Macromol. Symp. ***193****, 169–185 (2003)*

Ultraviolet (UV) Curing of Phosphated Polyurethane-Acrylic Dispersions

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SUMMARY: Phosphate-containing polyurethane-acrylic dispersions were synthesised for UV curing studies. The effects of light intensity, substrate-dependent temperature increase, soft-segment content and water on conversion were investigated. The effect of the light intensity on conversion was twofold. At first, conversion increased with light intensity. This was attributed to the inability of shrinkage to keep pace with the polymerisation and crosslinking, resulting in the creation of free volume, thereby facilitating reaction and enhanced conversion. At higher intensities, conversion was found to be reversed or, at least, it remained constant, owing to increasing radical-radical termination reactions. Phosphated-polyurethane coatings with high soft-segment content show improved conversion with exposure time. This was found to be related to the chain mobility, caused by the low glass transition temperature of the soft segment. The effect of water on conversion was also twofold. On the one hand, water had a plasticising effect on the UV curing and the polymerisation rate was fast. On the other hand, the gel content was found to be lower when films were cured before the evaporation of water.

Introduction

The use of ultraviolet (UV) to cure vinyl-terminated coatings is well established and documented [1]. The primary advantages of using UV for curing are the high cure speeds that can be used and the fact that the coating formulations are solvent-free. Most commercial UV-curing coatings use acrylic-based monomers and resins, which cure by a free-radical mechanism. However, the high level of the acrylic diluent used to reduce the viscosity of the composition has an adverse effect on the cured film. UV curing is generally accompanied by shrinkage, because non-bonding distances between the monomers are converted to shorter bonding distances in the polymers. Following the onset of polymer network formation, shrinkage may lead to internal stresses because of a

CCC 1022-1360/00/$ 17,50+.50/0

restricted relaxation process. This problem is further exacerbated in rapid-curing systems, in which relaxation processes may not keep pace with polymerisation [2,3]. 8-20% shrinkage occurs during the polymerisation of monofunctional acrylates and methacrylates. Internal stresses generally have adverse effects on the mechanical properties of coatings and their adhesion to substrates. Relatively small volume changes and even expansion may occur during the polymerisation of monomers which undergo ring-opening reactions, as a consequence of bonding distances being converted into longer non-bonding distances in the ring-opening process.

From the health point of view, the use of high proportions of acrylic monomers is unacceptable, particularly for spray applications. Low-molecular-weight diluents can easily be adsorbed into the substrate (if porous) during the time between application and curing. The part of the diluent being shielded from the UV light would not be polymerised and could cause failure of the coatings and an unpleasant odour. It is not only the monomers but also the photoinitiators that, due to the high content of initiator extractables after cure, that are considered to be a potential threat in the packaging industry. Hence the ‘once best, volatile organic compound-free technology’ is under new scrutiny [4,5].

Most photoinitiators absorb in the 300-430 nm region. The medium-pressure mercury arc lamp offers maximum UV output within this range. In addition to the lamps, complete UV-assemblies for commercial coating lines require: a power source, lamp reflectors, suitable shielding to reduce UV leakage, adequate cooling and ventilation. In practice, multiple lamps are mounted perpendicular to a moving conveyer, which is placed a few centimeter away from the coating.

Waterborne UV curing has recently become increasingly important [6] and a substantial amount of work is being done to develop co-polymerisable photoinitiators to minimise the extractables [7,8]. In this article we report on the UV-curing properties of phosphated polyurethane-acrylic dispersions as possible candidates for use as metal coatings.

Experimental

Preparation of the Phosphated Polyester Macroglycol

A polyester macroglycol that contains phosphorus in the main chain was synthesised from 1,4-cyclohexane dicarboxylic acid (Eastman Chemicals, USA), neopentyl glycol (Perstorp Polyols, Sweden) and 1,2,4-phosphonobutane tricarboxylic acid (Bayer, Germany) in a standard polycondensation reaction to a low acid value (less than 4mgKOH/gm). The macroglycol was then dried at 90^{0}C under reduced pressure to remove any traces of moisture before use.

