Polymer Bulletin 15, 51–58 (1986)

Polymer Bulletin

Photoinitiators

Light Screening Effects of Photoinitiators in UV Curable Systems

J. Guthrie[1]*, M.B. Jeganathan[1], M.S. Otterburn[1], and J. Woods[2]

[1] Department of Chemical Engineering, The Queen's University of Belfast, 21 Chlorine Gardens, Belfast BT9 5DL, Northern Ireland

[2] Loctite (Ireland), Tallaght, Co. Dublin, Ireland

ABSTRACT

The effect of initiator concentration and sample thickness on the photocuring properties of acrylate and methacrylate monomers has been investigated. It has been shown that as the concentration of photoinitiator increases the degree of polymerisation reaches a maximum and then decreases. This effect is very marked for film thicknesses greater than 1 mm. The optimum level of initiator corresponding to a maximum cure decreases as the sample depth increases. Photoinitiators with a high extinction coefficient at the principal wavelength of the UV source give rise to optimum concentrations at lower initiator levels. It should therefore be possible to predict the appropriate initiator concentration for a particular film thickness.

INTRODUCTION

It has been known for sometime that the efficiency of photoinitiators in free radical polymerisations decreases beyond a certain optimum concentration of the initiator due to screening by the initiator itself.[1] As a consequence of this screening, it can be expected that there is a critical relationship between photoinitiator concentration and the cure depth or sample thickness. Current reports of this relationship are however conflicting. Holman and Rubin[2] have reported that the maxima obtained in plots of power absorption versus photoinitiator concentration shift to lower values of initiator concentration as the sample thickness increases. On the other hand, Clarke and Shanks[3] have observed that the optimum initiator concentration increases with increasing sample thickness.

Due to the growing importance of applications requiring large through depth cures (up to 10 mm) it is necessary to clarify the relationship for typical multifunctional methacrylate based UV compositions. This work describes the determination of residual gel fractions for a variety of compositions over a range of initiator concentrations and different depths. As described by previous workers(1,3,4) it has been found that there is an optimum value of initiator concentration for a given sample thickness.

---

* To whom offprint requests should be sent

EXPERIMENTAL

Materials

The monomers trimethylol propane trimethacrylate (TPM), tripropylene glycol diacrylate (TGA), ethoxylated bisphenol A dimethacrylate (EPM) and the initiators 1-benzoylcyclohexanol (BCH), 2-butoxy-2-phenylacetophenone (BPA) and 2,2-dimethoxy-2-phenylacetophenone (DPA) were supplied by Loctite (Ireland).

Photopolymerisation

Photopolymerisation was carried out using two 400 watt MB/U lamps. These were mounted in a cabinet equiped with a shutter device. The distance between the sample and the UV source was adjusted to give an intensity of 25 watts/cm^2. Short wavelength UV radiation was absorbed by a trough of water located between the sample and the light source.

A solution of photoinitiator in monomer was placed in a "well" of accurately known depth in a block of Teflon. Five depths were investigated viz. 0.5, 1.0, 2.0, 3.0, 4.0 mm. The photoinitiator concentration was varied over the range 0.5-10% on weight of monomer. The sample block containing the mixture was weighed and irradiated for 30s. The contents of the well were removed and extracted with acetone on an electric shaker for 5 min. The residual polymer was air dried and reweighed. The extent of polymerisation could thus be calculated from the difference in weight. Each determination was carried out four times and an average value obtained. The degree of cure was plotted against photoinitiator concentration for each sample depth. From such plots it was possible to obtain a graph of initiator concentration corresponding to maximum cure versus sample thickness.

Determination of the extinction coefficients of photoinitiators

UV absorption spectra of the photoinitiators in ethanol were obtained using a Pye Unicam SP1800 recording spectrophotmeter. All measurements were carried out in quartz cuvettes.

