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Study the Curing Behavior and Mechanical Properties of Pigmented UV Curable Epoxy Acrylate in the Presence of Different Acrylate Monomers

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ABSTRACT

Non-pigmented and pigmented UV-curable coatings are being used extensively in adhesive, printing and electrical industries. One of the main obstacles for the extension of their use in other industries is the inferior curing of thick pigmented formulations. In this work, the pigmented and non-pigmented formulations containing different acrylate monomers with different structures and functionalities were applied to obtain pigmented acrylate films by UV exposure. The conversion and mechanical characteristics of the systems were correlated. The results showed that there was a significant interaction between the presence of pigment, the type of reactive diluents and mechanical properties of the coatings. It seems that cured films containing isobornyl acrylate had a good tensile strength. For obtaining higher hardness and T_g, monomers with higher functionality such as dipentaerythritol pentaacrylate and dipentaerythritol hexaacrylate was needed. Prog. Color Colorants Coat. 7(2014), 237-244 © Institute for Color Science and Technology.

1. Introduction

The use of UV curable coatings increased significantly in the recent years. This is due to their excellent characteristics such as rapid processing and environmental friendliness of this technology. Moreover, these coatings are highly crosslinked due to the use of multifunctional reactive diluents in their formulations. In general, these coatings have very good physical, mechanical and chemical properties [1-6].

Despite these merits, there are still some challenges associated with UV-curable coatings. One of the most important challenges is the inferior curing of pigmented UV-curable systems which leads to the poor physical and mechanical properties of the cured films. In the pigmented systems, the pigment particles usually absorb and scatter some part of the UV light and prevent the penetration of photons through the deep layers. In the past two decades,

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*Corresponding author: ebrahimi@aut.ac.ir many attempts were accomplished to overcome this problem by the modification of photo initiator systems and the formulations. For example, Decker et al. showed that organophosphorus compounds i.e. acylphosphine oxide photo initiators, could considerably improve the polymerization rate and the cure extent of pigmented systems mainly because of their fast photolysis [7].

Macarie et al. employed a combined photo initiator system (i.e acylphosphine oxide with conventional photo initiators) and found that the conversion improved considerably (about 10-15%) in comparison with the system which had only acylphosphine oxide photo initiator [8].

On the other hand, several researches were carried out to investigate the effect of formulations (i.e. the type and amounts of the oligomer and reactive diluents) on the curing and mechanical properties of non-pigmented UV-curable coatings [9-15].

However, there are a few open literatures on the effect of formulation on the pigmented UV-curable coatings [16-18]. For instance, Pietschmann et al. studied a pigmented UV-curable coating in 2002 and reported that multifunctional acrylate monomers with higher functionality showed a higher reactivity with respect to chain growing reactions and hence had a higher potential for crosslinking.

In another research, Macarie et al. used different pigments in a UV-curable formulation and claimed that titanium dioxide was the most difficult pigment for UV-curable coatings due to its absorbing and scattering effect in a wide range of UV region. To best of our knowledge, there are a few articles on the curing and mechanical properties of pigmented UV-curable coatings.

The present work was devoted to study the influence of TiO_2 pigment and reactive diluents type on the mechanical properties of the UV-cured epoxy acrylate coatings. The formulations contained conventional UV curable photoinitiator systems (i.e. benzophenone) and acrylate monomers with different structures and functionalities were prepared to observe the role of pigmentation on the curing and mechanical properties of different acrylated systems.

2. Experimental

2. 1. Materials

Bisphenol A epoxy diacrylate resin (EA), isobornyl acrylate (IBOA), 1,6-hexandiol diacrylate (HDDA), tripropyleneglycol diacrylat (TPGDA), trimethylol-propane triacrylate (TMPTA), pentaerythritol triacrylate (PETA), dipentaerythritol pentaacrylate (DiPEPA) and dipentaerythritol hexaacrylate (DPHA) were obtained from Jintianyoumao international Co., China. The chemical structures of the multifunctional acrylate monomers are shown in Figure 1.