Synthesis of the Phosphated Polyurethane-acrylic Resin

A 1L-glass reactor equipped with a mechanical stirrer, a charging and sampling port, a nitrogen inlet and outlet was charged with the phosphated polyester macroglycol and excess dicyclohexane-methane-diisocyanate (Bayer Germany). The reaction took place at 95^{0}C over 90 min. The temperature was then reduced to 60^{0}C and 2,2-hydroxymethyl propionic acid (Perstorp, Sweden) was added and allowed to react with the isocyanate for 1 h. During this stage the acrylic monomer of choice, selected from methylmethacrylate (MMA), ethylmethacrylate (EMA), butylmethacrylate (BMA), or ethylene glycol dimethacrylate (EGDMA) was added to reduce the viscosity of the reaction mixture. Finally, 2-hydroxyethylmethacrylate was added as a chain extender and allowed to react with the –NCO groups for 2 h, to complete the reaction. The reaction temperature was kept to 60^{0}C to prevent thermal polymerisation of C=C. The acid groups of the 2-hydroxyethylmethacrylate-terminated phosphated polyurethanes were neutralised using triethylamine. Water was then added to form the dispersion. The total solids content was adjusted to 35% in all cases.

Photoinitiator

Hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184, CIBA-GEIGY Corporation) in 2% concentrations was used as photoinitiator. It is a highly efficient photoinitiator, used to in many polymer systems for coating application.

Substrate Preparation

All the substrates used in this study were products of ISCOR and Hulett S.A. Of the possible substrates available for coil coating, only the hot-dipped galvanised steel and aluminium were used. The panels were cut to sizes of 10 cm x 20 cm. Their thickness was approximately 0.6 mm. Before application of the coating, all the panels were first dried at 120^0C for 5 min in an oven to remove any traces of moisture adsorbed during transportation and storage. After cooling to room temperature the panels were immediately coated with the phosphated polyurethane acrylic dispersions.

Film Applicator

A wire-wound drawdown bar was used to apply the coating to the substrate. Since the diameter of the wire wound on the bar controlled the thickness of the wet film, the choice of the bar was important in controlling dry-film thickness. In the coil-coating line, coating thickness is controlled by varying the pickup or applicator roll speed and nip adjustments. The wire-wound drawdown bar resembled a roller.

Preparation and Curing of Coatings

The UV-cured coatings were obtained by depositing a mixture of the phosphated polyurethane-acrylic dispersion and photoinitiator onto the substrates. Before applying the coatings, a mixture of the photoinitiator and the phosphated UV-curable polyurethane dispersion was homogenised at 40^0C for 10 min. The coated substrate and irradiated using a medium-pressure mercury lamp (of varying intensities), equipped a with semi-elliptical reflector. The distance between the sample and the lamp was 30 mm and the films obtained were 5-30 microns thick. The conversions (polymerisations) of the C=C bonds were studied by FTIR spectroscopy.

Results and Discussion

Verification of Complete UV-Curing

The UV-curing reactions are radical polymerisations involving the vinyl groups of the 2-hydroxylethyl methacrylate and the acrylate diluent. Complete reactions were verified by the disappearances of the acrylate C=C absorption bands at 820/cm and 1635/cm after irradiation.

The Effect of Light Intensity on Polymerisation

One of the unique advantages of light-induced reactions is that the initiation rate can be easily varied by changing the intensity of the UV beam that impinges on the sample. When the light intensity (I_0) was increased the polymerisation took place more rapidly, as a result of the increased rate of initiation. The conversion of the C=C bonds versus UV exposure time for the phosphated-polyurethane acrylic dispersions exposed to UV radiation of various intensities are presented in Figure 1. After a short induction period, due to the inhibitory effect of oxygen dissolved in the formulation, the rate of polymerisation increased sharply to a maximum value and later decreased before it levelled off. The polymerisation reaction was found to develop faster as the light intensity was increased to a certain value, above which it did not increase any further.

