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Use of 2-(*N*-methyl-*N*-phenylamino)-1-phenylethanol as synergist in UV-curing applications

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Abstract

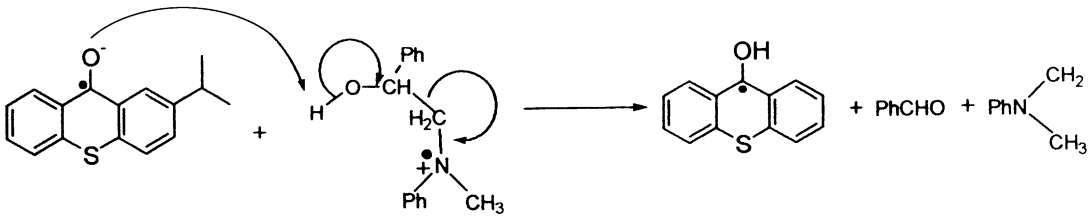
2-(*N*-Methyl-*N*-phenylamino)-1-phenylethanol in formulations was used as an aminoalcohol to help reduce the effect of oxygen inhibition and to act as synergist with a Type II initiator. When the aminoalcohol in the formulation containing Trimethylolpropane triacrylate (TMPTA) is replaced by the NMDEA at the 10% level, the same amount of cure is obtained after one pass as when 1% aminoalcohol is used. It was found that the aminoalcohol was efficient at reducing oxygen inhibition and act as an excellent synergist for isopropylthioxanthone.

Keywords: Aminoalcohol; Synergist; UV-curing; Photoinitiators

1. Introduction

UV-curing is finding application in the manufacture of a wide range of products [1], e.g. compact discs [2], optical fiber [3–5], printing [6,7], production of electronic components [8,9], floor tiles, etc. The physical characteristics of the coatings produced by UV-curing have to meet many different criteria with the application being so varied. These criteria are in the main meet by choosing the appropriate resin(s) and prepolymer(s) for the system but also it is important to have the correct initiator system and in order to achieve the right cure speed, and stability of the coating to light, etc. [10–13]. Free radical mediated polymerisation processes dominate the UV-curing market accounts for >80% of the market/despite the fact that oxygen inhibition of cure, reduces cure speed and has a deleterious effect a film surface properties [14–17].

We now describe the use of an aminoalcohol (1) in formulation to help reduce the effect of oxygen inhibition and to act as synergist with a Type II initiator. Use of the aminoalcohol with a Type I initiator (2-Methyl-[4-(methylthio)phenyl] -2-morpholino-propane-1-one) in this case allows are to assess its effectiveness in reducing oxygen inhibition and when used with isopropylthioxanthone as a synergist. The aminoalcohol will react over the triplet state of the thioxanthone to generation an α-aminoalkyl radical which will initiate polymerisation



2. Experimental

2.1. Material

2-(*N*-Methyl-*N*-phenylamino)-1-phenylethanol was used as an aminoalcohol. 2-Methyl-[4-(methylthio)phenyl]-2-morpholino-propane-1-one (Irgacure-907) was supplied by Ciba Geigy Ltd. (Macclesfield) and Isopropylthioxanthone (ITX, a mixture of 2 and 4 isomers) and by International Octel Ltd. Trimethylolpropane triacrylate (TMPTA) was obtained from Aldrich and used as received. Sartomer 259 [polyethyleneglycol (200) diacrylate], Sartomer 344

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[polyethyleneglycol (400) diacrylate] were obtained from Cray Valley and Photomer 4094 (aliphatictrifuctionalacrylate, viscosity 100 cps/25 °C), Photomer 4194 (aliphatictrifunctionalacrylate, viscosity 70–45 cps/25 °C) were supplied by Harcross Chemical Company.

2.2. Syntheses

2.2.1. 2-(N-methyl-N-phenylamio)-1-phenylethanone

A mixture of 2 g triethylamine and 2.1 g of *N*-methylaniline in 10 ml of toluene was added to 4 g of phenacylbromide in 20 ml of dry toluene. The mixture was stirred under nitrogen for 12 h. After 12 h, the yellow precipitate was formed and the solution was filtered. The toluene was removed from the filtrate and yellow crystals were obtained. Clear yellow crystals were obtained after recrystallization from absolute ethanol.

