of hardness was reached (see Section 2).

In Fig. 14 the kinetic behaviour obtained by using PGCDA as a diluent of BGEDA at two concentration levels is reported. The results obtained confirm the previous observations and different final unsaturation levels are attained.

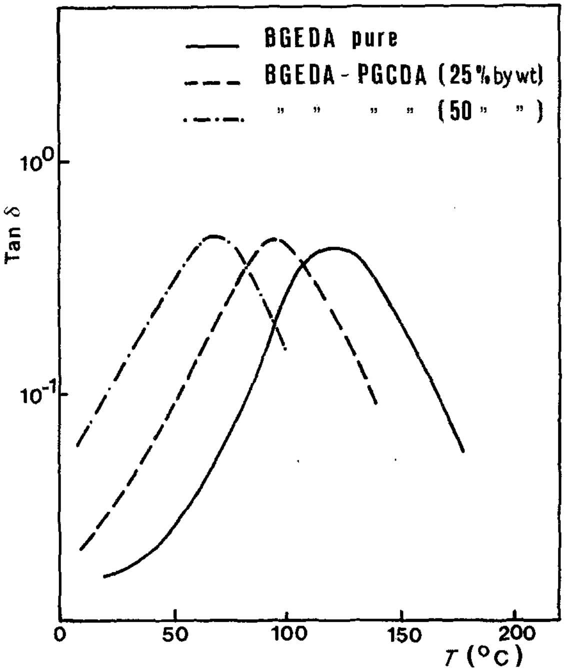

Figure 10 Tan δ plotted against temperature for films from mixtures BGEDA–PGCDA.

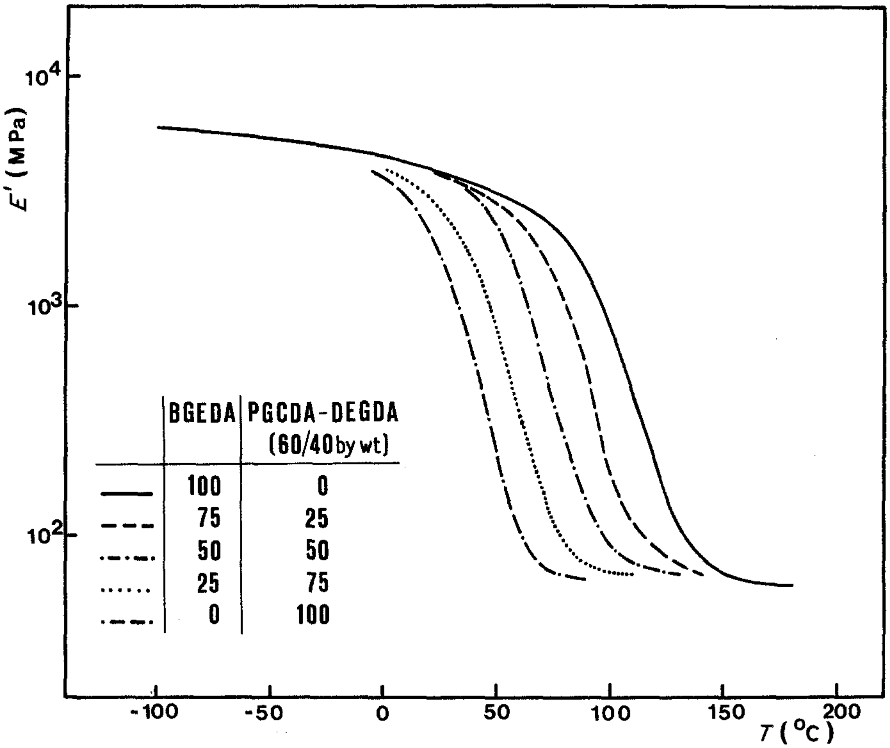

Figure 11 Dynamic moduli plotted against temperature for films from mixtures of BGEDA with PGCDA–DEGDA (60/40).