The effect of the light intensity on conversion was twofold. At first, conversion increased with light intensity. This is attributed to the inability of shrinkage of the polymer to keep pace with the polymerisation and crosslinking, resulting in the creation of free volume, thereby facilitating the reaction and enhanced conversion. At higher intensities, conversion was found to be reversed or, at least, it remained constant, owing to increasing radical-radical termination reactions. Since radical concentration increases with light intensity, termination reactions, which are second order in radical concentration, are expected to take place more rapidly than chain propagation reactions, which are first order in radical concentration [9]. Decker et.al [10] recently proposed that a decrease in initiation rate, rather than termination, is responsible for the levelling off of the polymerisation rate. According to their study, a given number of radicals must be generated by photolysis of the initiator to consume the oxygen dissolved in the formulation and, accordingly, the reciprocal of the induction time was found to vary linearly with light intensity. This proposal, however, needs more clarification before general acceptance. Initial conversion increased with I_0 and only high conversion decreased at higher I_0. Thus, a decrease in the number of initiating radicals at higher I_0 is not a plausible explanation for the observed decrease in conversion.

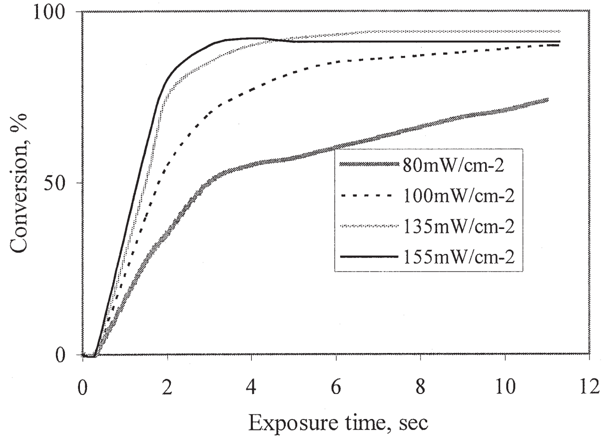

Figure 1: Influence of the UV light intensity and exposure time on the photopolymerisation of phosphated polyurethane-acrylic dispersions

The Effect of Temperature on UV Curing

During high-speed UV polymerisation, because of the great amount of heat evolved from reacting C=C double bonds, in addition to the heat emitted by the UV lamp, the temperature of the sample increases rapidly. UV-cured coatings are therefore, in reality, not polymerised at room temperature. To quantify the real polymerisation temperature, it was measured just after switching on the lamp. The time-dependent temperature build up under the UV-lamp is plotted in Figure 2. It clearly shows the temperature increase with time, as would be expected if continuous curing is carried out by conveying successive samples through the UV-chamber at an exposure time of, say, 12 s for each coating.

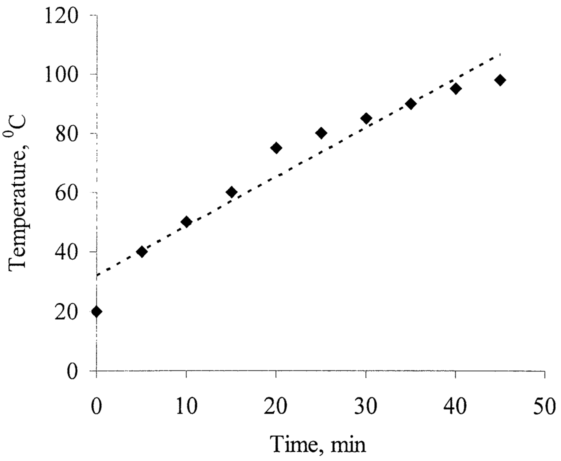

Figure 2: Time-dependent temperature increase under the UV lamp during UV-curing.

Though in practice the commercial UV-curing set-up is normally ventilated and therefore the temperature increase may be less than that recorded under the experimental conditions of Figure 2, temperature has a direct effect on the rate of polymerisation.

The instantaneous average chain length ν of a polymer formed during UV curing is given by [11],

$$\frac{dR_p}{dT} = (E_p + E_d/2 - E_t/2)/RT^2 \qquad \text{(equation 1)}$$

$$\frac{dv}{dT} = (E_p - E_d/2) - E_t/2)/RT^2 \qquad \text{(equation 2)}$$

where E_d, E_p and E_t correspond to activation energies of the initiator decomposition, propagation and termination rates. The effect of a small change in temperature during the curing could thus be estimated. Since Ed ≈ 0 and Ep-Et/2 ≈ 20 KCal mole^{-1} [11],

$$\ln\frac{R_p(T_2)}{R_p(T_1)} = \ln\frac{v(T_2)}{v(T_1)} = -20x10^3/R(1/T_2 - 1/T_1) \qquad \text{(equation 3)}$$

Thus a change in temperature from 30^{0}C to 40^{0}C induced a 25% increase in the polymerisation rate, R_p, of the phosphated polyurethane-acrylic dispersions.

