Properties of polymeric films obtained from u.v. cured poly(ethylene glycol) diacrylates

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The properties of u.v. cured poly(ethylene glycol) diacrylates (PEGDA) having MWs in the range 200–2000 and acrylic functionality near to two were evaluated. First, the properties of pure PEGDA oligomers, subjected to u.v. curing, were considered. Then, mixtures of different PEGDA oligomers with a typical epoxy acrylate resin were prepared and investigated. The double-bond conversion during the curing process was determined by *FT*i.r. analysis. D.s.c., t.m.a. and d.m.t.a. were used to evaluate the thermal and dynamic-mechanical behaviour of the networks obtained. As far as the pure PEGDA oligomers are concerned, the final double-bond conversion was always found to be complete, with the exception of the lowest MW oligomers. By using oligomers having MWs up to 1000, after the u.v. curing process, films having a completely amorphous structure were obtained. Oligomers having MWs higher than 1000 show, after curing, a partial PEG crystallinity. The T_g values of amorphous films were found to decrease by increasing the MW of the oligomer, i.e. by decreasing the crosslinking density of the network. Good agreement with the Nielsen equation was observed. The equilibrium swelling values in water were found to increase by increasing the oligomer MW. The investigation of mixtures of PEGDA oligomers with a typical epoxy acrylate resin confirms the above reported results as far as the double-bond conversion, the thermal and the dynamic-mechanical behaviour are concerned. By changing the oligomer MW it is possible to change the properties of the u.v. cured films over a broad range.

(Keywords: u.v. curable coatings; reactive diluents; poly(ethylene glycol) diacrylate; epoxy acrylate resin; structure–property relationships)

INTRODUCTION

Because of the favourable energetic and environmental aspects, radiation curable systems have become of increasing importance in the field of coating of wood, paper and plastics and in the field of inks, adhesives, lithography and printed circuits.

Several reviews[1,2] have discussed the principles of radiation curing and the main applications. Some problems concerning the mechanical properties of these coatings, their flexibility and adhesion are still present; they require further investigation of the structure–property correlations for these systems.

In this context we have undertaken a study of the properties of reactive diluents used in these systems.

Different types of reactive diluents are used at present[1,2]. They include monomers having one, two or three acrylic functionalities per molecule. The monofunctional monomers (2-ethylhexyl acrylate, *N*-vinylpyrrolidone) generally increase the flexibility of the network and the total double-bond (d.b.) conversion, but decrease the curing rate. Moreover, the obtained films often show low surface properties, low hardness and scratch resistance.

In general, the monomers having two acrylic functionalities show better properties and are widely used. However, on using these products, and especially the products having higher functionality, there is often formation of a very dense network in which the mobility of the reactive species is very low and polymerization may be stopped before there is complete conversion of the acrylic d.b. Under these conditions very rigid materials are obtained, but they are also often brittle with low flexibility. Low weathering properties, due to the presence of residual unsaturations, must also be considered[3–5].

Thus, it is important to investigate the type of reactive diluent and to choose its structure and functionality to have the best properties of the resulting cured films.

Therefore, we have considered the use, as reactive diluents, of oligomers having flexible chains whose length can be changed and which can be acrylated at both the ends of the chain. Examples of these oligomers are polyether α–Ω diacrylates and, in particular, poly(ethylene glycol) diacrylates (PEGDA).

By increasing the MW of the oligomers, the crosslinking density of the network decreases and thus the properties of the films can be changed gradually. The characteristics of poly(ethylene glycol) chains are reported in the literature[1,6]. They include high flexibility, high reactivity, good polarity and compatibility with different acrylic resins.

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Some of the PEGDA products are well known and are currently used as reactive diluents in commercial u.v. curable formulations, but a systematic study of their properties as a function of their MW has not been reported.

In this work we have considered PEGDA oligomers having MWs in the range 200–2000. They were cured as pure products and the properties of the obtained networks were evaluated.

Moreover, we examined mixtures of these different oligomers with a typical commercial epoxy acrylic resin to evaluate the modification of the properties of the resin in the presence of different reactive diluents. A preliminary account of systems containing PEGDA or poly(propylene glycol) diacrylate oligomers has been reported by us[7]. In the literature, only a few studies of the curing reaction of single poly(ethylene glycol) diacrylate[8] or dimethacrylate derivates[9] have been reported so far.

EXPERIMENTAL

Materials

TEGDA and PEGDA 600 were commercial products supplied by U.C.B. (Belgium) and PEGDA 400 was a Polyscience product; they were used as received. The other PEGDA oligomers were prepared by acrylation of the corresponding dihydroxy-PEG oligomers (Fluka) (see below).