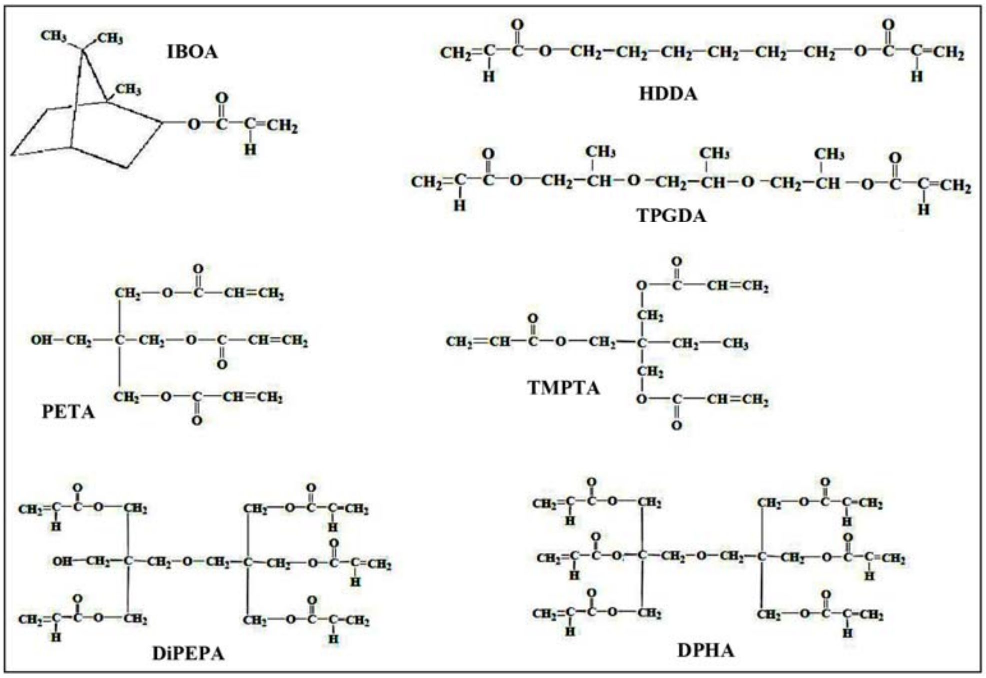

Figure 1: The chemical structure of different acrylate monomers .

Benzophenone (photoinitioator) and triethylamine (co-initiator) were obtained from Merck. The rutile type titanium dioxide pigment (TiO_2) was provided by Crystal Company of Saudi Arabia. This pigment is recommended for UV-curable systems by the supplier**.**

2.2. Sample preparation

For the preparation of non-pigmented samples, a specific amount of epoxy acrylate oligomer and one of the reactive diluents (i.e. weight ratio of 60:40) were well mixed. Then the benzophenone was added and mixed completely. Finally triethylamine was added to the mixture.

To provide pigmented formulations, a pigment content of 10%wt was chosen. First TiO_2 was added to the mixture of oligomer and monomer and well mixed and milled until a particle size of <5 microns was achieved. Then benzophenone and triethylamine were added to the mixture. The liquid coating formulations listed in Table 1 were applied to glass plates with a film applicator to obtain films of thickness of about 60 µm. The wet films were exposed to UV radiation using a medium-pressure mercury lamp (80 W. cm^{-2}, belt speed 0.5 m. min^{-1}).

2. 3. Degree of conversion

The degree of photopolymerization of all formulations was determined by using an FT-IR spectrophotometer (Perkin–Elmer1600).