The heat generated from the reaction, excluding the heat emitted by the UV lamp, started to rise as soon as the polymerisation began. It reached a maximum value once the reaction slowed down, because of gelation, and decreased later as air cooling became predominant over the small amount of heat evolved in the latter stage, as shown in Figure 3. For the sample that contained no photoinitiator, the temperature increase from the lamp was relatively low during a 15 s exposure (from 25 to 43^{0}C).

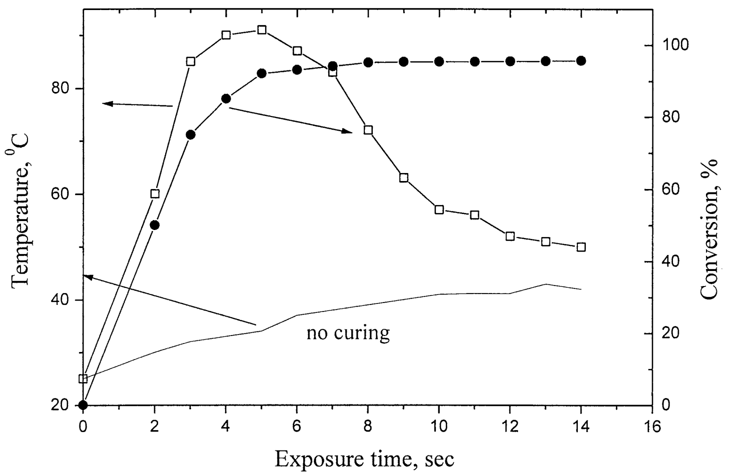

Figure 3: Temperature and conversion profiles for the UV curing of phosphated polyurethane acrylics

A linear relationship existed between the increase in temperature and the maximum rate of polymerisation $(R_p)_{max}$, calculated from the slope of the conversion versus time curve in Figure 1, as shown in Figure 4.

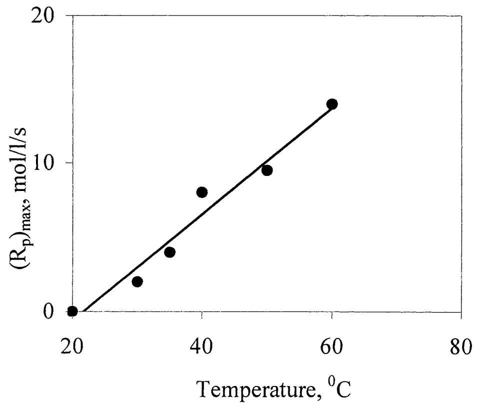

Figure 4: Dependence of (Rp)max on temperature.

The maximum temperature (T_{max}) reached upon UV exposure was also found to increase with the film thickness of the coatings, as shown in Figure 5. This is because the total amount of heat evolved upon polymerisation increases with an increase in the sample weight (film thickness).

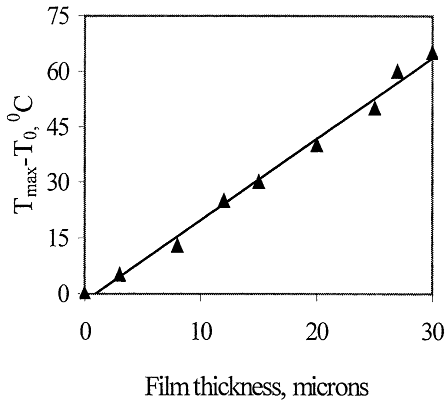

Figure 5: Dependence of temperature increase upon UV exposure with film thickness of the coatings

The heat transfer coefficient of the substrate also showed a significant increase in temperature and hence rate of polymerisation. The specific heat transfer coefficient of aluminium is much higher than that of the steel or galvanised steel.

Figure 6 shows the temperature increase with time for the two substrates used. The aluminium surface reached a higher temperature because of the higher heat transfer of the metal.