As a typical epoxy acrylate resin, a product obtained by acrylation of a commercial sample of bisphenol-A-diglycidyl ether having an epoxy equivalent of 195, according to the conditions reported elsewhere[10], was used. Benzyl dimethyl ketal (Ciba–Geigy) was employed as a photoinitiator at 4 wt% concentration.

PEGDA synthesis

PEGDA 1000, 1500 and 2000 were prepared by the same procedure. In the case of PEGDA 1000, 10.0 g of PEO 1000 (Fluka) were dissolved in benzene (80 cm^3), 50 mg of hydroquinone and 1.60 cm^3 of acrylic acid (10% stoichiometric excess) were added and the mixture was refluxed for 2 h in a glass flask equipped with a reflux column. Subsequently, 0.5 cm^3 methanesulfonic acid was added and the system was refluxed for 9 h with azeotropic distillation of water. The reaction mixture was treated with K_2CO_3 to eliminate the catalyst and free acrylic acid, stirred for 2 h and filtered. The solvent was evaporated in a vacuum evaporator at 0.2 mmHg. A final yield of 10.5 g was obtained; $T_f = 36.0°C$; acrylic functionality = 1.71; acid number = 7.2.

Curing procedure

The mixtures were coated onto glass plates with a calibrated wire-wound applicator to obtain a thickness of about 100 μm. Coated sheets were then irradiated with a medium-pressure mercury lamp with a light intensity at the film of about 3 mW cm^{-2} working in a small box equipped with a quartz window under pure N_2 atmosphere (O_2 content < 20 ppm). Free films were obtained by peeling them from the glass plate and completing the curing process by irradiating the other side of the film. The irradiation was continued until a constant d.b. conversion was reached.

Analyses and film characterization

*FT*i.r. analysis was performed on the product before and after u.v. curing, using a Bruker IFS 45 spectrometer and coating the film on a KBr disk.

Acrylic functionality was determined by the saponification method using an alcoholic 0.5 N KOH solution according to the reported procedure[11].

Viscosity measurements were performed with a Contraves Rheomat 15 viscometer at 25°C.

M_n determinations were carried out with a Gonotec Osmomat 070 in $CHCl_3$ solution at 37°C.

G.p.c. analyses were performed on a Varian 5020 instrument, using THF solutions at 25°C, two Styragel columns (Polymer Laboratories) having 50 and 100 Å porosity, and a u.v. detector.

Film thickness was measured with a Minitest 3000 instrument (Elektrophysik Köln, Germany).

D.s.c. measurements were performed with a Mettler DSC-3000 instrument, equipped with a low-temperature probe.

Dynamic mechanical analyses (d.m.a.) were performed with a Polymer Laboratories instrument at a frequency of 5 Hz in the tensile configuration. E_1 and $\tan\delta$ were measured as a function of temperature. The size of the specimen strips was about 20 × 40 × 0.1 mm.

Swelling in water was performed on sheets by measuring the area increase after 16 h water treatment. Gel content was determined by measuring the weight decrease after 16 h treatment with $CHCl_3$.

RESULTS AND DISCUSSION

Properties of pure PEGDA oligomers

The PEGDA oligomers used can be represented by the structure:

$$CH_2{=}CH{-}COO{-}(CH_2{-}CH_2{-}O)_n{-}CO{-}CH{=}CH_2$$

in which the number of structural units, *n*, was changed from 3 to about 45.

In *Table 1* some characteristics of the different PEGDA oligomers used are reported. The first oligomers are liquid at room temperature with low viscosity values. By increasing the MW, they crystallize; the melting point increases with an increase in the MW to the asymptotic value of the PEG T_f[6]. The $\bar{M}_n$ values obtained by vapour pressure osmometry together with the values of acrylic functionality obtained by the saponification method with alcoholic KOH are also reported.

The synthesis of bifunctional oligomers becomes more difficult by increasing the MW; in general, a decrease in the acrylic functionality was observed.

Table 1 Properties of PEGDA oligomers

Oligomer	Viscosity[a] (cP)	$\bar{M}_n$	Acrylic groups (mol^{-1})	Acid number[b]	T_f[c] (°C)
TEGDA	18	252	2.04	1.6	–
PEGDA 400	46	514	2.06	1.5	−8.7
PEGDA 600	66	733	1.80	9.8	+19.2
PEGDA 1000	–	821	1.71	7.2	+36.0
PEGDA 1500	–	1579	1.83	16.2	+43.3
PEGDA 2000	–	2017	1.14	24.5	+47.6

[a] At 25°C

[b] KOH (in mg) to neutralize 1 g sample

[c] By d.s.c.