RESULTS AND DISCUSSION

A typical set of results for the effect of initiator concentration on the extent of polymerisation can be seen in fig. 1. For sample depths of 0.5 and 1.0 mm. the screening effect is very small. For the 0.5 mm depth a maximum cure of 95% is reached at an initiator concentration of approximately 2%. Further increases in concentration do not result in a higher degree of conversion.

As the sample thickness increases, increasing the concentration of photoinitiator results in a reduction of the extent of polymerisation. It should be noted that a distinct maximum photoinitiator concentration can be observed corresponding to a maximum degree of cure. This maximum moves to lower values as the sample depth increases.

This type of behaviour was observed for all the monomer/initiator systems investigated. The decrease in extent of polymerisation at larger sample depths is in agreement with work carried out by Hutchinson and Ledwith[1]

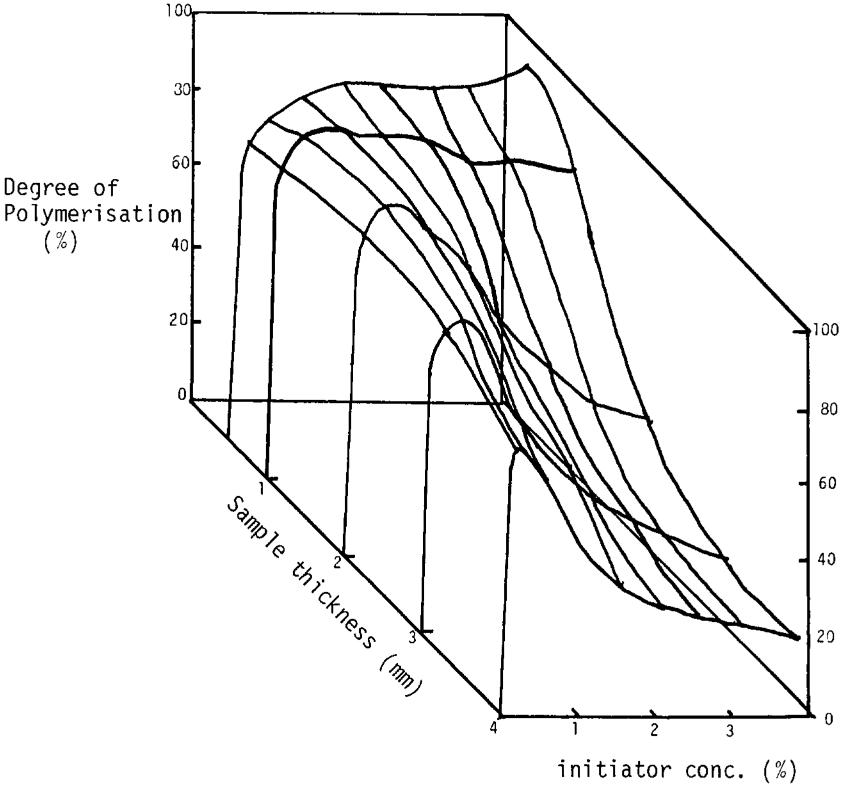

Fig. 1

The effect of sample thickness and photoinitiator concentration on the degree of polymerisation of TPM

who demonstrated that the rates of photopolymerisation of methylmethacrylate initiated with benzoin and benzoin methyl ether reached a maximum value followed by a decrease in rate as the initiator concentration increased. This was explained in terms of a non uniform distribution of radicals, the majority of the initiating species being concentrated in a region close to the light source. As the reaction is half order with respect to the initiator this non uniformity will give rise to an overall reduction in the rate of polymerisation. As the time of irradiation was identical in