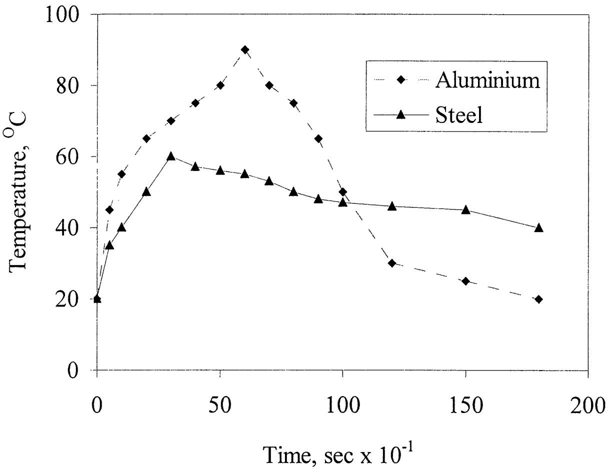

Figure 6: Effect of substrate on heat transfer during UV-curing of polyurethane dispersion coatings

The Effect of Soft Segment Content on Conversion

The conversions versus exposure times for phosphated-polyurethane dispersions (as formulated in Table 1) with different soft segment contents, but the same quantity of acrylic monomer, are presented in Figure 7. Film thicknesses, the drying conditions used to evaporate the water, the curing conditions and all the other conditions were the same for all coatings.

Table 1: Coating compositions of phosphated polyurethane-acrylic dispersions.

Soft segment content (g)	**Hard-segment content (isocyanate, DMPA, 2-HEMA), (g)**	**EGDMA content (g)**	**% soft segment**
60	40	20	50.00%
65	35	20	54.16%
70	30	20	58.33%
80	20	20	66.66%

As seen in Figure 7, the coatings with high soft-segment content had improved conversion with exposure time. This was found to be related to the chain flexibility caused by the low glass transition temperature of the soft segment.

When crosslinked networks are formed by low-temperature UV polymerisation, incomplete conversion of the monomer into polymer is observed [12]. This is caused by vitrification, and is also true for step-growth reactions involving, for example, the curing of epoxy resins with polyamines below the Tg of the cured polymer [13]. During UV crosslinking, the glass transition temperature of the composition increases. The reduction in the mobility caused by increasing viscosity and crosslinking first suppresses the termination process, then later the mobility of the monomer. The radicals are also suppressed and the polymerisation rate becomes diffusion controlled. On further crosslinking, the diffusion coefficient is decreased and so is the rate of polymerisation. Therefore, the assumption advanced by early researchers that the same polymer can be made at room temperature by photopolymerisation as was formerly made at higher temperature, does not hold true [12]. The reason for the bumpy pattern on the conversion curves in Figure 7 is not understood. Such a non-steady pattern should not have been observed.

Phosphated-polyurethane coatings with higher soft-segment content lead to crosslinked coatings that are elastomeric, where mobility restrictions are expected to be less pronounced than those coatings with low soft-segment content. Thus, as crosslinking progressed, coatings with low soft-segment content became less mobile before high conversion was achieved. It can also be seen from Figure 7 that the trapped, immobilised radicals were essentially inactive after continued irradiation.

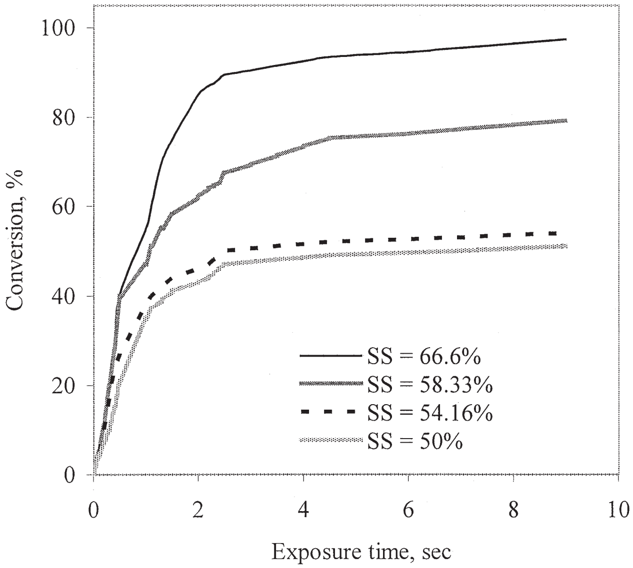

Figure 7: The effect of the soft segment (SS) content on the conversion of phosphated polyurethane-acrylic dispersions.