In *Figure 1* the MW distribution of the oligomers as evaluated by g.p.c. is reported; a calibration curve with standard monodisperse PS samples was used. The chromatograms indicate a narrow MW dispersion with small amounts of oligomers having lower or higher MW.

In *Table 2* some properties of the pure u.v. cured PEGDA oligomers are reported. The results of *Table 2* show a complete d.b. conversion for all the monomers with the exception of TEGDA, which revealed a small amount of residual unsaturation. Evidently in this case the high d.b. conversion causes a high crosslinked network with low mobility of the chain. Therefore, the curing reaction stops before all the double bonds are consumed[12].

In *Figure 2* the *FT*i.r. spectra of a PEGDA 400 film before and after the irradiation process are reported. The complete disappearance of the main double-bond signals at 1635, 1620, 1408 and 811 cm^{-1} is evident. In the case of TEGDA film, a small amount of residual unsaturation after u.v. treatment was evident.

In *Table 2* the results of d.s.c. and t.m.a. studies of the u.v. cured films are also reported. Oligomers having MWs lower than 1000 give completely amorphous products with low T_g values which decrease by increasing the oligomer MW. In the case of TEGDA, the T_g region was not evident from d.s.c. measurements.

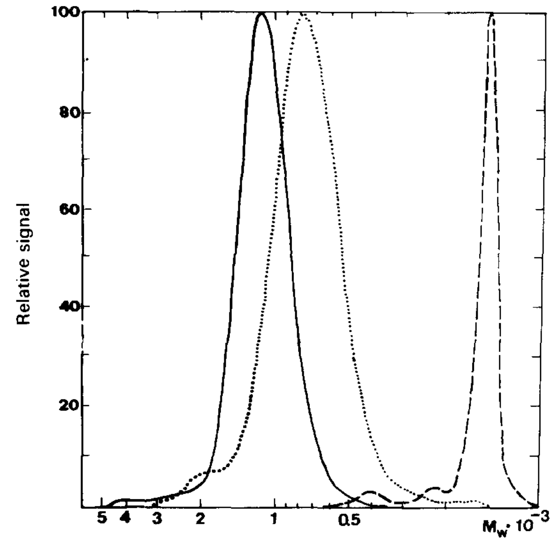

Figure 1 G.p.c. chromatograms of PEGDA oligomers: ——, PEGDA 1000; ···, PEGDA 600; – – –, TEGDA

Table 2 Properties of u.v. cured PEGDA oligomers

Oligomer	T_g^a (°C)	T_g^b (°C)	T_f^a (°C)	Gel content^c (%)	Swelling^d
TEGDA^e	^{f}	+19.6	^{g}	99.1	16.4
PEGDA 400^h	−29.8	−32.4	^{g}	98.2	34.1
PEGDA 600^h	−55.3	−47.5	^{g}	98.1	40.2
PEGDA 1000^h	−57.8	−51.8	^{g}	95.3	82.0
PEGDA 1500^h	−48.4	−39.5	+18.1	92.2	–
PEGDA 2000^h	−47.1	−45.2	+28.4	89.1	–

[a] By d.s.c.
[b] By t.m.a.
[c] Determined by $CHCl_3$ treatment
[d] At 25°C
[e] D.b. conversion = 94%
[f] The glass transition is not evident
[g] Crystalline phase is not evident
[h] Complete d.b. conversion

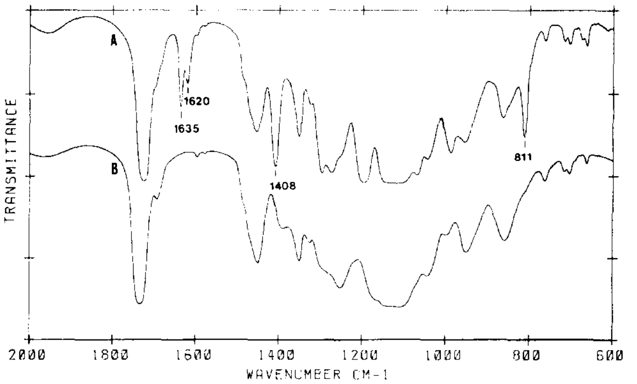

Figure 2 *FT*i.r. spectra of a PEGDA 400 film before (curve A) and after (curve B) u.v. irradiation