Calculated for: $C_{15}N_{15}NO$, C, 79.97; h, 6.71; N, 6.21. Found C, 80.01; H, 6.77; N, 6.20.

^{1}H NMR ($CDCI_3$): δ 6.88–8.12 (m, 10H, aromatic), 4.43 (m, 2H), 2.98 (M, 3H).

IR (KBr) ν: 3061, 2822, 1734, 1600, 1377, 850 cm^{-1}.

2.2.2. 2-(N-methyl-N-phenylamino)-1-phenylethanol

An amount of 0.4 g of sodiumborohydride was carefully added to the solution 2 g of 2-(*N*-methyl-*N*-phenylamino)-1-phenylethanone in 20 ml of dry methanol. The reaction mixture was allowed to stand at room temperature with stirring for 20 min. The methanol was removed and the residue was diluted with 40 ml of water. The mixture was extracted with ether (2 × 20 ml). The ethereal extract was dried over $MgSO_4$. The ether solution was filtered and ether removed by rotary evaporator. The aminoalcohol was obtained as red–brown oil.

Calculated for: $C_{15}N_{17}NO$, C, 79.35; H, 7.54; N, 6.16. Found C, 79.96; H, 7.63; N, 6.20.

^{1}H NMR ($CDCI_3$): δ 6.83–7.55 (m, 10H, aromatic), 4.98 (m, 1H), 3.457 (m, 2H), 3.07 (s, 1H), 2.75 (m, 3H).

IR (KBr) ν: 3061, 2822, 1589, 1571, 1501, 1370, 1121 cm^{-1}.

2.3. Irradiation methods

2.3.1. UV-curing

The UV-curing unit (Colordry) houses a medium pressure mercury lamp (80 W cm^2, 23 cm in length) situated 15 cm above the moving belt. The speed of the belt could be varied and was calibrated in metres per minute. Formulations were coated onto Gateway Natural Tracing Paper (Wiggins Teape Group Ltd.) using K bar (RK, Royston, Hertfordshire) giving a film of 12 μm thickness. The coated papers were passed under the lamp at a known belt speed. The degree of cure was measured arbitrarily using a hard rubber bulb. When no visible deformation of the surface occurred, the film was considered cured. This test was repeated on a minimum of three samples

2.3.2. FTIR

The films were coated on GTN paper. The film thickness was 12 μm and the spectra were recorded for each sample before and after irradiation. On exposure to UV irradiation the consumption of carbon–carbon double bonds of the acrylate group was monitored by the 810 cm^{-1} associated with the CH deformation of vinyl group and the doublet at 1640 and 1620 cm^{-1} associated with the carbon–carbon double bond stretch. The area associated with each peak was computed given a predefined baseline and from which peak ratio's were evaluated and the percentage of a given peak calculated.

2.3.3. IR spectroscopy

All solutions were coated onto a NaCl plate as a uniform layer of thickness ∼12 μm. The coated plates were passed under the lamp (UV-curing unit) at a known belt speed and plate was placed into an IR spectrophotometer before and after UV exposure.

2.3.4. Reaction mixtures

These were made up on a weight for weight basis and their compositions are shown in Table 1.

Table 1
Composition of reaction mixtures

Mixture	Irg-907 (%)	ITX (%)	NMDEA (%)	(1) (%)	P.4094 (%)	P.4149 (%)	S-344 (%)	S-259 (%)	TMPTA (%)
C1	2			1				97	
C2	2			1			97		
C3	2			1					97
C4	2			1		97			
C5	2			1	97				
C6		2		1			97		
C7		2		1					97
C8		2		1		97			
C9		2		1	97				
C10		2	10						87
C11	2		10						87