The FT-IR spectrum was recorded at the beginning and after the end of photo-irradiation in transmission mode at a resolution of 4 cm^{-1}. The amount of double vinyl bonds remaining in the sample exposed to irradiation is shown by the intensity of the peak at 1637 cm^{-1} referring to the C=C stretching of the vinyl group and 816 cm^{-1} which refers to the C=C twisting. Both have been used in the study of polymerization of acrylates and methacrylates. We chose the 1637cm^{-1} absorption because it was stronger than the absorption at 816 cm^{-1}. The spectra were normalized with the carbonyl peak at 1719 cm^{-1} as an internal standard to account for variation in sample thickness and instrument recording. The degree of conversion was directly related to the decrease of 1637 cm^{-1} absorption on the FT-IR spectra as follows:

$$\text{Degree of conversion} = [(A_0 - A_t)/A_0] \times 100 \qquad (1)$$

where A_0 is the peak area at 1637 cm^{-1} before curing and A_t is the peak area at 1637 cm^{-1} after curing.

2. 4. Glass transition temperature (T_g)

The T_g values of the samples were determined by using a differential scanning calorimeter (DSC-Pyris 1, Perkin-Elmer) at a scanning rate of 10 °C min^{-1}. The T_g values were determined from the mid-point in the thermogram, as measured from the extensions of the pre- and post-transition baselines.

Table 1: The specifications of the used formulations.

Sample code ingredients	A	B	C	D	E	F	G	A1	B1	C1	D1	E1	F1	G1
EA	60	60	60	60	60	60	60	54	54	54	54	54	54	54
IBOA	40	-	-	-	-	-	-	36	-	-	-	-	-	-
HDDA	-	40	-	-	-	-	-	-	36	-	-	-	-	-
TPGDA	-	-	40	-	-	-	-	-	-	36	-	-	-	-
TMPTA	-	-	-	40	-	-	-	-	-	-	36	-	-	-
PETA	-	-	-	-	40	-	-	-	-	-	-	36	-	-
DiPEPA	-	-	-	-	-	40	-	-	-	-	-	-	36	-
DPHA	-	-	-	-	-	-	40	-	-	-	-	-	-	36
TiO_2 (wt% based on total formulation)	-	-	-	-	-	-	-	10	10	10	10	10	10	10
Benzophenone (wt% based on binder)	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Triethylamine (wt% based on binder)	4	4	4	4	4	4	4	4	4	4	4	4	4	4

2. 5. Pendulum hardness

The Konig hardness of the films was measured by monitoring the damping time of the oscillations of a pendulum hardness instrument by Sheen company. This test was done according to ASTM 4366 and the measurements should be applied on the glass panels.

2. 6. Tensile strength

Tensile strength of the samples was obtained using a Santam tester. Rectangular samples were pulled to rupture at a rate of 10 mm/min using the procedure defined by ASTM D 412. The values reported for tensile strength are the average of five replicates of each of the samples.

3. Results and discussion

3. 1. Extent of conversion

The conversions for the photopolymerization reactions of all formulations were evaluated on the basis of their FTIR spectra. The conversions of these samples are presented in Figure 2.

Figure 2 shows that by increasing the functionality of acrylates, the conversion decreases, since it is well known that the functionality of acrylates has a considerable impact on the extent of polymerization [19-21]. Formulations containing IBOA (i.e. A and A_1) has the higher conversion among other formulations, since there is higher distance between acrylate groups in the formulations containing IBOA due its special structure [22-23].

With rising acrylate functionality, the content of residual unsaturations picks up. Therefore, in case of formulations containing DiPEPA and DPHA (i.e. F, G. F_1 and G_1), the conversion decreases dramatically. This is mainly because of the higher viscosities of these formulations and more complexity of the formed network for higher functional systems. The viscosity affects the initiation step through the radical addition to the monomers, which can be dependent on the diffusion of the reactants in the medium.

Therefore, the conversion of the polymerization is controlled by the diffusion limitations of the reacting media and not by the amount of unreacted monomer in the system. Hence, the increase of the viscosity of the formulations may cause a decrease in reaction between the functional groups on account of diffusion limits of reactive species and influence the curing process of the coating.

