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Dual-Cure Processes: Towards Deformable Crosslinked Coatings

Abdelkrim El-ghayoury[a,c], *Chouaib Boukaftane*[b,c], *Barteld de Ruiter*[*a]
and Rob van der Linde[b]

a) TNO Industrial Technology, Department of Polymer Technology, De Rondom 1, P.O. Box 6235, 5600 HE Eindhoven, The Netherlands.
b) Eindhoven University of Technology, Coatings Technology Group, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.
a) c) Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, The Netherlands

Summary: Two dual-cure processes consisting of a UV-initiated radical polymerization followed by either a UV-induced cationic polymerisation, or a thermal addition reaction, were investigated. The feasibility of the processes was studied using an acrylate-oxetane monomer for the UV/UV combination, and an acrylated oligoester for the UV/Heat combination. It was shown by FTIR and Tg measurements, that both steps of each process could be performed efficiently and separately. This allowed the production of a deformable partially cured coating, whose cure can then be completed, leading to the required final properties. Furthermore, it was demonstrated that the increase of the functionality of the reactive diluent led to a decrease of the thermal crosslinking extent. This is probably due to the reduced mobility of the reactive species that is caused by an enhanced UV crosslinking taking place during the first step.

Keywords: dual-cure; coatings; acrylate; oxetane; polyester; crosslinking; UV-curing

Introduction

Photoinitiated polymerization or UV-curing of multifunctional monomers is widely utilized for rapidly producing highly crosslinked polymer materials.[1],[2] Among the advantages of this

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[*] Corresponding author: Dr. Barteld de Ruiter: e-mail: B.deRuiter@ind.tno.nl

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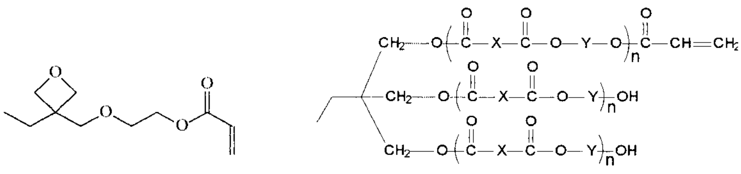
technology are the high cure speed, the reduced energy consumption and the very low organic emission. This allowed its rapid growth in a large variety of applications, in particular to achieve a fast drying of varnishes, printing inks and protective coatings, and a quick setting of adhesives and composites materials. [3],[4] A limitation of most photocrosslinkable systems, however, is the shrinkage occurring during the photopolymerization,[5] leading to a lack of adhesion on certain non porous substrates. Furthermore, the high crosslink density of the generated coatings often makes them very difficult to bend or to emboss, because of their brittleness. In this paper, we report on a two-step cure process that allows overcoming these problems.

The first process consists of the combination of two different UV steps based on different polymerization mechanisms. Few of such systems, combining (meth)acrylate with vinyl ethers[6],[7],[8],[9] or with epoxides[10],[11],[12] have been reported. However, in these studies the radical and the cationic steps were performed simultaneously. Moreover, only a few of them reported the efficient separation of the two steps such as compositions containing a photosensitive free radical reactive system and photosensitive cationic cure epoxy system. [13]

The second process consists in the combination of UV and thermal steps. Many of such systems have been reported where the formulations contain on one hand an acrylate function, and on the other hand a functionality having the ability to react at ambient temperature, like isocyanates or epoxy.[14] In addition to these systems, acrylates/amino resins were employed for radiation/heat technique that was more extensively studied.[15]

In our approach, the liquid formulation is applied on a flat substrate and then cured via a radical photo-initiated polymerization. This first step should lead to a tack-free, flexible and therefore deformable coating. In a latter stage, the coated sheet is shaped, and then the second cure, a cationic light-initiated or condensation/addition reaction, is performed to obtain a cross-linked hard coating, with improved physico-chemical properties. The feasibility of the dual-cure processes was investigated using acrylate-oxetane and acrylate-polyester systems for the UV/UV and the UV/Thermal combinations, respectively (Scheme 1).



