Progress in Organic Coatings 106 (2017) 60–68

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Synthesis and properties of spray-applied high solid content two component polyurethane coatings based on polycaprolactone polyols

Shan Huang [a], Juan Xiao [a], Yan'an Zhu [b], Jinqing Qu [a,*]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong, 510641, People's Republic of China
[b] Carpoly Chemical Group Co., Ltd., Jiangmen, Guangdong, 529085, People's Republic of China

ARTICLE INFO

Article history:
Received 8 October 2016
Received in revised form 10 January 2017
Accepted 11 February 2017

Keywords:
Small molecular polyol
Polycaprolactone polyol
Two component polyurethane
High solid content coatings
Blending curing agents
Film property

ABSTRACT

A series of polycaprolactone (PCL) polyols was synthesized via the ring-opening reaction of ε-caprolactone initiated by small molecular polyols including ethylene glycol (EG), 1,4-butanediol (BDO), diethylene glycol (DEG), neopentyl glycol (NPG), 2,4-diethyl-1,5-pentanediol (PD-9), 1,4-cyclohexanedimethanol (CHDM), trimethylolpropane (TMP), di-trimethylolpropane (Di-TMP), di-pentaerythritol (Di-PE) and maltitol. IR and ^{1}H NMR spectra of PCLs disclosed that ε-caprolactone reacted with the hydroxyl groups of small molecular polyols, then the target PCLs were successfully prepared and possessed similar molecular skeleton structures. The GPC data summarized the measured number-average molecular weights of PCLs approached to their theoretical values, and the polydispersity indexes (PDI) were ranged from 1.35 to 1.58. PCLs prepared with maltitol displayed the highest viscosity up to 42000 mPa s, while products obtained from diol substrates including EG, BDO, DEG, NPG and PD-9 exhibited the lower viscosities in the range of 160–300 mPa s. The cured films of PCLs prepared from polyisocyanate curing agents exhibited good impact resistance, adhesion, flexibility, higher hardness and displayed better thermal stability with 5% weight loss at 260 °C. PCLs obtained from TMP (PCL-7, TMP/3ε-CL) and Di-TMP (PCL-8, Di-TMP/4ε-CL) exhibited the higher films hardness and lower viscosities at 100% solid content. The viscosities of PCL-7 and PCL-8 were 1320 and 3900 mPa s, respectively, and the VOC contents of spray-applied 2K-PU coatings prepared from PCL-7 and PCL-8 were low to 180 g/L.

1. Introduction

As the increasingly stringent laws about the utilization and emission of the volatile organic compounds (VOC), the coatings industry is under great pressure to reduce the VOC contents of coating products. The options available for meeting the requirement on VOC of coatings are well known as waterborne coatings, powder coatings, UV curable coatings and high solid content coatings [1–4]. For obvious reasons of the excellent mechanical properties and the outstanding adaptability, the high solid content (HSC) coatings are the preferable routes to reduce the VOC level in coatings industry [3–5].

High solid content two component polyurethane (HSC 2K-PU) coatings are becoming increasingly accepted as an alternative to conventional solvent-borne systems in many diverse fields of the coatings industry because of their environmental, technical and low energy cure concern [6]. 2K-PU coatings are consisted of hydroxyl resins and polyisocyanate curing agents and the key technology of HSC 2K-PU coatings is preparing low viscosity, high solid content hydroxyl resins. Conventional hydroxyl resins used for the preparation of 2K-PU coatings are usually including alkyd resins, polyester resins and hydroxyl acrylic resins [7–11]. However, these resins are usually linear polymers with the higher molecular weights, and possessing high viscosities to be hard to formulate HSC 2K-PU coatings [10,11]. Meeting the requirements for high solid and low VOC contents without compromising on the coatings performance has always been a challenge [12].

