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Synthesis and characterization of flame retardant hyperbranched polyurethanes for nano-composite and nano-coating applications

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ABSTRACT

Flame retardant hyperbranched polyurethanes were prepared by reacting phosphorous containing triol, tris(bisphenol-A) mono phosphate, castor oil, and polyethylene glycol with different diisocyanates like TDI, IPDI and HMDI via A_2+B_3 method. In this method A_2 reactants were diisocyanates along with castor oil and polyethylene glycol whereas phosphorous containing triol was used as B_3 reactant and dibutyltin dilaurate (DBTDL) was used as catalyst. Synthesized polyurethans were characterized by gel-permeation chromatography (GPC), elemental analysis, Fourier transform infrared spectroscopy (FTIR) and ^{1}H NMR spectroscopic techniques. Neat polyurethanes were used for preparing films. Nano-clay composites were prepared with various concentration of organomodified montmorillionite nano-clay. Flame retardant, Thermal and mechanical properties of these hyperbranched polyurethanes and their nano-composites were found out. The polyurethanes and their formulations with nano-clay were also used for the coating of mild steel panels. Scratch, pencil, and impact hardness, flexibility and adhesion properties of coated panels were also determined. Observations show an increase in the scratch hardness and flexibility with the introduction of clay. All the coatings show excellent chemical resistance properties compare to their linear counterpart.

1. Introduction

During the last few years, there is a continuous search of advanced polymeric materials for coating applications which results in the development of non-linear hyperbranched polymers [1]. Due to their unique structures, a wide range of properties are observed in the end products. Different types of hyperbranched polyurethanes (HBPUs) having high solubility with high glossy, and flexible coatings are reported in literature [2]. Literature surveys show that most of the hyperbranched based structures are non-flame retardant. In this study attention has been made to synthesize flame retardant hyper branched polyurethanes by incorporating phosphorus moiety into the branched structure. With the presence of more number of end groups offering high crosslinking possibilities, use of these polymers in coatings improve the appearance as well as properties like scratch hardness, adhesion, flexibility, water resistance etc. These types of hyperbranched polymers, for certain specific coating applications can also be made flame retardant by the use of phosphorous, halogen, nitrogen and boron based monomers [3]. Therefore, it was thought to prepare flame retardant hyperbranched polyurethanes using phosphorous containing aromatic monomer. The combination of phosphorous based aromatic moiety with aliphatic castor oil and polyethylene glycol will maintain balance between various properties required for the development of an effective coatings. As the thermal degradation or burning of halogen based compounds release toxic gases [4] most of the users have turned toward phosphorous based compounds which are preferred for their less toxic and high char forming characteristics during burning [5].

Present work deals with the synthesis of phosphorous containing HBPUs for the development of flame retardant coating materials by reacting castor oil, conventional polyethylene glycol (PEG) and phosphorous containing triol tris(bisphenol-A) mono phosphate with different types of diisocyanates and characterized by various chemical and instrumental techniques. Thermal, mechanical and flame retardant properties of the hyperbranched polyurethanes have been found out. Organo-modified nano-clay in various concentrations have been used with HBPUs to develop nano-clay composites and coatings. Various properties of the nano-clay composites and coatings were found out and compared with the neat HBPUs.