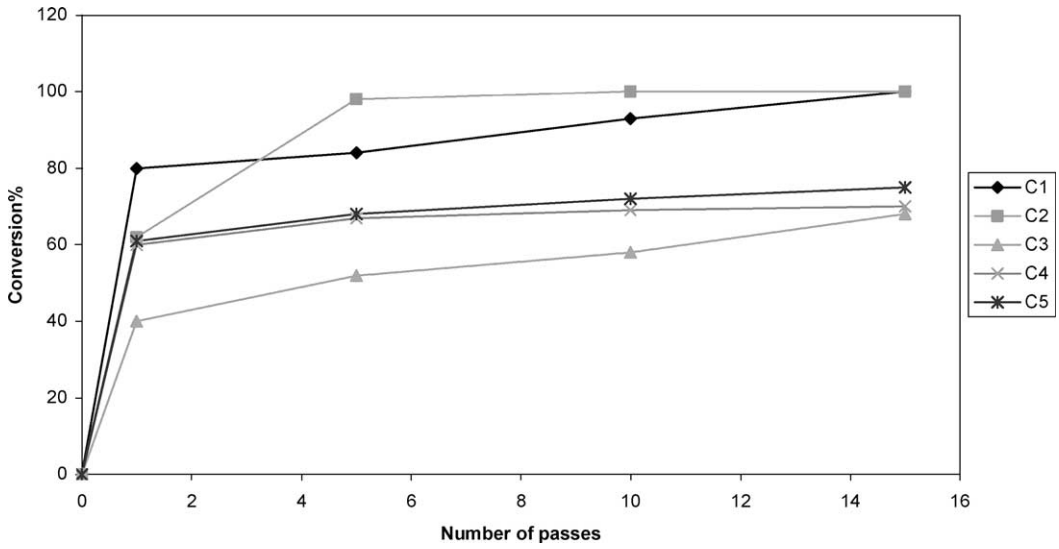

Fig. 1. The conversion percentage of samples (C1–C5) using IR spectrophotometer.

3. Results and discussion

The cure of the materials was determined by infrared spectroscopy. In one set of experiments the formulations were coated onto sodium chloride discs in the usual way. The infrared spectrum of the irradiated material was recorded and then the film subjected to further passes under the UV-curing lamp. With the IR spectrum of the films being recorded after appropriate number of passes under the lamp. The percentage conversion was calculated from the spectra and the results obtained are shown in Figs. 1 and 2.

Similar experiments were carried out with the formulations being coated onto paper. The coated paper were passed under the curing lamp and the IR spectra of the film being recorded using an FTIR spectrophotometer equipped with an attenuated total reflectance accessory. From these spectra the percentage conversion of the acrylate double bonds as a function of passes under the lamp was calculated.

Infrared spectroscopy can be used to determine the extent of cure as measured by the percentage conversion of the double bonds in the formulation. When the coatings were applied to a sodium chloride disc and the percentage conversion determined by transmission IR spectroscopy the calculated value related the average number of double bonds present in the film. When ATR–FTIR spectroscopy is used the analyzing IR beam only interogates the surface

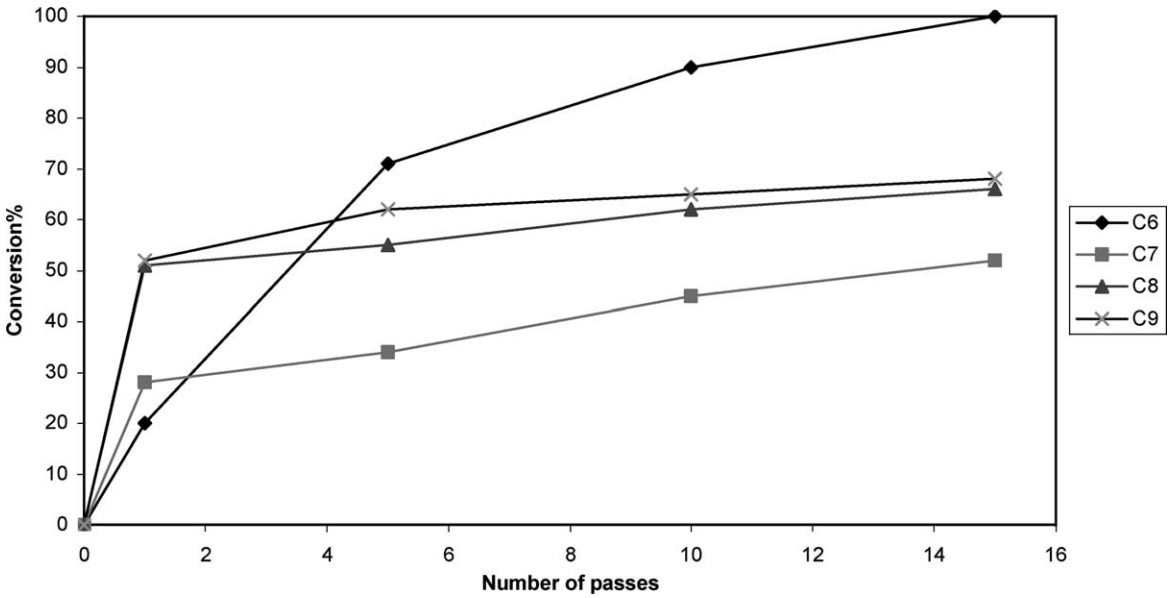

Fig. 2. The conversion percentage of samples (C6–C9) using IR spectrophotometer.