3.2.2. Properties of the coatings on a steel substrate

Some performance properties of films obtained from BGEDA and its mixtures with different commercial diluents coated onto steel sheets are reported in Table IV. The film hardness decreases by increasing the concentration of the flexibilizing agent. On the other hand, small percentages of diluents can determine a small increase of the hardness of the mixture as shown by the results in Table IV.

The tape adhesion of the BGEDA resin and of different mixtures is always incomplete. These data can be discussed on the basis of different factors which determine the adhesion of coatings onto the substrate [1, 4], i.e. (1) substrate wettability, (2) volume shrinkage during the curing reaction, and (3) flexibility of the film. The last two factors were changed without a clear influence on adhesion. We are now considering the superficial tension of the coatings in an attempt to explain these results.

The impact resistance and impact flexibility of the films increase with increasing concentration of reactive diluent.

Table V collates the properties of the mixtures BGEDA–PGCDA and BGEDA–(PGCDA–DEGDA 60/40 by weight). A similar behaviour

TABLE IV Properties of films from BGEDA and its mixtures with reactive diluents, coated on steel sheets

	PEGDA				EHA			HBA	
BGEDA (%)	100	90	80	60	90	80	60	80	60
Reactive diluent (%)	0	10	20	40	10	20	40	20	40
η, 25° C (Poise)	57000	–	388	25	480	62	3	197	20
Adhesion (cross-hatching) (%)	100	100	100	100	100	100	100	100	100
Tape adhesion (%)	30	0	0	20	0	5	30	0	40
König hardness	139	134	145	73	152	140	75	157	45
Impact resistance (kg cm)	2.5	2.5	2.5	75	2.5	2.5	17.5	2.5	150
Impact flexibility	0.5	0.5	1	40	1	2	2	2	20

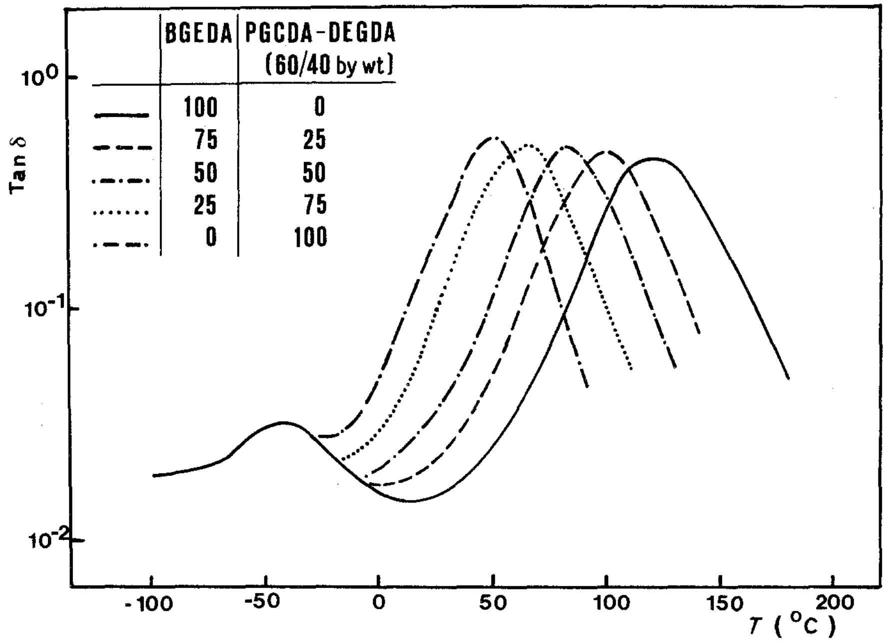

Figure 12 Tan δ plotted against temperature for films from mixtures of BGEDA with PGCDA–DEGDA (60/40).

is observed as in the results of Table IV. Fig. 15 shows the König hardness as a function of irradiation time for pure BGEDA and BGEDA–PGCDA mixture (50% by weight) coated in steel sheets. There is a fast increase in the hardness at the beginning, then an asymptotic value is attained.