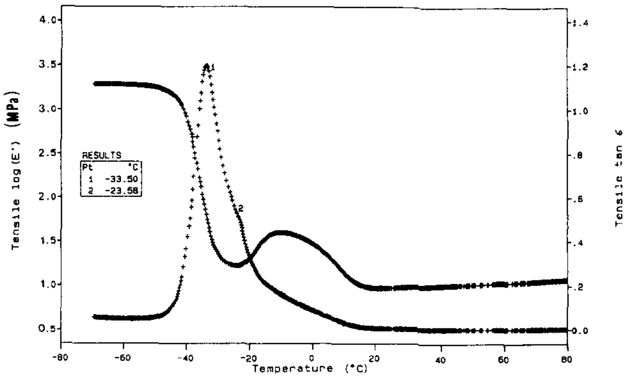

Figure 3 D.m.t.a. spectrum of a u.v. cured PEGDA 1000 film (thickness about 100 μm)

Oligomers having MWs higher than 1000 gave films with a partial crystallinity peak together with the glass transition region. The observed melting points were lower than those of the starting PEGDA oligomers. Similar results were obtained recently in a study on copolymers based on poly(ethylene glycol) monomethacrylate macromonomers having different MWs[13].

Dynamic mechanical thermal analysis (d.m.t.a.) was found to be a very sensitive technique for the network structure investigation. The use of this technique in characterizing the viscoelastic properties of polymeric films has received increasing attention[2,4,12]. In the d.m.t.a. spectrum of the TEGDA cured film, tan δ reaches its maximum value at 76°C which can be considered as the T_g of the material. For the same temperature interval the storage modulus, E_1, shows a sharp decrease confirming the occurrence of the glass transition.

In *Figure 3* a d.m.t.a. spectrum related to a u.v. cured PEGDA 1000 film is reported: a T_g at about −33°C is evident. Moreover, the spectrum exhibits peculiar behaviour at about −20°C, which could be attributed to a crystallization effect which increases the E_1 value. In fact these spectra were performed at a very low heating rate (2°C min^{-1}) and under a small tensile stress which could promote crystallization.

Considering the T_g values obtained by means of d.s.c., t.m.a. and d.m.t.a. (*Table 2*), it can be seen that d.s.c. and t.m.a. values are very close together whereas d.m.t.a. values are higher. This difference can be attributed to a frequency effect as reported in the literature[14,17].

It is well known that the T_g value increases by increasing the network crosslinking density. Relationships were proposed for this dependence by Nielsen and Di Benedetto[14]. Assuming that the mobility of the system is scarcely changed by introducing the acrylic double bond, we can attribute the T_g variation essentially to the length of the polyether chain between two acrylic double bonds.

Plotting the T_g values obtained by t.m.a. as a function of the reciprocal value of the chain length, M_c, a linear plot according to Nielsen's equation was obtained (*Figure 4*). The intercept T_g value at zero crosslinking density is about −66°C, in agreement with the T_g value of PEG reported in the literature[6].

We can conclude that a good correlation of the network properties as a function of crosslinking density for u.v. cured PEGDA oligomers is evident.

In *Table 2* the gel content values are reported together with the data relating to the equilibrium swelling of the cured films in water at 25°C. These values clearly increase on increasing the MW of the oligomers, in agreement with Flory's theory which relates swelling ratios to the network crosslinking density[16].

Properties of (epoxy acrylate resin)–PEGDA mixtures

With the aim of evaluating the possibility of modifying the properties of a typical acrylate resin in the presence of the oligomers, mixtures containing an epoxy acrylate resin (bisphenol-A-diglycidyl-ether-diacrylate) and PEGDA oligomers, at constant concentration (60/40 wt%), were prepared and subjected to the u.v. curing process.