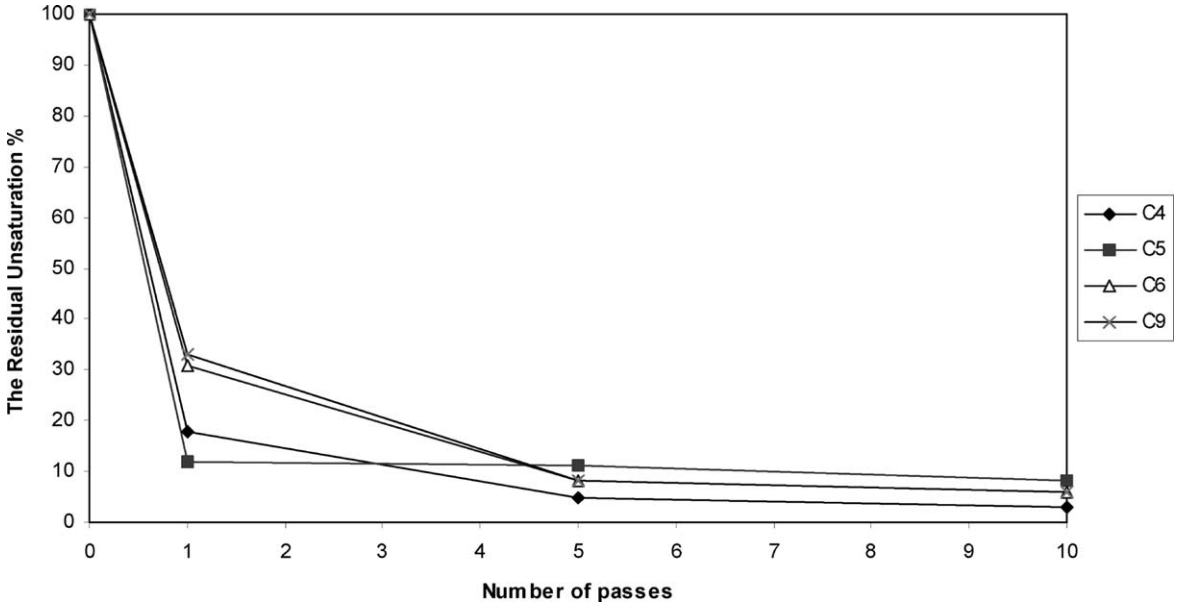

Fig. 3. The residual unsaturation of samples (C4–C6, C9) on paper by using of FTIR.

(∼2 μm-depth depending on the crystal and the angles of the end pieces) and therefore cure at the surface is being looked at. It was found that the 810 cm^{-1} peak was not markedly affected by the cellulosic substrate and therefore sample baseline techniques were applied to determine the area under the absorption band.

A quick inspection of Figs. 1–4 shows that the film on sodium chloride disc cured much slower than those a paper. The ATR–FTIR results show that the surface of the films are well cured and manually this present same difficulty and oxygen inhibition of are being more pronounced at the surface of the film compared with the middle of the film. Currently, we do not have an explanation for the differences in the rate of cure on the two substrates although it may be related to the different temperature which the coatings achieve in the UV-curing. When the Type I initiator (2-methyl-[4-(methylthio)phenyl]-2-morpholino-propane-1-one) is used extensive cure is obtained with the lower mol. weight PEG diacrylate formulation (C1) the high viscosity PEG diacrylate formulation (C2) cure a little slower but after two passes under the lamp cures to greater extent than the lower molecular weight PEG diacrylate. The two