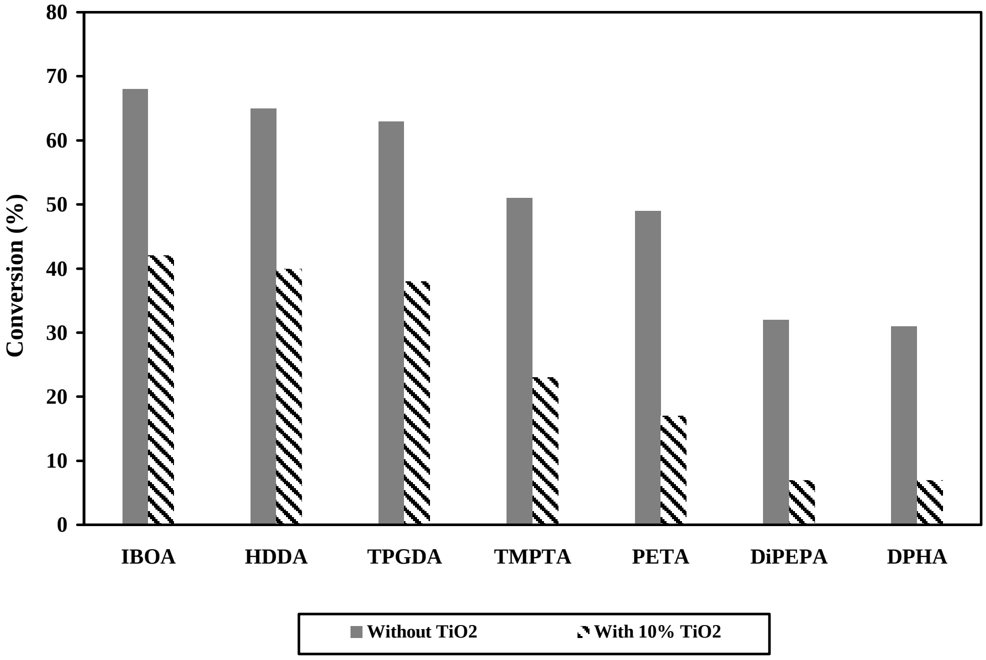

Figure 2: The conversion plots of different formulations with and without TiO_2.

The extent of reaction for pigmented formulations was considerably less than that for non-pigmented formulations which is because of filtering effect of TiO_2 particles. It seems that the interference effect of TiO_2 particles on the extent of curing was different for these formulations and followed the bellow order.

DPHA and DiPEPA> PETA > TMPTA>> TPGDA and HDDA>>IBOA

The least interference effect of the pigment particle on the curing of formulations A, B and C can be explained by the lower viscosity of these formulations and the least interaction between TiO_2 particles with these systems.

3. 2. Glass transition temperature

The T_g of the formulations is shown in Figure 3. As it is shown in Figure 3, the T_g of the formulations increased with increasing functionality of the systems. It is due to the formation of rigid networks and increasing of crosslink density of cured films. As a result, crosslinking restricts the mobility of chain segments, therefore causes the increasing of the T_g of the systems. The decrease of T_g for pigmented cured films could be explained by the lower conversions and filtering effects of the pigment particles on the curing of the films. Although TiO_2 could reduce the chain mobility in polymer network and therefore increased T_g, its filtering effect was more dominant.

3. 3. Pendulum hardness

The hardness of formulations is shown in Figure 4. As can be seen, the trends for hardness of the systems are almost the same as the trends for the T_g, since both are restrictly depending on the extent of crosslink density of the cured films. Therefore, similar discussion can be adopted for the hardness. The higher crosslink density results in the higher hardness.

3. 4. Tensile strength

The tensile strength plots of the formulation are shown in Figure 5. According to the trends in Figure 5, the formulations containing IBOA (i.e. A and A_1) have the high elongation on account of having long chains and cyclic structure.

