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Synthesis and properties of quick-drying UV-curable hyperbranched waterborne polyurethane coating

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ABSTRACT

Ultraviolet light (UV)-curable hyperbranched waterborne polyurethane (UVHWPU) resins were synthesized using polypropylene glycol (PPG)-1000, dimethylol propionic acid (DMPA), trimethylol propane (TMP), isophorone diisocyanate (IPDI) as core moiety, and 2-hydroxyethyl methacrylate (HEMA) as capping agent. The preparation methods of the UVHWPU resins were studied and an optimum recipe was given by selecting the proper dosage of DMPA, PPG-1000 and TMP. The structure of hyperbranched resins was characterized by C^{13}-NMR spectra and Fourier transform infrared (FTIR) spectroscopy. The type and dosage of photoinitiator were determined, and the properties of UVHWPU coating with excellent performance were examined.

1. Introduction

Ultraviolet (UV)-curable coating is a class of coatings having none or a little volatile organic compounds. This type of coatings offers many advantages including broad range of formulation, lesser energy consumption, instant drying, can coat heat sensitive substrate and low space. Additional advantage of UV-curable coating offers a very rapid curing evev at ambient temperature [1–3]. UV-curable coating is a kind of eco-friendly polymer which is initiated by photoinitiators and is then crosslinked [4,5]. This technique have been widely used in different industries such as solid printing plates, stereolithography that yield enhanced photo speed, adhesives and many more [2,6–11].

Waterborne coatings using UV-curing technology have gained increasing interest because they can decrease air pollution, reduce the risk of fire, improve aspects of occupational health and safety, lower energy consumption and have a high curing speed [12]. This offers some advantages of instant drying, broad range of formulation, economic, energy saving, and so on [13,14].

Since solvent-based UV-curable resin has higher viscosity, reactive diluents should be used to adjust its viscosity, rheological behavior, and curing velocity. Though most of the reactive diluents are spent in the reaction, the unreacted part is toxic to the human body and the environment. This problem can be solved using waterborne UV-curable coating, which does not need reactive diluents and is more environment-friendly than a solvent-based coating. However, studies show that it has some deficiencies like lower UV curing velocity and lower efficiency. Because of this the coating needs dewatering before UV curing. Waterborne UV-curable coating also has poor resistances to water and solvents [15,16].

Hyperbranched polymers belong to a class of synthetic tree-like macromolecules called dendritic polymers. They are polymers with densely branched structure and a large number of end groups. Dendritic polymers include dendrimers which have completely branched star-like topologies and hyperbranched polymers which have imperfectly branched or irregular structures [17–20]. Interesting physical properties of hyperbranched polymers is their considerably different viscosity characteristics in comparison with their linear analogues. It also has advantages like lack of intermolecular entanglements, and high chemical reactivity, solubility, and miscibility. The high-density functional terminal groups on hyperbranched polymers also offer the potential for tailoring their structure through the conversion of end groups to chemically suitable moieties [21,22]. Hyperbranched polyurethane (HPU) are mainly synthesized by modifying different hydroxyl-terminated hyperbranched polymers with various semiadducts of urethane monoacrylate [23]. As the hydroxyls in HBP are partially modified with anhydrides and neutralized with triethylamine, the HPU become waterborne [24]. HPU have been widely applied in coating, adhesive, photoresist, printing ink and nanocomposite as modifier, crosslinker and other additives to reduce viscosity, accelerate reaction, improve mechanical properties and enhance toughness of matrix [25,26]. Due to the nature of compactly packed periphery, high density, crosslinking and lack of chain entanglements, HPU are usually too brittle to form a freestanding films, and the mechanical performance of the films are weak [27].

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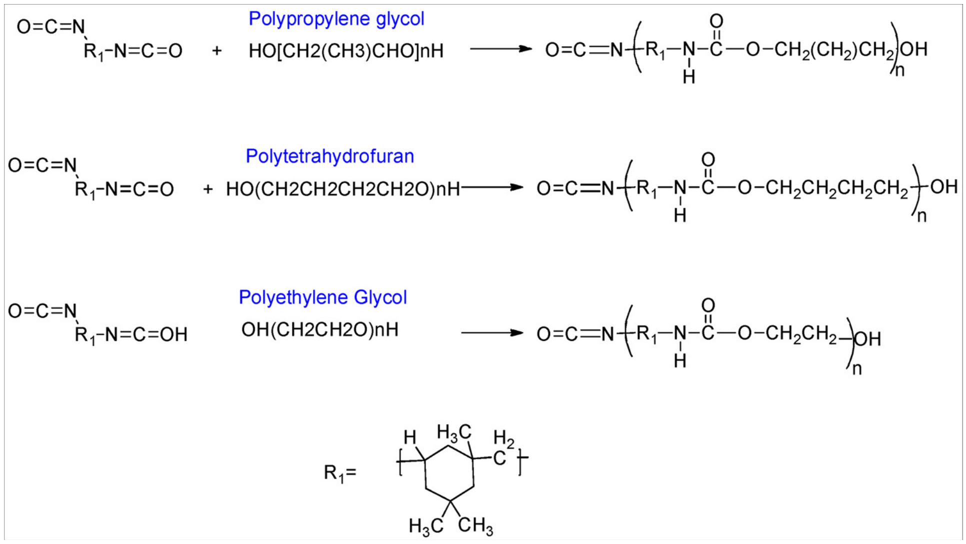

