

Synthesis of Triazole Ring-Containing Pentol Chain Extender and Its Effect on the Properties of Hyperbranched Polyurethane-Urea Coatings

K. G. Priyanka, Aswini K. Mishra, Sasidhar Kantheti, Ramanuj Narayan, K. V. S. N. Raju

Organic Coatings and Polymers Division, Indian Institute of Chemical Technology, Hyderabad 500 607, India

Received 16 September 2011; accepted 31 January 2012

DOI 10.1002/app.36921

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This article describes the synthesis and property evaluation of different hyperbranched polyurethane-urea (HBPUU) coatings based on a newly synthesized triazole ring-based pentol chain extender. For this initially, the chain extender was synthesized using acetylene azide click reaction and the structure of the intermediate compounds were confirmed by ^1H -, ^{13}C -NMR, FTIR, and ESI-mass spectrometry. In the further steps, the required HBPUU coatings were prepared by a systematic three-step reaction process. In the first step, a isocyanate terminated prepolymer resin was synthesized at NCO/OH ratio of 1.2 : 1, while the second and third step involves the partially chain extension followed by moisture curing. The excess NCO content in the prepolymer was calculated by standard dibutylamine titration method and partially (10, 20, 30, 50, and 70% of the excess NCO content) chain

extended with the pentol chain extender and remaining was moisture cured. The structure property relation of different HBPUU coating films were analyzed by FTIR peak deconvolution technique using Gaussian curve fitting procedure while, their viscoelastic and thermo-mechanical properties were measured by dynamic mechanical thermal analysis, thermo gravimetric analysis, differential scanning calorimetric, and universal testing machine instruments. These results showed that thermal stability, glass transition temperature (T_g), elongation at break increases but the storage and tensile modulus decreases with increasing the percent loading of the triazole chain extender. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: hyperbranched polyester; polyurethane; 1,2,3-triazole; TGA; DMTA

INTRODUCTION

In recent years, there has been an enormous growth in the application of hyperbranched polymers (HBPs), for the development of newer tailor-made functional macromolecules called dendritic polymers and possesses unique properties polymers with novel architecture and specific properties. HBP belong to a group of like highly branched structure, large number of reactive end groups, excellent flow and processing characteristics due to lower amount of inter or intramolecular chain entanglements and ease of synthesis on a larger scale at a reasonable cost.^{1–5} The requirements of new functional polymers with improved properties continuously fuel the induction of synthetic organic chemistry concepts into materials science.⁶ In this regard, Huisgen 1,3-dipolar cycloaddition reaction of azides and terminal alkynes catalyzed by copper (I) complexes,

commonly known as “Click Reaction” is one of the best organic methodology for the synthesis of polymeric materials with better properties.

The 1,2,3-Triazoles are nitrogen atom containing heterocyclic rings, thus incorporation of these triazole rings into polymer backbone will improve the thermal resistance and glass transition temperature value of the coating. The synthesis and improvement in thermo-mechanical properties of some 1,2,3-triazole-based polymers were reported.⁷ 1,2,3-Triazoles are extensively used in coating and other sectors such as corrosion protection, fabric coatings, anti microbial coatings, reactive and functional coatings, biodegradable polymers, energetic binders, biomedical applications, and so on. For example, Reed et al.,⁸ reported the synthesis of different crosslinked triazoles and their use as energetic binders for improving the mechanical properties and heat stability. Huang and coworkers^{9,10} synthesized a series of novel low temperature curing and heat-resistant polytriazole-based resins for various composite and coating applications. Wan, et Al.,⁷ in their work reported the synthesis of some polytriazoles which shows excellent processability along with good mechanical and thermal properties. Malkov et al.,¹¹ synthesized a novel hyperbranched poly([1,2,3]-triazole-[1,3,5]-triazine)s by a 1,3-dipolar cycloaddition

Correspondence to: K. V. S. N. Raju (drkvsnrju@gmail.com).

Contract grant sponsor: Council of Scientific and Industrial Research (CSIR, New Delhi, India).

reaction from AB₂ monomer-2-azido-4,6-bis-prop-2-yn-1-oxy-[1,3,5]-triazine (ABPOT). Rana et al.¹² have prepared biocompatible poly (ethylene glycol)-functionalized polyurethane using 1,2,3-triazoles. The results showed that the amphiphilic PEG-functionalized PU exhibits good biocompatible behavior, which supports the importance of functionalized PU with 1,2,3-triazoles for biomedical applications.

This work was aimed to develop moisture cured hyperbranched polyurethane urea (HBPUU) coatings through molecular engineering of hyperbranched polyester backbone using diisocyanate and pentol chain extender. For this initially, the pentol chain extender was synthesized by using azide-acetylene click chemistry and later on the required HBPUU coating films were prepared by a systematic three step reaction process. The first step involves the synthesis of isocyanate terminated prepolymer resins, while the second and third step involves the partially chain extension followed by moisture curing and amalgamation. The structure property relation of different HBPUU coating films were analyzed by FTIR peak deconvolution technique using Gaussian curve fitting procedure while, their viscoelastic and thermo-mechanical properties were measured by DMTA (Rheometric Scientific, NJ, USA), TGA (TA Instruments, Herts, UK), DSC (TA Instruments, Herts, UK), and UTM instruments. The base polymer along with the various HBPUU coatings prepared with 10, 20, 30, 50, and 70 wt %, of pentol chain extender (of the excess NCO content) are named as PU, PU-CL-10, PU-CL-20, PU-CL-30, PU-CL-50, and PU-CL-70, respectively. The different steps involved along with the reaction conditions used for the pentol chain extender and final HBPUU coating synthesis are shown in Schemes 1 and 2, respectively.