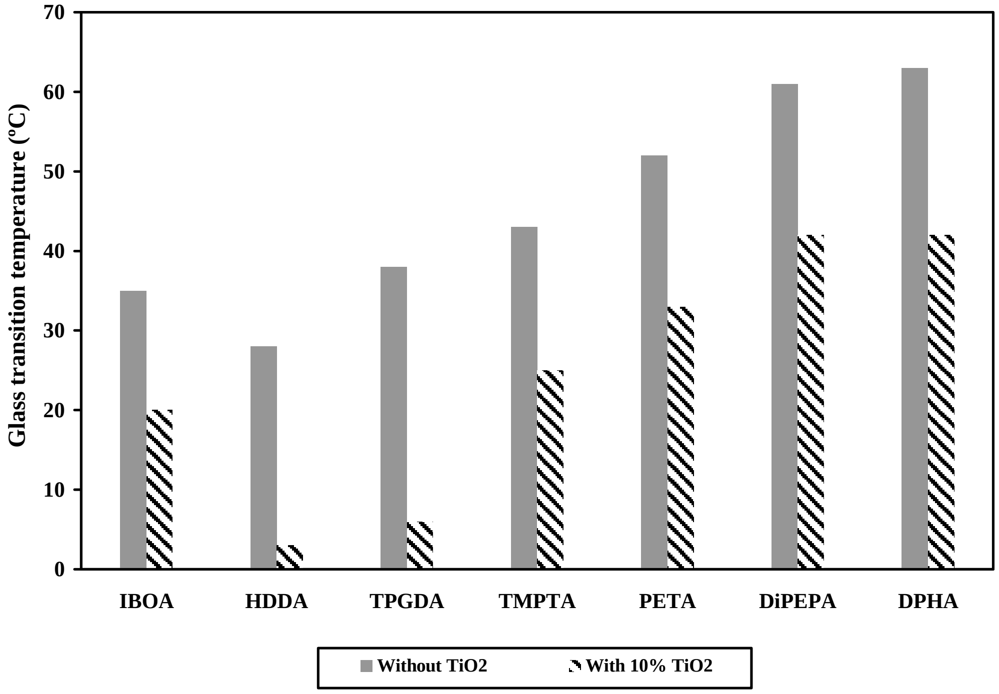

Figure 3: The T_g plots of different formulations with and without TiO_2.

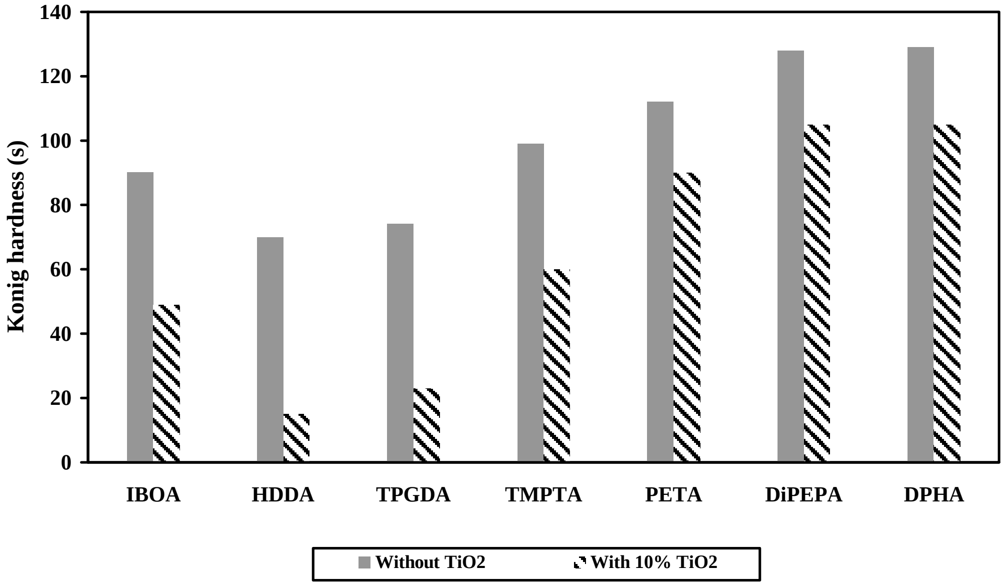

Figure 4: The hardness plots of different formulations with and without TiO_2.

