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Novel AB crosslinked polymer networks from telechelic 4-vinylbenzyl carbamate terminated polyurethanes and different vinyl monomers

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Novel AB crosslinked polymer (ABCP) networks were synthesized from telechelic 4-vinylbenzyl carbamate terminated polyurethanes and monomers such as styrene, 4-vinylpyridine, methyl methacrylate and butyl acrylate. Telechelic 4-vinylbenzyl carbamate terminated polyurethanes were synthesized from polypropylene glycol-based NCO-terminated polyurethane and vinylbenzyl alcohol. Effect of changing the molecular weight of polypropylene glycol on the static and dynamic mechanical properties of ABCP networks from polyurethane-polymethyl methacrylate was studied in detail. Dynamic mechanical thermal analysis results show that polymethyl methacrylate and polystyr-ene-based ABCPs have good damping over a broad temperature range. ABCP networks prepared from 4-vinylbenzyl carbamate terminated polyurethane and different monomers such as methyl methacrylate, butyl acrylate and styrene exhibit single tan δ_{max} value which implies excellent interlocking between the two polymers present in the ABCP networks. Static mechanical studies showed that methyl methacrylate and styrene-based ABCP networks exhibit better tensile properties compared to other ABCP networks from butyl acrylate and 4-vinyl pyridine monomers. Thermogravimetric analysis results revealed that the ABCP networks showed an improved thermal stability. Copyright © 2009 John Wiley & Sons, Ltd.

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INTRODUCTION

Polyurethanes are an important class of block copolymers for which the properties of the end product can be designed according to the need of the end-user.^[1] The main disadvantages of these segmented polymers are low thermal stability and poor mechanical properties to some extent. Mechanical properties and thermal stability of polyurethane (PU) can be improved by crosslinking amongst PU chains. Among the different type of crosslinking methods, AB crosslinked polymer (ABCP) network is relatively novel and its properties are unusual from the other crosslinked networks. In ABCP, polymer A is bonded to polymer B at both ends or at various points along the chain.^[2,3] Ideally a single network is generated in ABCP, i.e., polymer A is bonded primarily to polymer B and is not crosslinked itself.^[4-8] ABCP is generally prepared by reacting functional group containing polymer (polymer A) with vinyl monomers (source of polymer B) in the presence of a free-radical initiator.^[9] The polymer networks prepared by this method have improved physical properties such as increased tensile strength, less swelling behavior and increased damping.

Different types of ABCPs with improved properties were reported in the literature. ABCPs based on epoxy resin/benzoxazine-functionalized poly(oxypropylene),^[10] PU/poy(methyl methacrylate) (PMMA),^[11–17] polynorbornene/PMMA,^[18] PU/poly(N-isopropylacryl amide),^[19] chitosan/poly(N-isopropyl acrylamide),^[20] polystyrene/ polysiloxane,^[21] polyisoprene/polysiloxane,^[21] polyacrylamide/ PU,^[22] aqueous PU/polystyrene,^[17,23,24] polybenzoxazine/poly (imide-siloxane),^[25] PU/novolac resin,^[26–28] polycaprolactone/

PMMA,^[29] PU/polystyrene-co-acrylic acid,^[30] PU/polyhydroxyethyl acrylate,^[17] PU/polyvinyl acetate,^[17] and polycarbonate/ polystyrene^[31] are some of the examples of ABCPs which have been reported already. These ABCPs exhibit high damping over broad temperature range which finds applications in controlling vibration and noise. Some thermoplastic materials have damping properties comparable to ABCPs, but they have the disadvantage of flow above their T_g which is not a desired property for any engineering material. ABCPs have proved to overcome this disadvantage,^[32–36] by not flowing above their T_g due to the presence of crosslinking. Literature survey revealed that 4-vinylbenzyl carbamate terminated PU (TVBCPU) has not been used so far to synthesize PU/polystyrene, PU/4-vinyl pyridine and

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PU/butyl acrylate ABCP networks. Hence, in the present investigation, synthesis and characterization of novel ABCP networks from TVBCPUs and monomers such as styrene, 4-vinylpyridine, methyl methacrylate and butyl acrylate are reported.

EXPERIMENTAL

Materials

Poly(propylene oxide) gylcol of molecular weight 1000, 2000, 3000, and 4000 Dalton (PPG₁₀₀₀, PPG₂₀₀₀, PPG₃₀₀₀, PPG₄₀₀₀) were received from Aldrich, USA and dried under vacuum before use. Toluene diisocyanate (TDI; a mixture of 80% 2,4- and 20% 2,6-isomers) and dibutyltin dilaurate (DBTDL) were purchased from Aldrich, USA and used as received. Vinylbenzylchloride (VBC), styrene (Sty), and 4-vinylpyridine (4-VP) were purchased from Aldrich, USA and methyl methacrylate (MMA) and *n*-butylacrylate (BA) were purchased from SD Fine Chem., India. All the monomers were washed with aqueous NaOH to remove the inhibitor and washed further with water to remove NaOH. After storing them over sodium sulphate overnight, they were distilled under reduced pressure. The middle portions were stored at 0–4°C until use. Dimethyl formamide (DMF) was distilled at reduced pressure and the middle portions were stored over molecular sieves (type 4A) until use. Azobis isobutyronitrile (AIBN) was recrystallized from methanol and used as an initiator. p-Vinylbenzylalchohol (VBOH) was prepared from vinylbenzylchloride using the reported procedure.[37]

Synthesis of telechelic 4-vinylbenzyl carbamate terminated polyurethanes (TVBCPU)