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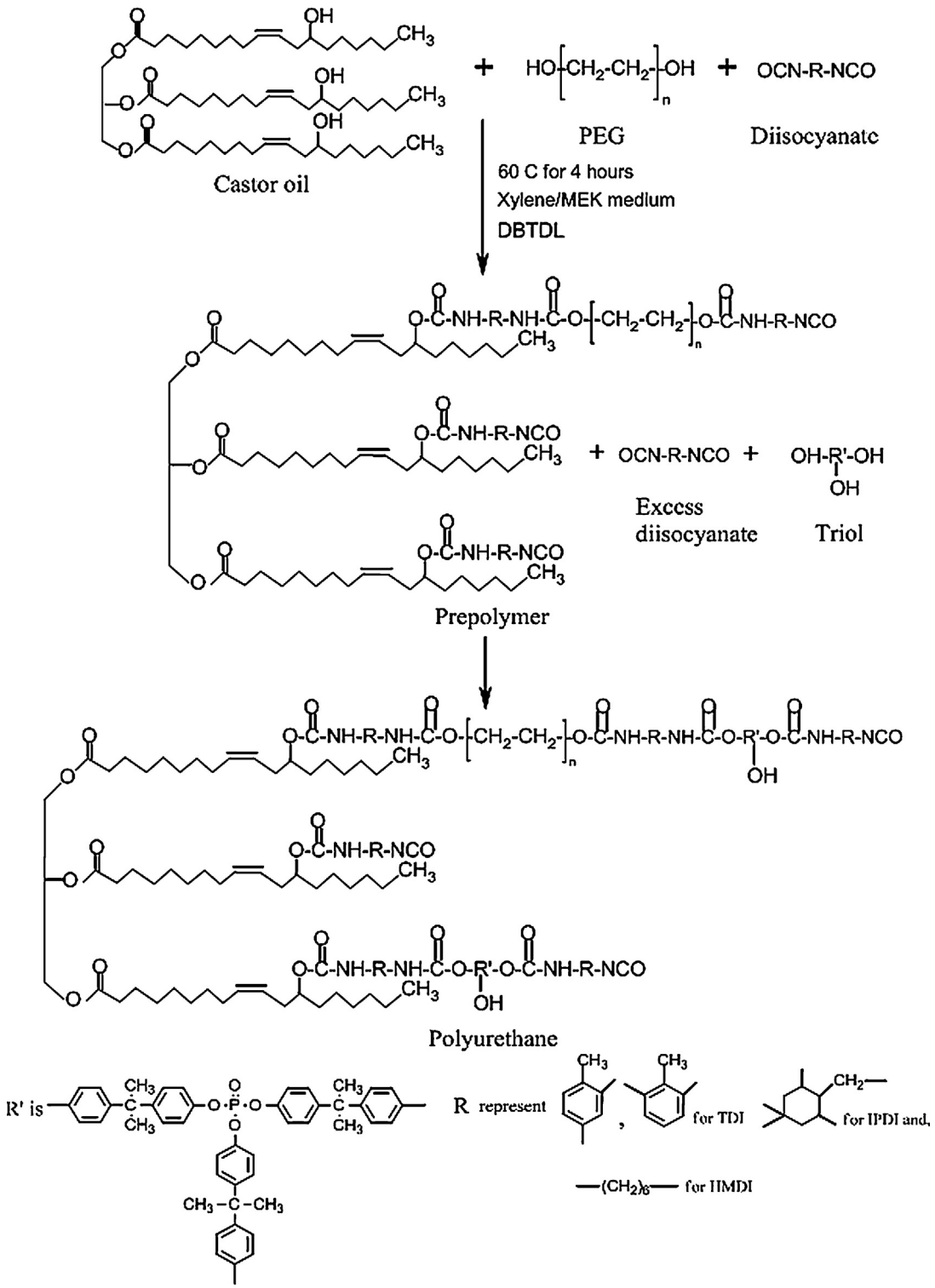

Fig. 1. Synthesis of hyperbranched flame retardant polyurethanes.

2. Experimental

2.1. Materials

The reagents, polyethylene glycol, phosphorous oxychloride ($POCl_3$), N,N-dimethyl aniline, toluene diisocynate (TDI), isophorone diisocynate (IPDI), hexamethylene diisocynate (HMDI), dibutyl tin dilaurate (DBTDL) were procured from Aldrich and were used without further purification. Montmorillonite-clay (MMT) was received from Fluka. Bisphenol-A and polyethylene-glycol (PEG-M.W. 392) were received from Mark. Castor oil was obtained from the local market having the hydroxyl value of 153. Solvent methyl ethyl ketone (MEK) and xylene (XL) were used after distillation. Mild steel panels (75 mm × 150 mm × 0.82 mm) were used as substrate for all the coating applications.