3.2.3. Abrasion resistance of the coatings

The abrasion resistance of the coatings obtained by using BGEDA resin and its mixture with PGCDA was tested on PMMA sheets with a Taber Abrader. The results are shown in Fig. 16 in which the behaviour of the uncoated material is also included. A strong increase in the abrasion resistance is observed by using BGEDA–PGCDA mixtures in comparison with pure BGEDA. This effect can be attributed to the network flexibilization induced by the presence of PGCDA in the coating. In fact, pure PGCDA, due to its elasometric character, shows the highest abrasion resistance, but in this case the hardness value is very low. Table VI gives some properties of these systems coated on PMMA sheets.

3.2.4. Chemical resistance and weathering of coatings

Table VII reports some results related to the chemical agent and solvent resistance of coatings obtained from BGEDA and its mixtures

TABLE V Properties of films from BGEDA and its mixtures with reactive diluents, coated on steel sheets

		PGCDA			PGCDA–DEGDA (60/40 by wt)			
BGEDA (%)	100	75	50	0	75	50	25	0
Reactive diluent (%)	0	25	50	100	25	50	75	100
η, 25° C (Poise)	57000	1006	180	8.7	225	19.7	2.5	0.6
Adhesion (cross-hatching) (%)	100	100	100	100	100	100	100	100
Tape adhesion (%)	30	15	20	0	0	10	30	0
König hardness	139	145	83	25	167	104	62	28
Impact resistance (kg cm)	2.5	2.5	30	63	2.5	2.5	75	17.5
Impact flexibility (%)	0.5	2.0	40	20	2.0	2.0	20	10

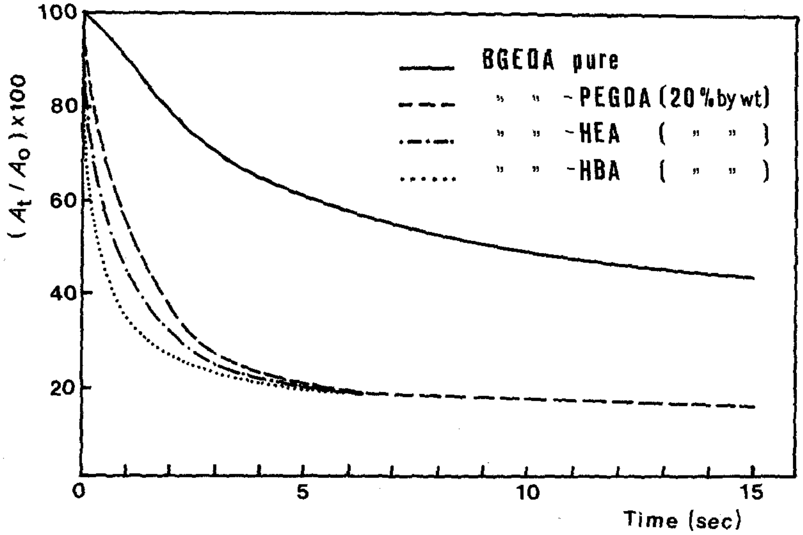

Figure 13 Kinetic curves through infrared analysis for mixtures of BGEDA with different diluents. Decrease in unsaturations as a function of irradiation time.

with different reactive diluents. Good resistance is shown by EHA mixture. PEGDA mixture shows good behaviour except towards H_2O and HNO_3. PGCDA, at a concentration of 25%, shows a good resistance towards all agents except HNO_3.

Table VIII collates the weathering behaviour results of coatings obtained from the different mixtures previously discussed. An interesting behaviour is shown by the mixtures BGEDA–PGCDA. They display the best results after WOM exposure, both from the yellowing and general aspect point of view. These results can be attributed to the high chemical stability and radiation [8, 9] of the cabonate group in these products.