In general, the VOC contents of 2K-PU coatings mainly depend on the properties of polyols and polyisocyanates, as well as the construction process [13]. Developing HSC 2K-PU coatings, one traditional approach is to reduce the viscosities of hydroxyl resins by lowering the molar weight or narrowing the molar weight distribution [4,14,15]. However, hydroxyl resins with the low molecular weight often result in poor drying behavior and mechanical property, such as long drying and recoating time, low hardness and abrasion resistance [15,16]. Moreover, the using of low molecular weight hydroxyl resins is always resulted only a moderate increase in the solid content compared with conventional high-molecular

* Corresponding author.
E-mail address: cejqqu@scut.edu.cn (J. Qu).

http://dx.doi.org/10.1016/j.porgcoat.2017.02.011
0300-9440/

systems [14,16]. Another approach, the use of reactive diluents, which become a part of the coating films after drying and indeed increases the solid content considerably [14–16]. But such formulations are usually much more expensive because of the higher amount of curing agents required [14].

Hydroxyl polyesters (HPs) always exhibit high viscosity because of the strong hydroxyl bonding effects, the high polarity and cohesive energy of ester groups in molecules of HPs [6]. Recently, several studies have reported that the partial replacement of the hydroxyl groups in HPs with the less polar acetoacetate groups leads to an increase in solid content at the application viscosity as well as increase in adhesion due to chelate effect [4,6]. Raju et al. [6] found that the structural variation of diol and acetoacetylation help in significant reduction of viscosity of HPs and that is also reflected in an increase in solid contents of coatings. Meanwhile, there are many articles and patents focused on the oligomers contained potential reactive groups, such as oxazolidines, aspartate, aldimines and ketimines oligomers [17]. Those potential reactive groups are unblocked or activated and generated reactive groups when exposed to the air humidity. However, the slow unblocking reaction would lengthen the whole film-forming times, furthermore the unblocking reaction sometimes releases organic volatiles that contribute negatively to VOC [17–19].

Recently, the increase in molecular branching is performed along with the reduction of molecular weights of the polyols [15]. The highly branched hydroxyl-terminated polymers (i.e. dendrimer, hyperbranched polymer, star polymer, etc.) have been attracted great attentions and applied in coating formulations [15]. In our previous studies [20–22], we prepared a series of hydroxyl-terminated hyperbranched polyesters (HBPs) via "pseudo one-step" method, then used ε-caprolactone and different mono-carboxylic acids to modify these HBPs. The results showed that using lauric acid to cap part of hydroxyl groups and utilizing ε-caprolactone to react with end-hydroxyl groups of 2,2-dimethylol propionic acid then to extend the carbon chains could effectively reduce the viscosity of HBPs, and the lowest viscosity of the modified HBPs was only 7500 mPa s and the highest film hardness of 2K-PU coatings was F. However, these reported hydroxyl-terminated HBPs have always been synthesized through "pseudo one-step" method [20,23], the viscosities are still higher. In addition, the xylene homologues used as the water-carrying agent is difficult to be fully removed and will bring the environmental and health hazard [24,25]. DuPont Company developed polyesters based on star oligomers via the ring-opening polycondensation, and these polyester star oligomers have been used as the sole hydroxyl component in 2K-PU coatings to boost-up the solid contents with a good overall balance of properties, and the lowest VOC was about 3 lbs/gal [17,26–29]. Huybrechts et al. [17] prepared the star oligoethers by ring-opening polyetherification of mono epoxyesters with different polyols, and the lowest VOC contents of 2 K clear coatings based on the branched polyethers was at 2.1 lbs/gal with an acceptable overall balance of pot life, appearance, durability and productivity.

