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Studying the effect of hyperbranched polymer modification on the kinetics of curing reactions and physical/mechanical properties of UV-curable coatings

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ABSTRACT

A polyester-amide based hyperbranched polymer with hydroxyl end-groups is modified by the aid of acrylic functionalities. Two levels of modification, i.e. 40% and 65%, are considered. The unmodified hyperbranched polymer and the modified ones are added to UV-curable monomeric and oligomeric systems. Rheology measurements are conducted to investigate the effects of hyperbranched polymer on the rheological behavior. In order to assess the curing kinetics and physical/mechanical characteristics of the samples, photo-DSC and DMA experiments are exploited, respectively. The effect of viscosity and number of UV-curable functionalities of the hyperbranched polymer on the curing level and kinetics of the curing reactions are discussed. Dynamic mechanical analysis shows that the addition of hyperbranched polymer in the formulation increases a 25% in storage modulus of the glassy region and cross-linking density of the UV-curable coating. Furthermore, it is also seen that the existence of the hyperbranched polymer increases the viscosity of Trimethylolpropane triacrylate (TMPTA)-based system while it is decreasing the viscosity of oligomeric-based of the epoxy di-acrylate system. It is obtained that the hyperbranched polymer makes the curing level in the monomeric and the oligomeric system, improve up to 15% and 10% correspondingly. It is also observed that T_gs of the coatings containing the hyperbranched polymer increases up to 5.9 °C.

1. Introduction

Photo-polymerization technology, due to its favorable advantages, i.e. solvent free systems, optimized energy consuming and being altogether economical, is rapidly growing. The polymeric systems cured by radiation have numerous applications in the different industries such as coatings, paints and printing inks, adhesives, composite and dental remedial materials. Furthermore, the unique characteristic of such materials such as polymerization at irradiated regions, provides the possibility of obtaining high resolution images that are applicable in preparation of printing plates, optical disks and micro circuits [1–7].

On the other hand, the radiation-curable coatings face some challenging limitations in the research and industrial zones. Various approaches have been proposed in order to improve the curing behavior of these coatings. Utilizing multi-functional oligomers and monomers, exploiting multi-mechanism curing process, using glass beads which ease the radiation to penetrate and finally employing hyperbranched polymers are referable. This study is focused on investigating the effect of hyperbranched polymers on improving the curing behavior [2,3,8–12].

Hyperbranched polymers are highly branched structures on which multitude of functional end-groups exist. The particular structure of these polymers renders them an especial flow- and process-ability that puts them in the center of attention in recent years. The multiplicity of functional end-groups makes it possible to control the reactivity and other properties such as viscosity, solubility and adhesion characteristics [13–22].

Beside the nature and the structure of the backbone, the physical and chemical properties of hyperbranched polymers are largely dependent on the number and the nature of their end-groups, so the chemical modification of the end-groups gives the possibility of designing the macromolecules with desired properties for any particular applications. Chemical modification of end-groups can

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result changes in the solubility, reactivity, rheological behavior and polarity of the molecule [2,15–20].

In this present research, the effects of end-group modification of a hyperbranched polymer (polyester-amide based) by the aid of acrylic acid on the viscosity of monomeric and oligomeric systems have been studied. In the next step, the kinetics of curing reactions of these systems in the existence of the modified hyperbranched polymer is focused. Eventually, the physical/mechanical properties of the coatings made of the modified systems are investigated.

2. Experimental

2.1. Materials

The hyperbranched polymer is a polyester-amide based with ten hydroxyl end-groups under the trade name of Hybrane H1500 which was provided by DSM Company. Acrylic acid, Toluene, Benzoquinone, Calcium hydroxide, Ethyl acetate and DMF were purchased from Merck Company. TMPTA monomer, Epoxy di-acrylate oligomer (Code: 6215-100), Benzophenone initiator and amine co-initiator (Code: 641) were acquired from Eternal, Taiwan. TPO initiator was from BASF. Petroleum ether and p-Toluenesulfonic acid were purchased from Taw Faravar Shimi and Kimia Tehran Acid companies, respectively.