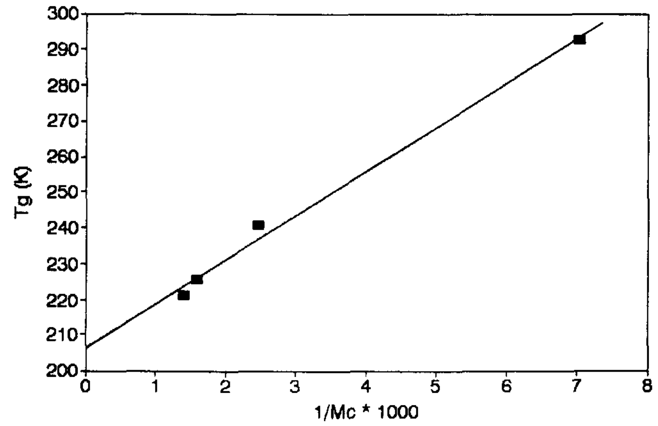

Figure 4 T_g *versus* $1/M_c$ for u.v. cured PEGDA oligomers

Table 3 Properties of u.v. cured epoxy acrylic resin–PEGDA 60/40 wt/wt mixtures

Oligomer	D.b. conversion[a] (%)	Swelling[b] (%)	T_g^c (°C)	T_g^d (°C)	Gel content[e] (%)
TEGDA	76.4	3.1	73.5	-	99.4
PEGDA 600	89.5	9.6	37.8	19.1	99.2
PEGDA 1000	90.4	10.1	41.5	22.1	98.1
PEGDA 1500	90.6	10.5	18.5	18.3	96.5
PEGDA 2000	90.2	12.5	-	16.7	95.1

[a] By *FT*i.r. analysis
[b] In water at 25°C
[c] By d.m.t.a.
[d] By t.m.a.
[e] Determined by $CHCl_3$ treatment

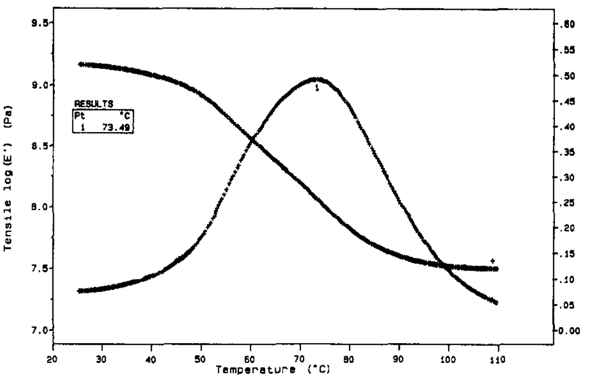

Figure 5 D.m.t.a. spectrum of a u.v. cured epoxy acrylate–PEGDA 600 mixture, 60/40 wt% (film thickness about 100 μm)

In *Table 3* some properties of the u.v. cured films are reported.

The d.b. conversion was found to increase in the presence of the PEGDA oligomers. It should be noted that in the presence of pure epoxy acrylate resin only about 65% d.b. conversion[3,4] is obtained; in the presence of PEGDA oligomers the d.b. conversion clearly increases. Moreover, the d.b. conversion increases by increasing the MW of the PEGDA oligomers, indicating that a higher flexibilization effect is obtained in the presence of the higher MW oligomers.

The u.v. cured films were examined by d.s.c., t.m.a. and d.m.t.a. All the products showed almost complete absence of crystallinity of the PEG type. No glass transition region was evident on performing d.s.c. on these products.

However, the presence of a glass transition was clearly revealed by t.m.a. and d.m.t.a. The values obtained for T_g are reported in *Table 3*; they confirm that the T_g values obtained by d.m.t.a. are clearly higher than those obtained by t.m.a.

In the literature[4,10] very high T_g values for the pure epoxy acrylic resin (> 100°C) are reported. In the presence of PEGDA oligomers a strong decrease of the T_g value is obtained, indicating a flexibilization effect on the network structure. Moreover, the T_g value decreases by increasing the MW of PEGDA.

In *Figure 5* a d.m.t.a. spectrum of a typical epoxy acrylate–PEGDA 600 mixture after u.v. curing is reported.

The gel content was almost 100% for all the systems investigated. The equilibrium swelling data for the cured films in water at 25°C are reported in *Table 3*. By increasing the MW, the swelling value increases as expected because the network crosslinking density decreases. Similar behaviour was shown by the pure PEGDA oligomers. These results may be important for predicting the behaviour of the films in the presence of water.

CONCLUSIONS

By examining the properties of networks obtained after u.v. curing of PEGDA oligomers having MWs in the range 200–2000, the following conclusions can be drawn:

(i) The double bond conversion is always complete except for the lowest MW oligomers.

(ii) The T_g values of the cured films increase by decreasing the oligomer MW, i.e. by increasing the network crosslinking density.

(iii) A linear plot of T_g values *versus* the reciprocal of the value of the chain length was obtained according to the Nielsen equation.

(iv) The swelling ratios of the cured films in water increase by increasing the oligomer MW.

Similar behaviour was observed with mixtures of PEGDA oligomers with a typical epoxy acrylate resin.

By changing the concentration of the oligomer and its MW, it is possible to modify, over a broad range, the properties of the u.v. cured films.

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