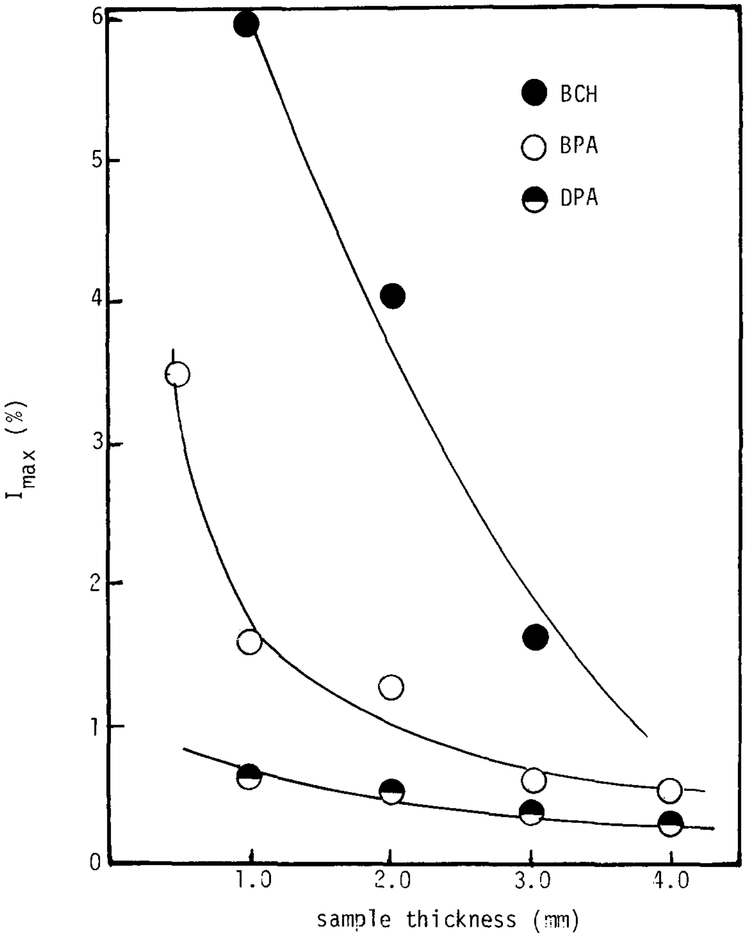

Fig. 2 The variation of I_{max} with sample thickness for formulations based on trimethylol propane trimethacrylate.

each case, the extent of reaction would be expected to decrease with increasing photoinitiator concentration. Similar results have been obtained by Clarke and Shanks[3] for the photopolymerisation of butyl methacrylate initiated with benzoin. Fig. 1 illustrates that this decrease in the extent of reaction with increasing photoinitiator concentration becomes more apparent as the thickness of the sample increases. This can be attributed to the filtering or screening effect predicted by Holmin and Rubin.[1] These workers have shown that the radiant power absorption of the reaction media falls to very low values at points deep in the polymerising sample. Consequently the rate of initiation and the distribution of radicals will be non uniform resulting in overall lower rates of reaction in thick samples. This effect will be more exagerated in very thick films. It also follows that the reduction in extent of polymerisation with increasing film thicknesses will become more marked as the concentration of photoinitiator increases.