4. Conclusions

The flexibility of a typical epoxy acrylic resin can be increased by using suitable reactive diluents as shown by mechanical and dynamic-mechanical measurements. In addition, some technological properties, weathering and chemical resistance of the coatings can be increased. In this context,

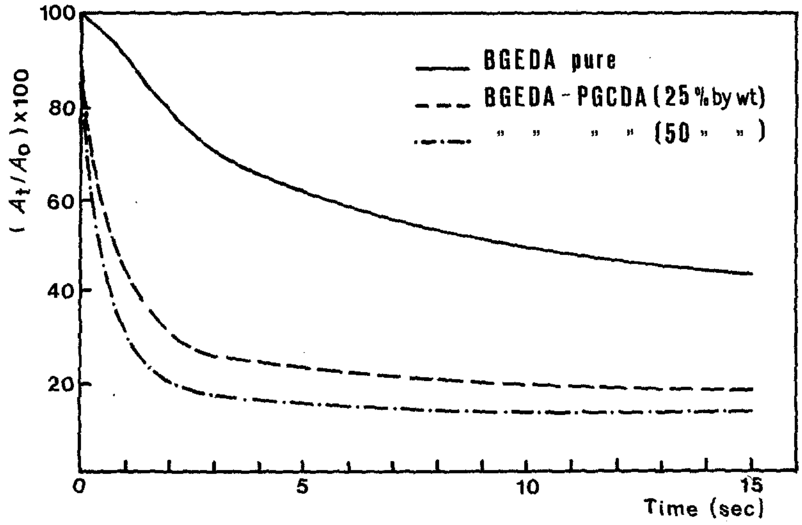

Figure 14 Kinetic curves for BGEDA–PGCDA mixtures.

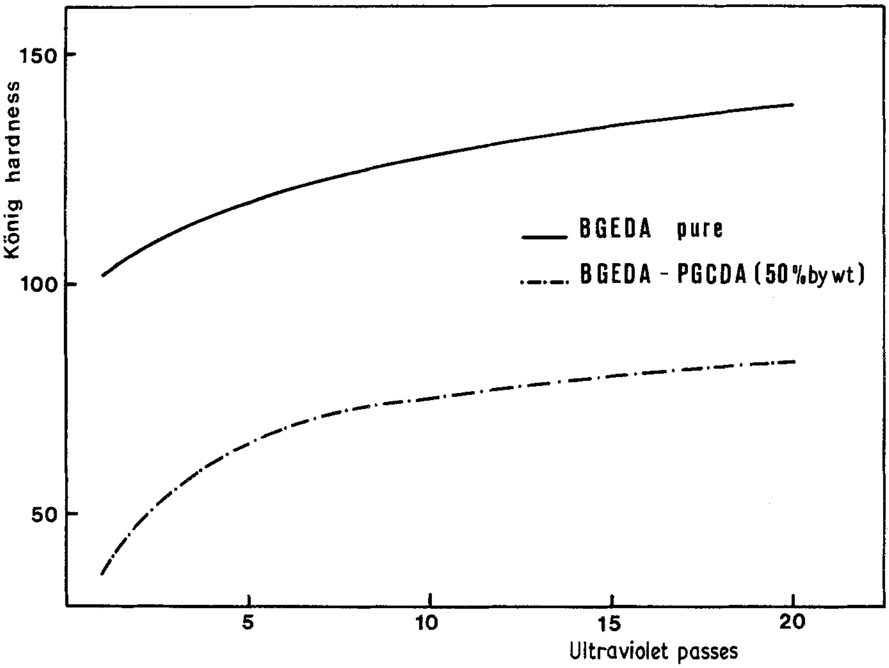

Figure 15 König hardness as a function of irradiation time for pure BGEDA and BGEDA–PGCDA mixture.