Scheme 1. Polyurethane formation from reaction of isophorone diisocyane and polyols (PPG,PTHF,PEG).

Table 1
Effect of polyether diols on the UV curing rate of the linear polyurethane coating.

Polyether diols	Appearance and viscosity (Ford 4# viscosity cup) of coating	Curing rate of coatings
PEG-1000	blue light, translucent, 120s	No curing over 50 min
PPG-1000	blue light, translucent, 42s	Curing in 30 min
PTHF-1000	translucent, 680s	Curing in 65 min

Isophorone diisocyanate (IPDI) is one of the most widely used aliphatic isocyanates. IPDI consist of two different types of isocyanate: aliphatic and cycloaliphatic groups. Given this two groups in one compound, IPDI have unequal reactivity of primary and secondary isocyanate groups in making prepolymer with low molecular distribution [28].

Although many researches have concerned about UV-Hyperbranched Waterborne Polyurethane (UVHWPU), little work has been reported on the selection of photosensitive resin in hyperbranched waterborne urethane coating and the performance comparison of UVHWPU with the linear coating. The aim of present work is to prepare hyperbranched waterbase polyurethane (HWPU) resins based on the choice of UV-sensitive polymeric diols and to examine their characteristic properties. The obtained hyperbranched resins were characterized by Fourier transform infrared (FTIR) and C^{13}- NMR spectra.

2. Experimental

2.1. Materials

Polypropylene glycol (PPG)-1000), polyethylene glycol (PEG)-1000 and polytetrahydrofuran (PTHF)-1000 (where Mn is 1000 g/mol, Tianjin, China), were dried and degassed at 90 °C for 6 h under vacuum.

Table 3
Effect of carboxyl content on the property of UVHWPU.

Sample	Carboxyl group content(mmol/g)	Appearance of 30% resins	Stability
PU1	0.28	light yellow	deposit within one week
PU2	0.30	milky white with light yellow	part deposit within three months
PU3	0.40	light white and translucent	more than one year stable
PU4	0.50	light white and translucent	more than one year stable
PU5	0.60	light white and translucent	more than one year stable

2-Hydroxyethyl methacrylate (HEMA, Dow Corning reagent, Gangzhou, China). Dimethylol propionic acid (DMPA, Shanghai Meichen Chemical Co., China), were dried over 5 Å molecular sieve before use. Isophorone diisocyanate (IPDI, Bayer Co., German), 2,4,6-trimethyl benzoyldiphenyl phosphine oxide (TPO, Suzhou Taiyang Chemical Co., China), 2-hydroxy-2-methylphenyl-propan-1-one (Irgacure 1173, Shanghai Ciba-Gao Qiao Chemicals Co., China) and 1-hydroxy-clohexylphenylketone (Irgacure 184) were used without further purification. Dibutyl tin dilaurate (DBTDL) and triethylamine (TEA, Tianjin Guangcheng Reagent Co., China), N-methylpyrrolidone (MPD) and acetone (AC), from industrial products, were dried from moisture using 5 Å molecular sieves.

2.2. Synthesis of UVHWPU resins

The UVHWPU oligomers were prepared by a three-step reaction. In the first step, PEG-1000 (105–120 mg KOH/g), PPG-1000 (111 mg KOH/g) or PTHF-1000(112 mg KOH/g), DMPA, TMP, diisocyanate IPDI (mole ratio of –CNO/ – OH was 1.5: 1.0) and MPD were charged into a 250 ml four-necked round bottom flask equipped with a heating

Table 2
Effect of dosage of TMP in the hyperbranched PU on the curing time of films.

Molar ratio (TMP: PPG-1000)	1:3	1:4	1:5	1:5.4	1:6	0:1
UV curing rate /min	–	0.5	8	17	26	38
Appearance of films	Coating thick and water insoluble	Smooth, hard pliable and transparent	Smooth, hard pliable and transparent	Smooth, hard pliable and transparent	Smooth and slightly sticky	Smooth and sticky

Note: The dosage of photoinitiator Irgacure 184 is 3% in the coatings and the samples were irradiated under a 1kw UV tube 20 cm blow.

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