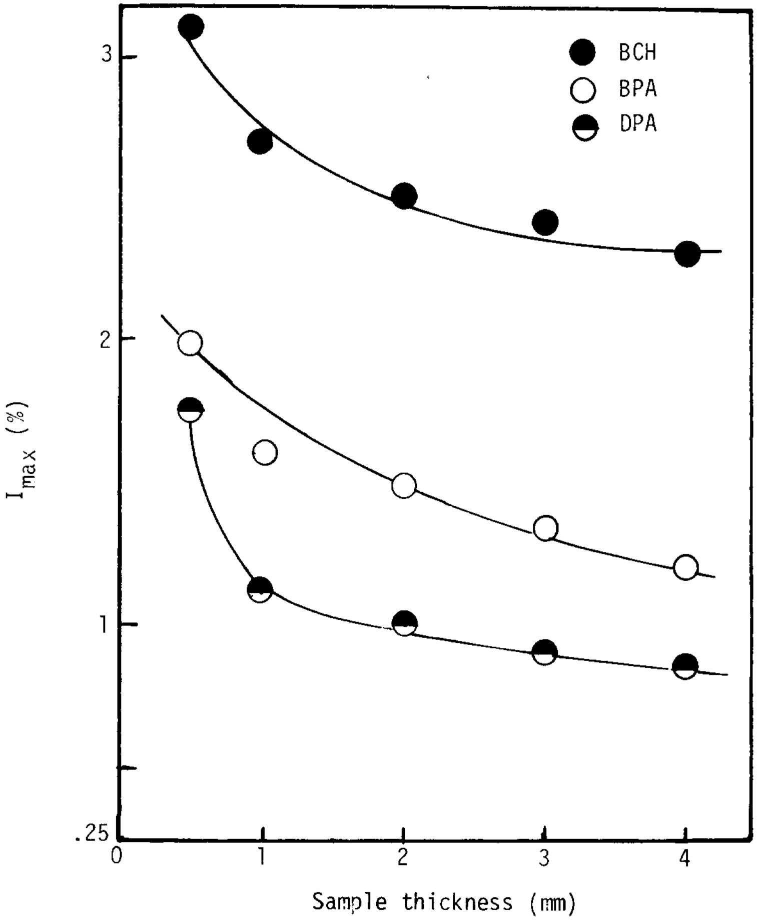

Fig. 3 The variation of I_{max} with sample thickness for formulations based on tripropylene glycol diacrylate.

Similar results were obtained for this monomer initiated with the other two catalysts under investigation. The photocuring properties of formulations of ethoxylated bisphenol A dimethacrylate and tripropylene glycol diacrylate with the three initiators gave results showing the same trends.

Using fig. 1 as a typical example it can be seen that for each sample thickness there is a maximum degree of polymerisation corresponding to a particular or optimum photoinitiator concentration. Figs. 2, 3 and 4 show how this optimum initiator concentration (I_{max}) varies with sample thickness for all the formulations studied. In all cases

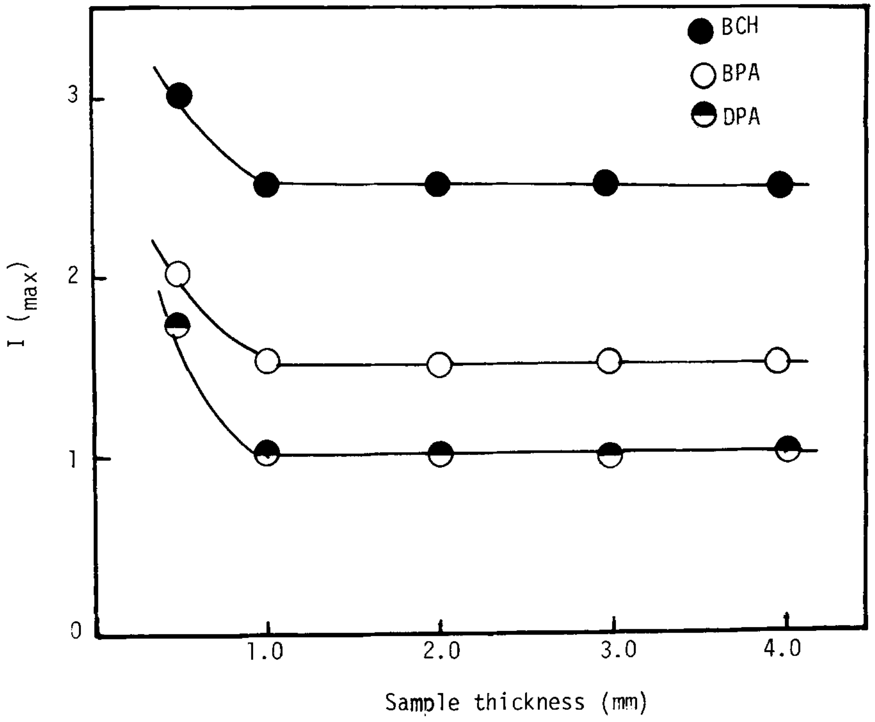

Fig. 4 The variation of I_{max} with sample thickness for formulations based on ethocylated bisphenol A dimethacrylate