Dried polyol (0.02 M) was placed in a three-necked round bottomed flask fitted with a mechanical stirrer, nitrogen inlet, and heated in an oil bath. When the temperature reached 65°C, TDI (0.04 M) was added drop-wise with stirring. Then the temperature was increased to 70°C and the reaction was allowed to proceed till the isocyanate content reached half of the initial quantity (as determined by dibutylamine titration). Then the temperature was reduced to 50°C, and VBOH (0.04 M) and DBTDL (2 mol % based on TDI) were added successively. The reaction was allowed to proceed until the complete disappearance of NCO peak in the Fourier transform infrared (FTIR) spectrum and the resulting viscous TVBCPU was stored at 0-4°C until use. Different types of TVBCPU were prepared by using PPG with different molecular weights and TVBCPU₁₀₀₀, TVBCPU₂₀₀₀, TVBCPU₃₀₀₀, and TVBCPU4000 are the TVBCPUs prepared from PPG1000, $\mathsf{PPG}_{2000},\,\mathsf{PPG}_{3000}$ and $\mathsf{PPG}_{4000},$ respectively.

¹H NMR of TVBCPU₁₀₀₀ (300 MHz; CDCl₃): δ (ppm) = 8.5–9.5 (N-<u>H</u>), 7.0–7.4 (aromatic ¹H), 2.19 (C<u>H₃</u> of 2,4 TDl), 2.11(C<u>H₃</u> of 2,6 Dl), 3.3 (OC<u>H₂</u> of PPG), 1.1 (C<u>H₃</u> of PPG), 4.1 (OC<u>H₂</u> attached to urethane), 3.3–3.6 (OC<u>H</u> of PPG), 4.5 (OC<u>H</u> attached to urethane), 4.05 (C<u>H₂</u> of benzyl), 6.20 (CH=C<u>H₂</u>) 7.10 (5H ring protons and vinyl CH).

Synthesis of ABCP

To prepare ABCP, first, 50 wt% of already prepared TVBCPU was thoroughly mixed with 50 wt% of a monomer. To this homogenous mixture, a calculated amount of free radical initiator (AIBN, 0.02% w/w) was added and mixed again at room

temperature. This mixture was injected into a glass mould and placed in a thermostated water bath at 75°C for 48 hr. The glass mould (toughened glasses of thickness 4 mm) is used in such a way that 2 mm thick sheets were produced after polymerization. The resulting films were placed in a vacuum oven at 60°C for 48 hr to remove unreacted monomers and solvent. Further, to remove traces of unreacted monomers, the resulting films were soaked in DMF for 48 hr and Soxhlet extraction was carried out for 6 hr. Finally, all the films were removed from DMF washed thoroughly with water and dried in vacuum at 50°C for 48 hr.

Measurements

The FTIR spectra were recorded with Nicolet Avatar 360 infrared spectrophotometer equipped with HATR accessory. Fouriertransform nuclear magnetic resonance (FT-NMR) spectrum of TVBCPU was recorded on a Bruker DPX-300 NMR instrument using deuterated dimethyl sulfoxide as the solvent and tetramethylsilane as the internal standard. Number-average (\overline{M}_n) and weight-average (\overline{M}_w) molecular weights and molecular weight distribution (MWD) of TVBCPU were determined by gel permeation chromatography (GPC) using polymer laboratories GPC 50 integrated system equipped with a differential refractometer (RI Detector) and PLgel 5 µm MIXED-C column. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL min⁻¹ and the molecular weight calibrations were done using polystyrene standards. Differential scanning calorimetry (DSC) of TVBCPU was carried out using DSC Q200 instrument (TA instruments, USA) at a heating rate of $10^{\circ}C \text{ min}^{-1}$ under N₂ atmosphere and thermogravimetric analyses (TGA) were carried out using Du Pont 910 thermogravimetric analyser at a heating rate of 10°C min⁻¹ under N₂ atmosphere. Strips ($20 \times 10 \times 2 \text{ mm}^3$) of each material were examined with DMA 2980, Dynamic Mechanical Analyser (TA instruments) in the tensile mode (tension film) in the temperature range of -100° to $+150^{\circ}$ C, at a heating rate of 5° Cmin⁻¹, strain amplitude of 20 μ m and frequency of 1 Hz. The samples (three specimens each) for stress-strain analyses with the specification of 40 mm length, 10 mm width and 2 mm thickness were kept for conditioning at a temperature of $20 \pm 2^{\circ}$ C and relative humidity of $65 \pm 2^{\circ}$ C for 24 hr before testing. The tensile testing was done using an Instron Universal Testing machine model 4501 at an elongation rate of 100 mm min^{-1} .

RESULTS AND DISCUSSION

Synthesis of TVBCPU and ABCP networks

Scheme 1 shows synthesis of TVBCPU and ABCP networks. When NCO-terminated PU was reacted with VBOH, TVBCPU is formed. Table 1 gives synthesis details of different TVBCPU. As the molecular weight of PPG is increased, \overline{M}_n of TVBCPU also increases. This is due to the simple reason that the high molecular weight polyol forms the high molecular weight NCO terminated prepolymer which subsequently forms a high molecular weight TVBCPU after adding VBOH. As the molecular weight of PPG increases, T_g of the TVBCPU decreases. As the TVBCPU molecular weight increases the flexibility of the TVBCPU chain and consequently T_q decreases.

After successful synthesis of TVBCPU, it was used further to synthesize ABCP from different monomers. Table 2 shows