One of the limitations of conventional UV-curing of coatings is the presence of high levels of reactive diluents used to reduce the viscosity. Such reactive diluents are mainly multifunctional acrylates and, as a result, the crosslink density of the coatings is very high. This in turn leads to properties of films that are not required for coating flexible surfaces. Koshiba et.al [14] found that increasing the reactive diluent content to more than 20% lead to the development of a second, high glass-transition temperature, that lead to decreased conversion due to mobility restrictions. However, a 20% reactive diluent is normally not enough to bring the viscosity of the polymer to application viscosity, such as for spray and roller coatings.

When EGDMA (in Table 1) was substituted with MMA, EMA and BMA, the conversions with exposure time were found to increase in order of MMA < EMA< BMA. This is directly related to the mobility caused by the lower Tg of the diluent and the overall resulting polymer.

Comparison of UV-cured Coatings with Coatings from Internally-Crosslinked Dispersions

Crosslinked dispersions made from the phosphated-polyurethane dispersion 'seed' by copolymerising monofunctional and difunctional acrylate monomers in the dispersed phase were compared with UV-cured films. The UV-curable dispersions had the same compositions as the crosslinked dispersions. When coatings prepared by UV-curing were compared with those of the crosslinked counterpart dispersions, significant property differences in the resultant coatings were observed. The main one was the flexibility of the coatings, as determined from impact tests, as shown in Figure 8. The results of the impact tests are expressed in kg/m, that is, the height required to produce cracking on the deformed area, using an 1.8kg mass at 25^0C.

Internally-crosslinked phosphated polyurethane dispersions are typical core-shell polymers with a low glass-transition temperature soft segment core and a hard shell that contains the urethane and the acrylic groups. Since polymerisation is carried out in the dispersed phase stabilised by carboxylic acid monomer, particle growth occurs in the absence of secondary nucleation and no homopolymer formation of the acrylic monomer is observed. Thus, coatings from internally-crosslinked dispersions show better impact resistance because the applied energy is absorbed by the soft and flexible soft segments. However, homopolymersation of the reactive diluent under UV-curing conditions is very likely and homopolymers of the acrylic diluents are brittle. Since the homopolymer chains are less chemically bonded to the phosphated polyurethane particles, they may act as weak areas and result in poor flexibility. Shrinkage of the coatings during UV exposure, that could result in internal stress of the coatings, may also be responsible for the low impact resistance of the UV-cured coatings.

Another possible reason for the observed difference in flexibility may be the non-homogeneity of the acrylate phase caused by the high speed UV curing. In UV-curing, the light is mounted perpendicular to the coating surface and crosslinking begins at the outer layer. This is because photoinitiators at the interface absorb light faster than those in the deeper layer and initiate the crosslinking. Thus, the acrylate diluent may diffuse to the reaction site, causing non-homogeneity [9].

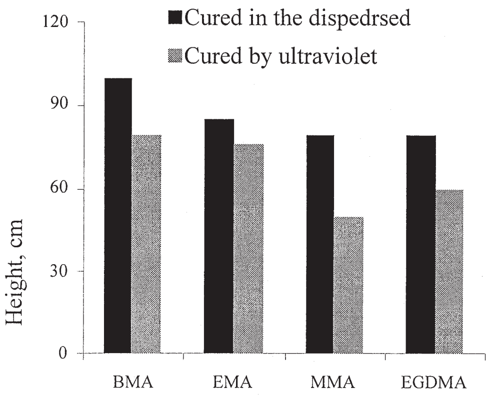

Figure 8: The effect of crosslinking method on the impact resistance of various phosphated polyurethane-acrylic coatings

The Effect of Water on UV-Curing

For a UV-curing system, it is important that all water be removed (by evaporation) before irradiating, for increased network formation. The effect of residual water on the gel content of samples that were irradiated without prior water evaporation was significant. Figure 9 shows that when the flash-off time between coating and curing was 3 min, gel content was low. In a commercial application, water evaporation is normally done either by an infrared lamp or in a hot oven at a temperature of 80^0C, before curing. It must be emphasised, however, that loss of the photoinitiator at the drying temperature may also occur. Davidson [7,15] and Anderson et.al [16] studied the use of polymeric photoinitiators in efforts to avoid the potential loss of low molar-mass photoinitiators during the water evaporation stage at elevated temperatures; reduced volatility during flash-off time was reported. Studies by Catalina et.al. [8] on the use of copolymerisable photoinitiators to overcome photoinitiator losses have also shown reduced steam volatility.