Acrylate-oxetane

Acrylate-polyester

Scheme 1: Schematic representation of the compounds

Materials and Methods

Materials

1. Acrylate-oxetane monomer[†]

The acrylate-oxetane monomer was obtained after four steps reactions.

2. Acrylate-polyester

To have a binder bearing both UV and thermally reactive functionalities, one third of the hydroxy groups are converted into an acrylate function. Acrylation consists of adding dropwise at 0 °C in a dry medium, a solution of acryloyl chloride (ACl) (0.05 g/ml) to a solution of an oligoester obtained by direct catalysed esterification of trimethylolpropane (0.15 mole), neopentylglycol (1.21 mole), adipic acid (0.20 mole) and isophtalic acid (1 mole). For example, 0.5 g of ACl (5.5 10^{-3} mole) is added to a solution of 5g (1.65 10^{-2} mole OH) and 0.56 g of triethylamine (6.0 10^{-3} mole) in dichloromethane. After the reaction, the solution is washed with an aqueous solution of ammonium chloride and water to remove the produced salt, $(CH_3CH_2)_3NH^+Cl^-$. It is then dried with $MgSO_4$. The solvent and remaining TEA are removed under reduced pressure. The degree of acrylation of the polyester is 30% (NMR) and its molecular weight is 1970 g/mole (GPC).

3. Material mixtures used for the experiments

UV/UV dual-cure

93 % (w) Monomer

4 % (w) Irgacure 819 (Ciba Specialty Chemicals)

3 % (w) Cyracure UVI-6974 (Dow Chemicals)

Substrate: KBr plate

UV/Thermal dual-cure

39.6 % (w) Binder: Acrylated polyester

39.6 % (w) Thermal crosslinker: Blocked polyisocyanate (Desmodur BL3272 MPA, Bayer)

19.8 % (w) Reactive diluent (see text)

1% (w) Photoinitiator: Irgacure 819 (Ciba)

Methods

1. UV/UV process

For all experiments with the acrylate-oxetane monomer, 20-30 microns liquid films were prepared. A cut-off filter (allowing only wavelengths higher than 385 nm, where the radical photoinitiator is solely absorbing light) was combined with the lamp in the first step of the process in order to initiate only the radical polymerization. The second step was performed without the filter to allow the cationic photoinitiator to absorb light and start the second cure. The samples for FTIR and DSC (Perkin Elmer) measurements were applied on KBr plates and irradiated using a Uvicube curing system (Dr. Hönle), which was equipped with an F lamp (400 W). The samples were irradiated for 5 minutes and the UV and the visible doses were measured using an UV Power Puck radiometer. The measured doses were: Vis.= 10.6 mW/cm^2, UVA= 21 mW/cm^2 and with the filter: Vis. = 10.6 mW/cm^2. Inhibition of the radical polymerization by O_2 was prevented by exposing the samples to radiation either under a N_2 atmosphere or by applying a polypropylene foil on the liquid film.

2. UV/Thermal process

30-50 micron liquid films were irradiated under nitrogen using a Dr. Honle UV curing system equipped with an H lamp. At 20 cm height, the light intensity is (mW/cm^2) (UV Power Puck): Vis. =17; UVA= 24. The UV dose received by the coatings is 0.24 J/cm^2. The thermal curing was performed without vacuum or gas extraction. The coatings were cured at 120 °C for two hours.

3. FTIR and DSC (Tg) measurements

The dual-cure processes were studied by transmission FTIR using a Bio-Rad infrared spectrometer. Liquid films were applied on KBr plates using a wire bar coater. For the study of the UV/UV system, the cure was evaluated by following the decrease of the acrylate C=C (1630 cm^{-1}) and oxetane C-O-C (985 cm^{-1}) bands, after the UV induced radical and cationic steps, respectively. As for the UV/Heat system, the extent of the cure of the UV and thermal steps was assessed by monitoring the disappearance of the acrylate C=C (810 cm^{-1}) and OH (3450 cm^{-1}) bands, respectively. Tg measurements were carried out using a Perkin Elmer DSC.

