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Cross-linking kinetics of hyperbranched epoxy cured hyperbranched polyurethane and optimization of reaction conversion by central composite design

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HIGHLIGHTS

- Efficacy of hyperbranched epoxy with poly (amido amine) as cross-linker in polyurethane curing was explored.
- DSC kinetic study was done to evaluate cross-linker's efficiency.
- The cross-linker effectively reduces the activation energy and curing time.
- On-set and peak temperature of curing was influenced by the cross-linker.

ARTICLE INFO

ABSTRACT

Study on cure kinetics and optimization of various curing parameters of thermosetting polyurethane are very important for its industrial utility. Hence, an attempt has been made to study the cure kinetics of hyperbranched polyurethane by using a hyperbranched epoxy with and without poly(amido amine) as a cross-linker. The kinetics study was conducted by Differential Scanning Calorimetric (DSC) measurements. Different kinetic parameters were evaluated by fitting the DSC data to an autocatalytic kinetic model using Advanced Pyris® 10.1 analytical software. The results clearly indicated the efficacy of the used cross-linker. The study witnessed greater conversion of curing with reduction in activation energy from 44.78 kJ/mol to 30.05 kJ/mol by hyperbranched epoxy and poly(amido amine), as a combined cross-linker. Dynamic calorimetric measurements suggested the effect of cross-linker on on-set, peak and end-set temperature of the curing reaction. The cross-linker effectively reduced the on-set curing temperature. Further, exothermic heat flow and other kinetic parameters such as order of reaction, rate constant, pre-exponential factor were found to be influenced by the cross-linker. A response surface model was also employed to optimize the conversion of curing with variation of time and temperature. A significant quadratic influence of the variables on the response was observed with model co-efficient > 0.93. Thus, the cure kinetics and optimization of curing parameters of a hyperbranched polyurethane by a hyperbranched epoxy in the presence of a poly(amido amine) was demonstrated for the first time.

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1. Introduction

Polyurethane, being a versatile polymer has drawn the copious interest of both scientific and industrial communities for its development and applicability. Both thermoplastic and thermosetting polyurethanes have enormous applications (Delebecq et al., 2012). In this context, thermosetting polyurethane presents an important class of material with high thermal and chemical stability (Raquez et al., 2010; Zia et al., 2007; Jia et al., 2005; Chen et al., 1992). Basic chemistry of thermosetting polyurethane relies on the reaction of isocyanate terminated pre-polymer, di-functional chain extender and a cross-linker. In this milieu, nature of the cross-linker is very important, as the same can greatly influence the extent of reaction and hence the property of the thermosetting material (Kalita and Karak, 2013; Wu et al., 2013). A perusal of literature has shown the use of different types of cross-linkers in polyurethane curing reactions which include hydroxyl terminated polyesters, poly(ester amide)s, amine terminated polyamides etc. (Nasar et al., 2003; Van Benthem, 2000; Lin et al., 2011). In the quest of developing thermosetting polyurethane, we found epoxy as an interesting option because of its excellent material properties viz. good thermostability; high mechanical strength; excellent adhesive strength; high corrosion, weather and

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chemical resistance; dimensional stability; good processability etc. (Hodgkin et al., 1998; Levchik and Weil, 2004; De and Karak, 2013; Barua et al., 2014). Successful use of linear epoxy for curing of polyurethane is also cited in the literature (Kalita and Karak, 2013; Deka and Karak, 2010).

In addition to the chemical nature, the architectural feature of a polymer is also important in relation to its efficiency as a cross-linking agent. In this regard, polymer with hyperbranched architecture is an apt option (Mezzenga et al., 2001; Bruchmann, 2007). Favorable attributes like low solution and melt viscosity, large peripheral functionalities, compact structure and good compatibilizing ability make such kind of polymer attractive for various applications (Boogh et al., 1999). The use of hyperbranched polymers as cross-linkers is documented in the literature. Oh et al. showed superiority of hyperbranched polyester as a cross-linker over its linear analog for epoxy curing reaction in terms of lower activation energy and shorter curing time (Oh et al., 2001). Further, Wan et al. witnessed efficient cross-linking ability of a branched polyamine over its linear analog for an epoxy resin (Wan et al., 2012). Although, accessible literature reports the curing of polymeric resins by hyperbranched cross-linkers (Maji and Bhowmick, 2009; Deng and Shi, 2004), but information regarding cure kinetics of hyperbranched polyurethane cured by hyperbranched epoxy is not available as per the authors' knowledge.

Thus, the authors like to carry out a study on bulk cross-linking of a hyperbranched polyurethane based on isocyanate terminated pre-polymer and a dihydroxyamine compound by using a glycerol based hyperbranched epoxy with a fatty acid based poly(amido amine) as the cross-linker. The main objective of the study is to corroborate the relationship among the reaction parameters like temperature, time and degree of conversion as well as to establish the function which dictates the rate of the reaction. Thus, the use of epoxy and polyurethane with hyperbranched architecture is the main highlight of the present study. Differential scanning calorimetric (DSC) method was chosen as the tool to demonstrate the efficiency of the cross-linker. As the cross-linking kinetics of polyurethane is very complex due to the involvement of multiple competing reactions, a phenomenological model would be followed. DSC is well compatible to carry out such kind of kinetics study (Nzihou et al., 1999; Yousefi et al., 1997). Based on the kinetics results, a statistical model would also be developed in order to optimize the conversion with variation of time and temperature by surface response methodology following a central composite design. Such optimization of reaction conversion based on time and temperature would be immensely helpful to design similar types of thermosetting polymers.

