Bio-based Hybrid Non-Isocyanate Polyurethane (NIPU)/Epoxy Foams

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Abstract – The hybrid isocyanate-free polyurethane/epoxy foams were obtained by reaction of carbonized soybean oil and epoxies with diamines. The first stage involves the synthesis of carbonized soybean oil, which was carried out by reaction of carbon dioxide with epoxidised oil in the presence of tetrabutylammonium bromide (TBABr) as a catalyst. At the next stage, hydroxyurethane pre-polymers were obtained by aminolysis of cyclic carbonate of soybean oil with diamines such as aminoethylpiperazine (AEP) and isophorone diamine (IFDA). The adjusting of the molar ratio of IFDA, AEP, compared to carbonized vegetable oil was carried out for receiving pre-polymers with structure and physical properties, which are optimal for further reaction(s). At the last third stage, hybrid NIPU/Epoxy foams were synthesized from hydroxyurethane prepolymer and epoxy resin, in presence of polymethylhydrosiloxane (PMHS) as a reactive foaming agent. The final hybrid NIPU/Epoxy foams were obtained by curing at 80 ◦C during 14 hours. The synthesized foams were investigated by FTIR and DSC, TGA analysis.

Keywords – NIPU/Epoxy foams, cyclic carbonates, carbonized vegetable oil, hydroxyurethane polymers, prepolymers, foaming agent.

Introduction

Polyurethane foams (PUFs) are becoming increasingly important and are very common materials that find many applications in various fields [1-2]. Recently, there has been an increasing number of studies on environmentally friendly ways to replace traditional isocyanates in polyurethane synthesis. Non-isocyanate polyurethane foams (NIPUFs) can be come as promising alternative to conventional polyurethane ones. As main way for NIPU-synthesis is reaction of cyclic carbonates with (di)amines. Such polyaddition recation does not lead to gas formation and foaming unlike reaction of isocyanate with water, which turn in limits the application of such polymers for foam preparation. To overcome this disadvantage, using of foaming agent is necessary.

Therefore, the aim of this work is procedure developing for the synthesis of bio-based hybrid NIPU/Epoxy foams. At the first stagethe synthesis of carbonized soybean oil (CCSO) was carried out in an autoclave by passing CO2 through the epoxidized soybean oil in the presence of a TBABr catalyst under stirring, at a temperature of 120 °C, pressure (4-5) atm, for 10 hours [3]. To control the reaction progress, samples were taken at regular intervals and analyzed by titration and FTIR spectroscopy. At the next step two reactive oligohydrixyurethanes (prepolymers)were obtained based on cyclocarbonate of CCSO and IFDA or AEP aminesrespectively. Reaction was carried out by the isocyanate-free method due to the interaction of the cyclocarbonate and amino groups. At the last stage the NIPU/Epoxy foams were synthesized with the followingratio of components: 1.5/1 amine/cyclic carbonate (prepolymer), 5-50% epoxy resin (DER-332, Aldrich), and 5-10% w/w polymethylhydrosiloxane (PMHS) as a reactive foaming agent, the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used as urethane formation catalyst (0.05 eq.). The progress of gelling reaction was investigated by rheological measurement of the reaction mixture at different temperatures. The curing of the final NIPU/Epoxy foams was carried out at 80°C during 14 hours (Fig 1.) The cross-linked network formation was evaluated by FTIR spectroscopy. Moreover, curing reaction kinetic parameters during NIPUF solidification were determined using

DSC analysis [4]. The thermostability of both NIPUFs - CCSO-IFDA and CCSO-AEP was determined by thermogravimetric analysis (TGA) in inert gas (nitrogen) - Td30% were 360 and 355 °C respectively.The thermal properties were measured by differential scanning calorimetry (DSC) - the glass transition temperature values Tg obtained for CCSO-IFDA, CCSO-AEP foams are equal to 55 and 62 °C respectively. These results are in good correlation with the analogous NIPUFs formulations which differ only in the nature and content amines.

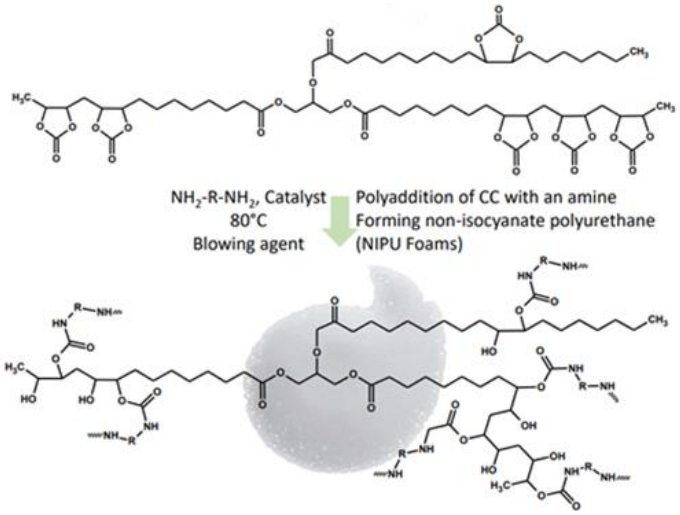

Fig.1. Schematic presentations of the syntehesis of NIPUFs.

Conclusions

Hybrid NIPU/Epoxy bio-based foams based on soybean oil were successfully synthesized by the isocyanate-free method. Reaction kinetic of hydroxyurethane formation as well as curing of aminourethane/epoxy was investigated by FTIR and DSC methods. Thermal properties of the synthesized foams were investigated by TGA, DSC. Thermal properties of the new developed foams correlate with analogous NIPU systems developed by other scientific groups.

References

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