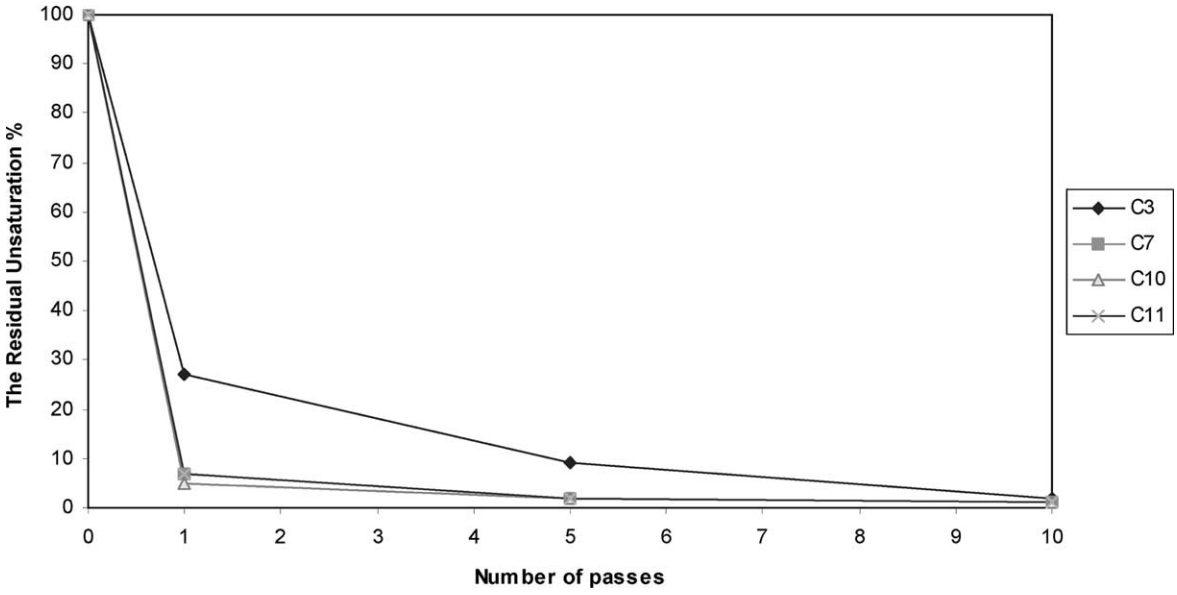

Fig. 4. The residual unsaturation of samples (C3, C7, C10, C11) on paper by using of FTIR.

urethane acrylate formulation (C4 and C5) are not similar. The TMPTA formulation cures very slowly but 4094 conversion have occurred after one pass.

When formulation containing the Type I initiator are coated onto paper, the TMPTA percentage conversion was 75% after one pass, i.e. significantly higher than when sodium chloride is the substrate. The trifunctional urethane acrylate formulation (C4) cures at a similar rate. A formulation containing TMPTA and NMDEA (10%) was above aminoalcohol and after two passes under the lamp almost full cure was achieved. Given that NMDEA is better than the aminoalcohol at reducing oxygen inhibition and that it is used at a much higher concentration it can be seen that the amino alcohol performs relatively well in these formulation. When isopropylthioxanthone is used as initiator the role of the aminoalcohol is both that of a synergist and as a reducer of oxygen inhibition. The results obtained for formulation applied to a sodium chloride disc shown once again that the one containing TMPTA (C7) is the lowest to cure and exhibits the lowest conversion after 15 passes under the lamp. Although the formulation containing the PEG acrylate (C6) is slow to cure, total conversion is achieved after 15 passes under the lamp. The two formulation containing urethane acrylates (C8 and C9) are not similar scale.

When formulation containing ITX (C6 and C7) are applied to paper, much higher conversion are achieved and a substantial amount of are obtained after one pass. When the aminoalcohol in the formulation containing TMPTA is replaced by the NMDEA at the 10% level, the same amount of cure is obtained after one pass as when 1% aminoalcohol is used. The aminoalcohol is efficient at reducing oxygen inhibition and act as an excellent synergist for isopropylthioxanthone.

4. Conclusion

We have shown that the extent of cure of formulation containing acrylates is influenced by the substrate to which they are applied. Cure was found to be for slower a sodium chloride plates than a paper this may be related to the temperatures that the films each on the UV-curing. The results show that the aminoalcohol when used with a Type I initiator behaves as reducing the effect of oxygen inhibition and as a synergist with isopropylthioxanthone. The aminoalcohol is effective when used at a low level as 1%.

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