ε-Caprolactone is an excellent chemical raw material, which easily occurs ring-opening reaction with hydroxyl-terminated compounds without reducing the number of hydroxyl groups and generates high-active primary hydroxyl groups. In the meanwhile, the introduction of flexible hexa-carbon chain can effectively reduce the viscosity and enhance the flexibility of the modified products. Hong et al. [30] used ε-caprolactone to modify the hydroxyl-terminated HBPs and obtained a hyperbranched polyol with long flexible chains on the surface of molecule, then the hyperbranched polyol was added into epoxy resin to prepare cationic UV curing films and found that the flexibility and impact resistance of the films increased significantly. Morell et al. [31] prepared multiarm star hyperbranched poly(glycidol)-b-poly(ε-caprolactone) by cationic ring-opening polymerization of ε-caprolactone from a poly(glycidol) core and used it to modify diglycidylether of bisphenol A (DGEBA) formulations. Their study showed that the addition of star-like structures modifiers decreased the global shrinkage, and increased the conversion at gelation, and led to a more toughened fracture of the thermoset in comparison to pure DGEBA. Smet et al. [32] prepared hyperbranched aliphatic copolyesters by the copolymerization of ε-caprolactone and 2,2-bis(hydroxymethyl)butyric acid, and the results displayed that the introduction of ε-caprolactone decreased the viscosity of polyesters and the flexibility of coating film also greatly increased. Nowadays, polycaprolactone diols have been wildly used as macrodiol extender in the preparation of PU materials [33,34]. However, there are few literatures have reported the utilization of polycaprolactone polyols as the sole hydroxyl component in the preparation of spray-applied 2K-PU coatings.

The purpose of this study is to synthesize star-like polyols via a simple method and to prepare spray-applied HSC 2K-PU coatings based on the star-like polyols. We synthesized a series of polycrprolactone (PCLs) polyols via the ring-opening reaction of ε-caprolactone initiated by ten kinds of small molecular polyols, and used FTIR, NMR and GPC to characterize their structures and molecular weights. The cured films of PCL polyols were prepared using polyisocyanate curing agents and their comprehensive properties were tested. The influence of the categories of small molecular polyols and the molar ratios of raw materials on the viscosities of PCL polyols and their 2K-PU film properties were investigated. Since the performance of polyisocyanate component is also important for the VOC contents of 2K-PU coatings, the influence of different polyisocyanate on the 2K-PU film properties were investigated and the high performance, low VOC, high solid content 2K-PU coatings were prepared.

2. Experimental

2.1. Materials and reagents

Ethylene glycol (EG), 1,4-butanediol (BDO), diethylene glycol (DGE), neopentyl glycol (NPG), 2,4-diethyl-1,5-pentanediol (PD-9), 1,4-cyclohexanedimethanol (CHDM), maltitol and anhydrous zinc acetate were all analytical grade reagents and were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Trimethylolpropane (TMP, 99%) and ditrimethylolpropane (Di-TMP, 97%) were industrial products and were obtained from Wuxi Baichuan Chemical Industrial Co., Ltd. (Wuxi, China). Di-pentaerythritol (Di-PE, 90%) was industrial product and was supplied by Yunnan Yuntianhua Co., Ltd. (Zhaotong, China). ε-Caprolactone (ε-CL, 99.5%) was industrial product and was purchased from Perstorp Group (Sweden). H137H-80 (alkyd resin, with solid content of 80% in xylene, hydroxyl value = 140 mg KOH/g, η/25 °C = 20000 mPa s) and toluene diisocyanate/trimethylolpropane (TDI/TMP) adduct curing agent L-75 (industrial product, with solid content of 75% in ethyl acetate, NCO% = 13 wt%, η/25 °C = 2000 mPa s) were kindly provided by Carpoly Chemical Group Co., Ltd. (Jiangmen, China). Diphenylmethane diisocyanate curing agent (MDI-50) (industrial product, 100% solid content, NCO% = 33.5 wt%, η/25 °C = 30 mPa s), and polymeric methylene diphenyldiisocyanate curing agent (PM-400) (industrial product, 100% solid content, NCO% = 31.1 wt%, η/25 °C = 400 mPa s) were supplied by Wanhua Chemical Group Co., Ltd. (Yantai, China). Solid raw materials (i.e. NPG, CHDM, TMP, Di-TMP, Di-PE and maltitol) were dried in vacuum oven at 100 °C for 4 h to remove moisture prior to use. Liquid raw materials (i.e. ε-Cl, EG, BDO, DEG and PD-9) were dried over 3 Å molecular sieves for 3 days before use. All the materials were used as received without further purification.