Results and Discussion

UV/UV system

A two-step UV/UV coating process is possible by developing a monomer that combines two different functional groups. One of those groups can be polymerized via a radical mechanism (acrylate) and the second via a cationic mechanism (oxetane). In such a system, the free-radical step is to be carried out first, because during the cationic step, the photoinitiator undergoes photolysis through a radical reaction.[16] Therefore, the cationic photoinitiator would, if activated in the first step, initiate both the radical and the cationic polymerizations. The free-radical photoinitiator will not initiate the cationic step. The selected photoinitiators have different absorption spectra. The radical photoinitiator (Irgacure 819) is absorbing light between 200 and 420 nm. The cationic photoinitiator (Cyracure UVI-6974) is only absorbing light below 380 nm. Therefore, by using a filter that cuts off the light between 200 and 385 nm, we can selectively excite the radical photoinitiator during the first step and initiate only the free-radical photopolymerization.

The efficiency of the dual-cure process, that is the occurrence of subsequent UV-initiated radical and cationic polymerizations, was studied using the acrylate-oxetane monomer from scheme 1. The transmission FTIR spectra depicted in Figure 1 show that the first step, namely the radical cure, was performed successfully since the FTIR spectrum shows an almost complete disappearance of the acrylic C=C peak at 1630 cm^{-1}. This generated a soluble polymer with polyacrylic linear chains bearing oxetane side chains. When the second irradiation (without the filter) had been performed, the large decrease of the absorption of the oxetane C-O-C peak at 985 cm^{-1} indicated that the second cationic polymerization had also taken place. This latter allowed the formation of an insoluble 3D network. These findings could be confirmed by DSC measurements. The film obtained after the first step shows a glass transition temperature (Tg) of −16 °C. When the cationic polymerization step had been performed, the resulting cured film had a Tg of +34 °C. This large increase of the Tg observed between the first and second step is indicative of the formation of a highly crosslinked polymer film.

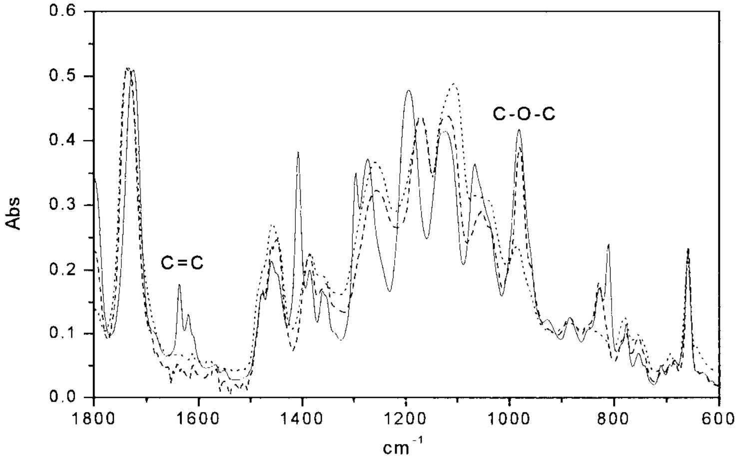


Figure 1. Dual-cure of acrylate-oxetane: Before cure (solid), step 1 (dash) and step 2 (dot); (UV dose (J/cm^2): 3.6 (step1), 12.6 (step2))

UV/Heat system

The formulation used for this study contains hexanedioldiacrylate (HDDA, UCB) as reactive diluent, besides the components mentioned previously. The coating obtained after the UV step is touch dry and has a Tg of 2 °C. Occurrence of the cure is confirmed by the disappearance of the acrylate double bond peak at 810 cm^{-1} (Figure 2.a). After the thermal step, the Tg of the coating increased by 35 °C, thus indicating that the second step was successful. This is also consistent with the large decrease of the OH band at 3550 cm^{-1} (Figure 2.b). These results show that the two steps of the dual-cure process can be performed separately and efficiently.