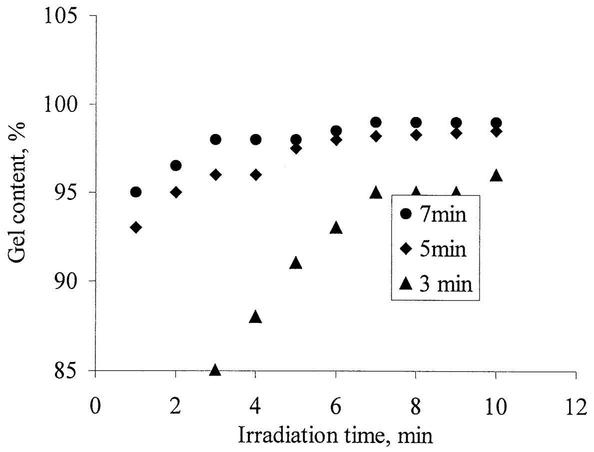

Figure 9: The effect of water on gel content of a UV-cured phosphated polyurethane-acrylic dispersion coatings

The gel content of coatings irradiated after all the water had been completely removed at 80^0C is presented in Figure 10. An UV exposure time of only 1.5 sec was adequate to crosslink 80% of the dispersion coatings.

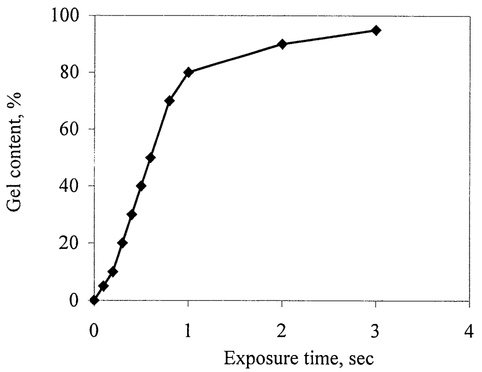

Figure 10: Gel content versus irradiation time for a completely dried dispersion coating

On the other hand, water can be a positive contributing factor for polymers cured by UV. For example, a non-reactive diluent can be added into the acrylic monomer before irradiating to decrease the glass transition temperature of the growing polymer during polymerisation and to drive the polymerisation to completion at room temperature. It has been reported [17] that the addition of polar solvents, like water, have a plasticising effect on the UV-curing of acrylic monomers and the polymerisation rate is fast. On the basis of this, the effect of water on the gel content of the UV-cured phosphated polyurethane dispersions was not directly related to lack of conversion of the reactive diluent to polymer, since FTIR studies showed the complete disappearance of the C=C bond in dispersions irradiated before water evaporation. For waterborne dispersions used in UV curing, it is essential to achieve initial film formation before curing commences. This means that the water must be evaporated from the particles to allow the particles to coalesce and form a coherent film. If no film formation is obtained before irradiation, then crosslinking will occur inside the individual particles separated by water, and a coherent film will not be obtained. Another possible reason for the low gel content is that homopolymerisation of the diluent could take place and the base dispersion may not be crosslinked. Thus, gel content, as determined by toluene and acetone extraction, may decrease as a result of incomplete crosslinking and not necessarily due to incomplete conversion. Network formation requires that the growing chains be in close proximity, which, in this case, they may not be. They were separated by water molecules and the water must be removed for crosslinking to take place.

Conclusions

Phosphorous-containing polyurethane-acrylic dispersions were synthesised for possible use in UV-curing applications, for coil-coating application. Results showed they had potential for use in environmentally safe coatings. However, waterborne UV-curing, like any other curing technique, is not without limitation; the slow curing of the above dispersions resulted from the need to first evaporate any water. Nevertheless, some striking advantages of the UV-curable phosphated polyurethane-acrylic dispersions are: their low viscosities at high molecular weight that allows thin-film coatings to be made, easy control of the rheology, tack-free coatings before cure, ease of application (spray, roller coatings, curtain coatings) and easy cleaning of the application equipment.

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