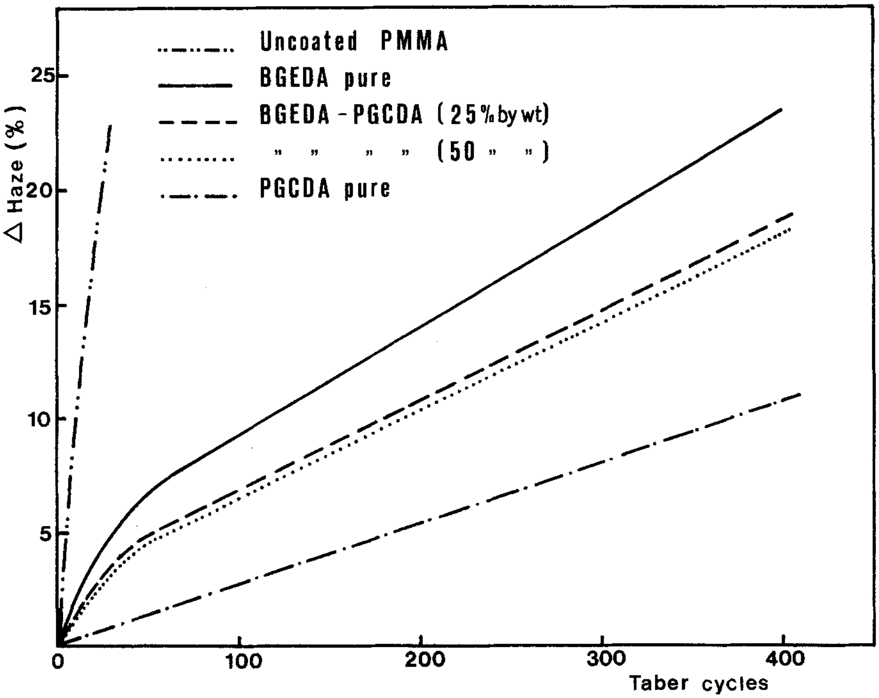

Figure 16 Abrasion resistance on PMMA of coatings from BGEDA–PGCDA mixtures.

TABLE VI Properties of coatings from BGEDA–PGCDA mixtures on PMMA sheets

	BGEDA pure	BGEDA–PGCDA (25% by wt)	BGEDA–PGCDA (50% by wt)	PGCDA pure
Initial haze (%)	0.54	0.67	0.54	0.61
Transmittance (%)	92.2	92.0	92.2	92.6
König hardness	132	135	81	24

TABLE VII Chemical resistance of coatings from ultraviolet cured mixtures of BGEDA and reactive diluents

		EHA	PEGDA	PGCDA	
BGEDA (%)	100	80	80	75	50
Reactive diluent or LT (%)	0	20	20	25	50
NaOH (10%)	A B	A B	A B	A B	A B
	G G	G G	G G	G G	S S
HCl (25%)	S S	G G	G G	G G	S S
HNO_3 25%	G G	G G	Is Is	S S	Is Is
1-Butanol	G G	G G	G G	G G	G G
Methyl-isobutyl-ketone	G G	G G	G G	G G	G G
Water absorption (%)	1.2	1.2	2.7	1.8	2.4

A = general aspect, B = blistering, G = good, S = sufficient, Is = insufficient.

an interesting behaviour is shown by using PGCDA diluent caused by the flexibility and stability of the carbonate group, confirming our previously obtained results [5].

The adhesion of the coatings on steel sheets was in all cases incomplete. Different factors may determine this behaviour as previously discussed [1, 4]. The abrasion resistance of the coatings on PMMA sheets increases sharply in the presence of PGCDA reactive diluent.

TABLE VIII Weathering behaviour of coatings obtained from different formulations (after 1000 h exposure)

	Yellowing	General aspect*
Pure BGEDA	Is	S
BGEDA–EHA (80/20)	Is	G
BGEDA–PEGDA (80/20)	S	G
BGEDA–PGCDA (75/25)	S	G
BGEDA–PGCDA (50/50)	G	G

*Based on loss of gloss, crazing and blistering.

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