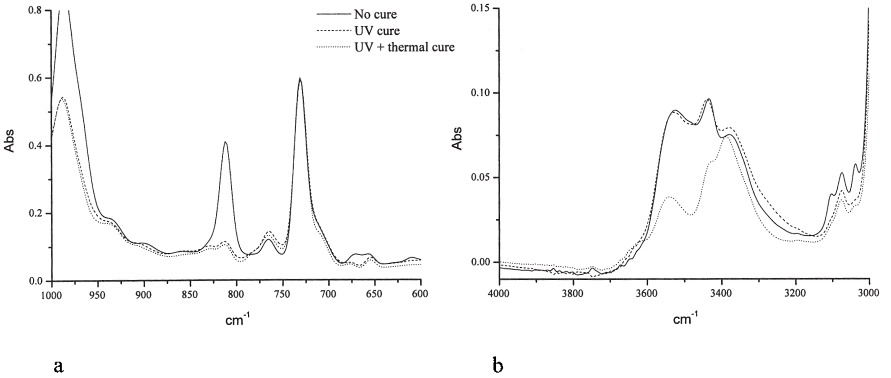


Figure 2. Study of the effectiveness of the UV/Heat process by FTIR

To study the influence of the reactive diluent on the second step of the process, three diluting acrylates having a functionality ranged between 1 and 3 were used. These monomers are isobornylacrylate (IBOA, UCB), hexanediol diacrylate and trimethylolpropane triacrylate (TMPTA, UCB). The extent of the thermal reaction involving OH and blocked NCO (OH/NCO=1) was evaluated by transmission FTIR. As shown by the FTIR spectra (Figure 3) of the three systems, higher functionality (IBOA<HDDA<TMPTA) of the reactive diluent, leads to lower conversion of the OH group, and therefore to a lower degree of thermal cross-linking. This behavior is probably due to the network generated by the UV step, since an enhancement of the functionality of the diluent leads to a denser UV generated network. This leads to a reduced diffusion of reactive species and thus to a lower conversion of the OH groups during the second step.

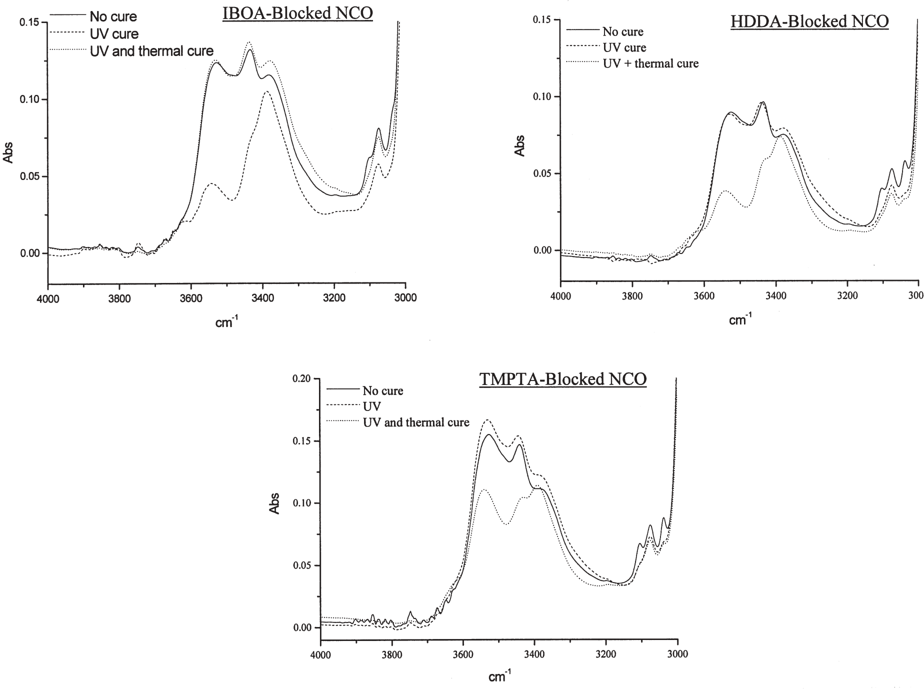


Figure 3. Effect of the reactive diluent functionality on the second step of the process

Conclusion

The two dual-cure processes combining on one hand a UV-initiated radical and on the other hand a cationic polymerization or a thermal addition reaction were shown to be effective in producing deformable cross-linked coatings in two separate steps. The efficiency of the second cure of the UV/Heat process was affected by the cross-linking density generated by the first cure.

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† Full synthetic details will be given elsewhere.

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