Development of Bio-Based Non-Isocyanate Polyurethane through CO_2 Insertion and Its Nanocomposites

ABSTRACT

Usually, polyurethanes (PUs) are manufactured by the polymerization reaction between polyisocyanate, long chain polyol (polyester or polyether) and low molecular weight polyols as a chain extender. However, the isocyanates used in this process are highly toxic chemicals that cause severe health hazards. Moreover, they are prepared from the reaction of an amine with phosgene which is also an extremely toxic gas. Therefore, recently various alternative routes for the synthesis of isocyanate-free polyurethane (NIPUs) have been developed. The main motivation of this research work is the synthesis of bio-based polyurethanes through isocyanate-free route by using renewable resources like vegetable oils and tannic acid, and improves their properties to make them suitable for applications. In this research, the properties of the prepared NIPUs are enhanced by blending with epoxy resin and preparation of nanocomposite by reinforcing various nano-filler. The nanocomposites are made by incorporating various nano-filler like modified graphene oxide, multi-walled carbon nanotubes and montmorillonite nanoclay into the polymer matrix. Chapter-wise summary of the work is given below:

Chapter 1: General Introduction

The general introduction includes the motivation and background of the present research work. The types, market and drawbacks of classical polyurethanes are discussed. In the second part, the various synthesis routes developed in recent years to prepare isocyanate-free polyurethanes are explained. Among the different approaches, the polyaddition reactions of cyclic carbonates with amines are the most attractive one, and the mechanism of formation, catalyst, reaction kinetics of this isocyanate-free polyurethane is discussed. Various synthetic methodologies of five-membered cyclic carbonates are also included. Finally, a detailed discussion about the chemistry and structure of vegetable oils, and some types of polymeric materials prepared from vegetable oils is described. This chapter also reviews various bio-based non-isocyanate

polyurethanes, prepared especially from vegetable oils like soybean oil and castor oil etc and discus about the various types of nano-filler.

Chapter 2: Solvent and catalyst-free synthesis of sunflower oil based polyurethane through non-isocyanate route and its coatings properties

This chapter deals with the synthesis of bio-based non-isocyanate polyurethanes (NIPUs) synthesized by the polyaddition of diamines with carbonated sunflower oil (CSFO). Carbonated vegetable oils were obtained by solvent-free mixture reaction of CO_2 with epoxidized sunflower oil under the conditions (120 °C, 50 bar) and characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR. Finally, the effect of the amine structure as well as CSFO/amine molar ratio (1:0.75, 1:1 and 1:2) on mechanical and chemical properties NIPUs were studied by using curing agents EDA (Ethylenediamine), DETA (Diethyltriamine) and IPDA (Isophorone diamine). IPDA and EDA showed good thermal, mechanical, chemical and anticorrosive properties. Furthermore, DETA based NIPU displayed high elongation at break.

Chapter 3: *In situ* development of bio-based polyurethane-*blended*-epoxy hybrid materials and its nanocomposites with modified graphene oxide via non-isocyanate route

In this chapter, we have reported a series of sunflower oil based non-isocyanate polyurethane (NIPU)-*blended*-epoxy hybrid materials (HNIPU) and its nanocomposites with amine functionalized graphene oxide (AF-GO). Firstly, the carbonated sunflower oil (CSFO) containing cyclic carbonates groups were synthesized by the reaction of epoxidized sunflower oil (ESFO) with CO_2. Then, a series of HNIPUs were synthesized by using a mixture of CSFO and the commercially available epoxy resin at different weight percentages (10, 20, and 30 wt% with respect to CSFO) by using isophorone diamine as the curing agent. The HNIPU with 30 wt% epoxy showed the highest mechanical properties. Finally, the nanocomposites of 30 wt% HNIPU based composition were prepared with different wt% of AF-GO (0.3, 0.6 and 1.0 wt%). These results emphasize the potentiality of this environmentally friendly approach to prepare renewable HNIPU and its nanocomposite materials of high performances.

Chapter 4: Development of sunflower oil based non-isocyanate polyurethane/multi walled carbon nanotube composites with improved physico-chemical properties

This chapter introduces sunflower oil based non-isocyanate polyurethane (NIPU)/ amine functionalized multi-walled carbon nanotube (AF-CNT) composites. NIPU was synthesized by reaction of CSFO with isophorone diamine (IPDA) and subsequently, the effects of different weight percentages (0-2 wt%) of AF-CNTs on physico-chemical properties of the NIPU/AF-CNT composites were examined. FT-IR, XRD and SEM analyses confirmed the formation of the polymer nanocomposites. The results of the studies showed that polymer nanocomposites exhibited better performance than that of the pristine polymer.

Chapter 5: A non-isocyanate approach towards the synthesis of polyurethane with high performance: Blending of cyclic carbonate based on soybean oil and glycerol

This chapter demonstrates the synthesis of bio-based polyurethane from soybean oil and glycerol derived highly branched structure via non-isocyanate route. The soybean oil based cyclic carbonates were synthesized by coupling of CO_2 with epoxidized soybean oil. In the second step, glycerol derived highly branched cyclic carbonate was synthesized from diglycidal ether of bisphenol A (DGEBA) and CO_2. The structure of prepared monomer was confirmed from FT-IR, ^{1}H and ^{13}C NMR spectra. Then a series of non-isocyanate polyurethanes (NIPUs) were synthesized. They exhibited satisfactory mechanical properties and thermal stability.

Chapter 6: Synthesis of tannic acid based polyurethane through non-isocyanate route and effect of organically modified clay on its physico-chemical behavior

In this chapter, tannic acid based isocyanate-free polyurethanes (NPT) is presented. NPT was synthesized by the reaction of carbonated tannic acid (CTAN) with polyamidoamine hardener. Bio-based CTAN were obtained by coupling reactions of CO_2 with modified epoxidized tannic acid (ETAN) under the conditions (75 °C, 50 bar) and the structure were confirmed by FT-IR spectra. Finally, the effect of organically modified clay on its physico-chemical of behavior was examined by altering its amounts (0.5, 1.0 and 1.5 wt% with respect to the resin). It was observed that with the addition of clay, the prepared polymer exhibited improved tensile strength, scratch hardness and good thermal stability. Thus, the synthesized bio-based and isocyanate-free polyurethane exhibited good physico-chemical properties.

Chapter 7: Conclusion and Future Scope

The concluding remarks outcomes and future scopes from this research work are outlined in this chapter. The procedure developed for the preparation of NIPU provides a number of advantages including environmentally friendly, low cost, bio-based and isocyanate-free process. Addition of nano-fillers significantly improves the properties of prepared NIPU. These results highlight the potentiality of this environmental friendly approach to prepare renewable NIPU materials for surface coatings purpose.