I_{max} decreases with increasing sample thickness. In other words maximum cure is obtained at lower catalyst concentrations for thick films. It should however be noted that the cure corresponding to I_{max} falls with increasing sample depth. Never the less I_{max} will produce the highest

TABLE 1

Maximum extents of polymerisation (P_{max}) obtained for various monomer/photoinitiator combinations

Pmax (%) Thickness (mm)					INITIATOR	MONOMER
0.5	1.0	2.0	3.0	4.0		
95.0	91.5	92.5	84.0	73.0	DPA	TPM
69.5	74.5	73.5	66.0	41.0	BPA	TPM
85.0	84.5	77.5	70.0	60.0	BCH	TPM
98.5	93.0	56.5	35.0	27.5	DPA	TGA
91.0	70.0	37.5	22.5	17.5	BPA	TGA
99.9	87.5	46.0	29.5	21.5	BCA	TGA
99.0	92.5	56.5	35.0	27.5	DPA	EPM
90.0	70.0	37.5	22.5	17.5	BPA	EPM
99.9	87.5	43.0	27.5	22.0	BCH	EPM

extent of reaction possible for a particular concentration range for a given depth.

The values found for the maximum degree of polymerisation are shown in Table 1. It is not possible to draw any real conclusion from the data in this table other than that for each formulation maximum cure is found for the thinnest sample depth. The relationship between degree of polymerisation and the chemical nature of the initiator/monomer system will be rather complicated, depending on a variety of factors such as quantum efficiency, extinction coefficient of monomer and initiator side reactions. The extinction coefficients of the three photoinitiators at 360 nm were found to be 358, 89 and 56 $mol^{-1}cm^{-1}dm^{3}$ for DPA, BPA and BCH respectively. From figs. 2, 3 and 4 it can be seen in all cases that the optimum initiator concentration is found at lower values as the extinction coefficient of the photoinitiator increases. This would be expected if the rate of polymerisation and hence the extent of cure after a given time depends on a uniform distribution of radicals in the reaction medium. Initiators having a high extinction coefficient would be expected to give rise to this uneven distribution more readily than initiators which do not adsorb UV light so strongly.

Trimethylol propane trimethacrylate appears to be particularly sensitive to sample thickness for the initiator 2,2'dimethoxy-2-phenylacetophenone. On the other hand ethoxylated bisphenol A dimethacrylate does not seem to be very sensitive to changes in sample thicknesses greater than 1 mm.

CONCLUSION

The extent of photopolymerisation of acrylate and methacrylate monomers in thick films reaches a maximum and then decreases with increasing concentration of photoinitiator. The effect becomes more marked as the thickness of the sample increases. This is attributed to a non uniform distribution of radicals within the reaction media. This non uniformity is exagerated if the initiator has a high extinction coefficient at the principal wavelength of the UV source. As a consequence an optimum initiator concentration corresponding to a maximum extent of reaction can be determined. This optimum moves to lower concentrations for large sample depths. For initiators with low extinction coefficients the optimum is found at higher initiator concentrations. From such studies it should be possible to predict the most appropriate level of initiator for a particular film thickness.

REFERENCES

1. HUTCHISON, J. and LEDWITH, A.: Polymer 14, 405 (1973).

2. HOLMAN, R.J. and RUBIN, H.: J. Oil Col. Chem. 61, 189 (1978).

3. CLARKE, S. and SHANKS, R.A.: Polym. Photochem. 1, 103 (1981).

4. VAN LANDUYT, D.C.: J. Rad. Curing 11, No. 3, 4 (July, 1984).

Accepted December 19, 1985

C