2.2. Modification of HP with acrylic acid

H 1500 was solved in toluene and loaded in a three-necked flask equipped with a contact thermometer lug, a nitrogen gas input and a Dean-Stark lug with a condenser and heated. The solution was stirred using a magnetic stirrer. To prevent the reaction of double bonds 1 wt% hydroquinone also added and the reaction was performed with toluene reflux at 110 °C. 1.5 wt% of catalyst p-TSA was also added. In the next step acrylic acid was added drop-wise. Two different methods were selected to perform the modifications. In the first rout, 20% excess acrylic acid reacted with HP1 during 2 h. The product is called HP2. In the second rout, 30% excess acrylic acid reacted with HP1 during 4 h. The product is called HP3. Calcium hydroxide was added subsequently to neutralize p-TSA, after which filtration under pressure was carried out. Precipitation was performed in petroleum ether to eliminate unreacted acrylic acid, followed by precipitation in distilled water.

2.3. Samples preparation

The modified hyperbranched polymer was solved in ethyl acetate prior to its addition to radiation-curable coating system. Then, 5 wt% of the hyperbranched polymer was added to the coating system. After being mixed and homogenized (magnetic stirrer and butterfly shaft mixer at 1500 rpm for monomeric and oligomeric system were used respectively), the samples were placed inside a vacuum oven at 40 °C for 24 h to ensure the solvent removal.

The prepared samples were then mixed by 4 wt% of Benzophenone, 4 wt% of amine co-initiator and 4 wt% of TPO. These materials were already solved in ethyl acetate. The final mixtures were placed inside a vacuum oven once more ($T = 40\,^{\circ}\mathrm{C}$, $t = 24\,\mathrm{h}$) in order to ensure solvent evaporation. They are now ready for curing behavior measurements and film formation.

2.4. Nomenclatures

HP1, HP2 and HP3 are used for unmodified, 40% modified and 65% modified hyperbranched polymer, H1500. E for samples based on epoxy di-acrylate and T for those based on TMPTA.

2.5. FTIR measurements

FTIR spectra of the hyperbranched polymers were collected on PerkinElmer-spectrum model one spectrometer in the range of 400–4000 cm^{-1}.

2.6. NMR measurements

NMR spectra were recorded on an Avance-300 spectrometer (Bruker) in deuterated chloroform. The frequency was adjusted at 300 MHz.

2.7. Rheological measurements

Viscosity measurements were performed by an MCR 300 rheomechanical spectrometer made by Anton Paar, Austria. Coaxial and parallel plates geometries were considered for monomeric and oligomeric samples, respectively. The measurements were conducted at 25 °C across the frequency range of 0.01–1000 s^{-1}. Neat monomeric and oligomeric samples along with those containing 5 wt% of modified hyperbranched polymers underwent rheological measurements.

2.8. Real-time photo-DSC measurements

Photo-DSC measurements were taken into consideration to investigate the curing behavior and kinetics of the samples. To this aim a DSC instrument model DSC1 made by Mettler Toledo, England was used. This device is equipped with a UV source model LC8 Lightning cure made by Hamamatsu, Japan. This source possesses a nominal power of 4500 $\mathrm{mW/cm}^2$ and is able to be adjusted at different $\lambda_{\max}$ by various filters. In this study $\lambda_{\max}$ is 365 nm and the power is equal to 4% of total power. The intensity of the radiation is 20 $\mathrm{mW/cm}^2$.

To perform these measurements, about 1–2 mg of each sample were placed inside an aluminum lidless pan and isothermal DSC during 180 s is continued at 25 °C. Irradiation lasted for 180 s one time and a further 3 s.

2.9. Dynamic mechanical analysis (DMA)

To assess the elastic behavior of the samples DMA measurements were carried out using a DMA device model DMA242C made by Netzsch, Germany. The device performs between the modulus range of 10^{-3} to 10^{6} MPa and frequency range of 0.01–1000 Hz. Tensile geometry was selected for conducting the experiments.

In order to prepare samples for DMA measurements, free films made of UV-cured coatings were prepared. To this aim, UV-cured coatings were applied on glass substrates at 60 μm thickness afterwards the samples were transferred inside a radiation cabin using a conveyor at 0.3 m/min speed and 25 $\mathrm{mW/cm}^2$ power to ensure complete curing.

3. Results and discussion

In the previous study by Mirshahi et al. [23], it is proved that the acrylic functionalities are replaced with hydroxyl end-groups of the pristine hyperbranched polymer. The unmodified and modified hyperbranched polymers, i.e. HP1, HP2 and HP3 have been characterized by FT-IR and NMR as shown in Figs. 1–3. The specifications are as Table 1.

Fig. 1 shows the normalized FT-IR spectrum of unmodified and modified hyperbranched polymer, comparing the peak corresponding to the hydroxyl group and carbonyl of ester functional group confirms the esterification reaction. There is a broad peak with medium intensity in the vicinity of 3200–3500 cm^{-1} which