2. Materials and methods

2.1. Materials

Isophorone diisocyanate (IPDI, Aldrich, Germany) and poly (amido amine) (PAA, HY 840, Ciba Geigy, Mumbai, India) with amine value of 6.6–7.5 equiv/kg were used as received. Poly (ethylene glycol) with molecular weight 200 g/mol (PEG 200, Merck, India), diethanol amine (DEA, Himedia, India), glycerol (Merck, India), epichlorohydrin (Merck, India) and tetrahydrofuran (THF, SD fine Chem., India) were used after vacuum drying in a oven at 55 °C for 12 h. ε-Caprolactam (Himedia, India) was recrystallized from cyclohexane and dried in a vacuum oven at room temperature for overnight. Bisphenol-A (BPA, G.S. Chemical Testing Lab. and Allied Industries, India) was recrystallized from toluene prior to use.

2.2. Preparation of the precursors of hyperbranched polyurethane thermoset

2.2.1. Preparation of 6-Amino-N,N-bis(2-hydroxyethyl)hexamide (dihydroxyamine compound, DHA)

DHA was prepared according to the method described elsewhere (Gogoi et al., 2014). Briefly, vacuum dried DEA (5.257 g) and ε-caprolactam (5.658 g) in 1:1 M ratio with CaO (1 wt% of the total reactant weight) were taken in a three necked round bottomed flask equipped with a mechanical stirrer, a nitrogen inlet and a thermometer immersed in a silicon oil bath. The reaction was carried out at 150 °C for 5 h under constant mechanical agitation in a nitrogen atmosphere. DHA formed was stored in a moisture free environment.

[**FTIR (cm^{-1}):** 1730 (C=O), 1576 (N–H bending), 3410 (O–H stretching); **^{1}H NMR (ppm):** δ 1.46 (–CH$_2$–), δ 1.58 (–**CH$_2$**–CH$_2$–NH$_2$, –**CH$_2$**–CH$_2$–C=O), δ 2.24 (–**CH$_2$**–C=O), δ 2.98 (–**CH$_2$**–NH$_2$), δ 2.52 -N(**CH$_2$**)$_2$, δ 3.48 (–**CH$_2$**–OH); δ 5.10–5.12 (amine and hydroxyl protons); **^{13}C NMR (ppm):** δ 20.2 (–CH$_2$–), δ 30.2 (–**CH$_2$**-CH$_2$-NH$_2$), δ 30.5 (–**CH$_2$**–CH$_2$–C=O), δ 36.8 (–**CH$_2$**–C=O), δ 41.9 (–**CH$_2$**–NH$_2$), δ 52.1 –N(**CH$_2$**)$_2$, δ 60.9 (–**CH$_2$**-OH), δ 172 (**C**=O)].

2.2.2. Preparation of –NCO terminated pre-polymer (PUP)

IPDI (4.44 g) was taken in a three necked round bottomed flask in the inert atmosphere of nitrogen. Exactly required amount of PEG 200 (2 g) was injected into the reaction vessel maintaining functional ratio of –NCO to –OH equal to two. The temperature was slowly increased under constant mechanical stirring and maintained at 65 ± 5 °C for about 50–60 min. The reaction was arrested by rapidly bringing down the temperature below 20 °C. The viscous pre-polymer so obtained was stored under cool (2–8 °C) and dry conditions.

2.2.3. Preparation of hyperbranched polyurethane (HBPU)

HBPU was prepared by reacting PUP (6.44 g) with DHA (1.45 g) compound at an equivalent functional ratio of –NCO and –OH. The reaction was carried out at 45–50 °C for 30–35 min under constant mechanical agitation in the inert atmosphere of nitrogen.

[**FTIR (cm^{-1}):** 3490 (N–H stretching), 1750 (C=O), 1572 (N–H bending), 1108 (N–H deformation); **^{1}H NMR (ppm):** δ 0.86–0.89 (–**CH$_2$**–)$_n$, δ 1.5-0.7 (–**CH$_2$** and –**CH$_3$** of aliphatic cyclohexyl ring system), δ 3.9–4.0 (–**CH$_2$**–O–C=O), δ 3.50 (–**CH$_2$**–OH), δ 3.62 (–**CH**N– urethane), δ 3.72 (–**CH**N– urea), δ 6.0–6.4 (–**NH** urea), δ 6.9 (–**NH**– *trans* urethane), δ 7.1 (–**NH**– *cis* urethane); relative integration of peaks at δ 3.9–4.0 and δ 3.50 confirmed the hyperbranched structure].

2.2.4. Preparation of hyperbranched epoxy (HBE)

HBE was prepared according to the method described in our earlier report (Barua et al., 2013). Briefly, required amount of glycerol (0.972 g) and BPA (19.01 g) were reacted with epichlorohydrin (36.815 g) (at 1: 2 M ratio of total –OH of glycerol and BPA to epicholrohydrin). Reaction temperature was maintained at 110 °C. A solution of 5 N sodium hydroxide was added drop wise through a pressure equalizing funnel. Reaction was carried out for 3 h. The resin formed was separated, washed and dried by following procedure described elsewhere (Barua et al., 2013).

[**FTIR (cm^{-1}):** 914–832 (epoxy ring), 1035 (alkyl-aryl ether group), 1241 (aryl-ether linkage), 3441 (–O–H stretching), 1608 (–C=C-); **^{1}H NMR (ppm):** δ 2.71, 2.72, 3.13 (oxirane protons); **^{13}C NMR (ppm):** δ 44.68, 50.43 (oxirane ring C atoms), δ 68.68 (dendritic tri-substituted glycerol) δ 68.49 (linear di-substituted glycerol) and δ 67.9 (terminal mono-substituted glycerol); degree of branching: 0.88].