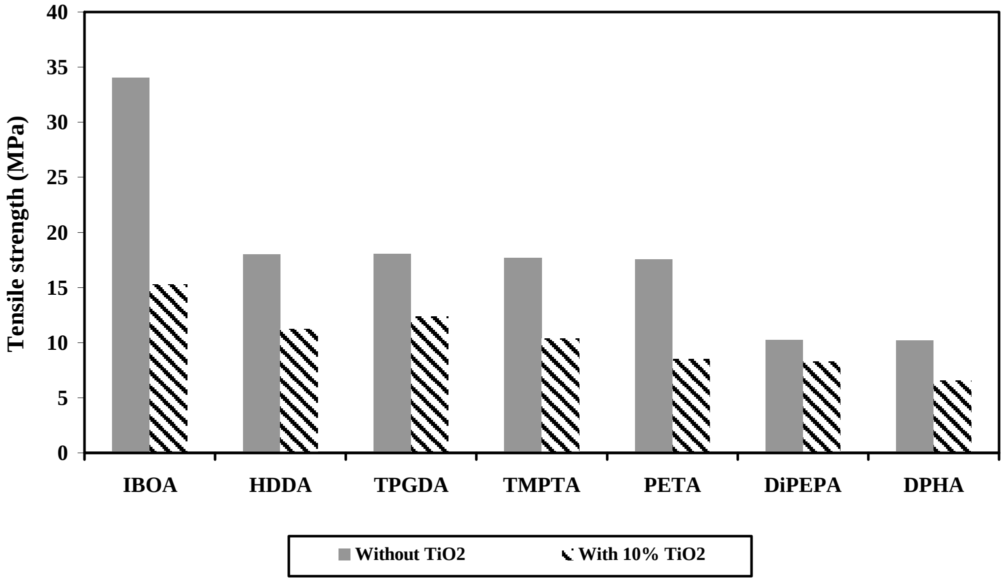

Figure 5: The tensile strength plots of the formulations with and without TiO_2.

On the other hand, formulations containing two and three functional monomers have higher tensile strength than formulations containing five and six functional monomers. Because of forming very rigid networks in the case of formulations containing DiPEPA and DPHA (i.e. F, G. F_1 and G_1) due to their high functionality, their tensile strength decreased. The comparison of tensile strength difference of these formulations reveals that there is remarkable difference between the tensile strength of non-pigmented and pigmented formulations especially in the case of lower functionalities. This behavior is the result of inferior effect of TiO_2 on the curing. However, in higher functional monomers (i.e. F, G. F_1 and G_1) the difference between the tensile strength of non-pigmented and pigmented formulations is less pronounced.

4. Conclusion

The formulations contained different acrylate monomers with different structures, functionalities and TiO_2, were used to obtain UV curable pigmented formulations. The conversion and mechanical characteristics were also calculated.

The comparison of conversion difference of these monomers reveals that there is dramatic difference between the conversions of non-pigmented and pigmented formulations. The T_g of the acrylate formulations increases with increasing functionality of monomer and the similar discussion can be adopted for the hardness. Also, there is a remarkable difference between the tensile strength of non-pigmented and pigmented formulations in the case of lower functionalities.

As a result, cured films containing IBOA are claimed to have good strength, even though to obtain higher hardness and T_g, formulations containing higher functional acrylate monomers such as DiPEPA and DPHA is needed.

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