EXPERIMENTAL

Materials

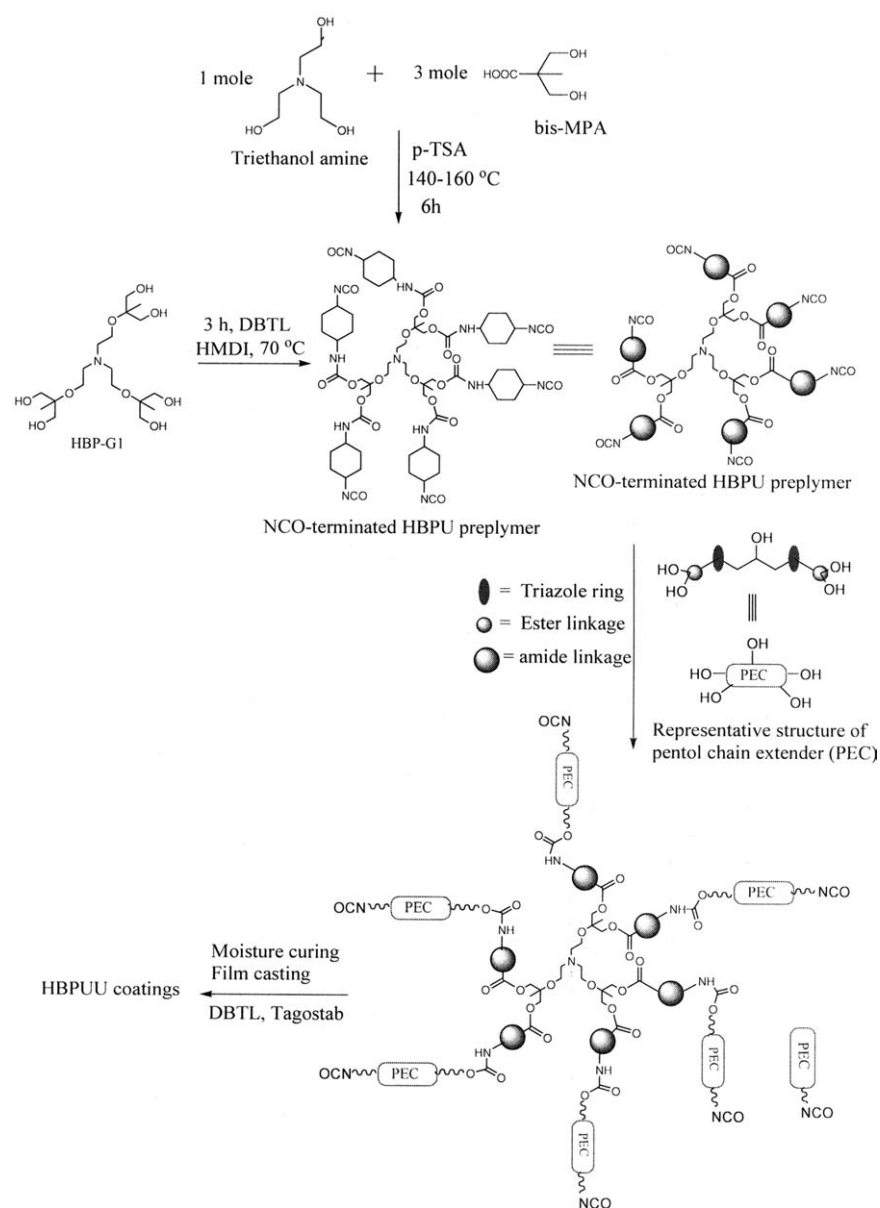
2,2-bis(hydroxymethyl)propionic acid (bis-MPA), Dibutyltindilaurate (DBTL) were purchased from Aldrich Chemicals (Milwaukee, WI), *N,N*-dimethyl formamide (DMF), Triethanolamine (TEA) were purchased from ranbaxy chemicals (Mumbai, India), *p*-toluenesulphonic acid (*p*-TSA), epichlorohydrin, sodium azide, dichloromethane, copper sulphate 5H₂O, copper turnings, acetonitrile, hexane, ethylacetate, dibutylamine, 2,2-dimethoxypropane, and sodium bicarbonate were purchased from S.D. Fine chemicals (Mumbai, India), Dimethylaminopyridine (DMAP), *N,N*-dicyclohexylcarbodiimide (DCC), propargyl alcohol were purchased from Avra chemicals (Hyderabad, India). All the chemicals are used for reaction process without further purification while the solvents are distilled before use.

Characterization methods

The ¹H- and ¹³C-NMR (Midland, ON, Canada) study of the synthesized polyester samples were done in VARIENE-200 and BRUKER-300 MHz spectroscopy by taking trimethylsilane (TMS) as standard at room temperature and dissolving in CDCl₃ solvent. Fourier transform IR spectra (FTIR) of the final HBPUU-cured films coated on dry KBr disc were obtained on a Thermo Nicolet Nexus 670 spectrometer. Each sample was scanned 128 times with resolution, 4 cm⁻¹ in the range 400–4000 cm⁻¹. The curve-fitting was performed using Origin 6.0 software. The ν(N–H) and ν(C=O) bands of different HBPUU coatings were deconvoluted considering peaks as Gaussian with a number of iteration to get the best fit Gaussian peaks. The thermal stability of the different HBPU coatings was studied using TGA Q500 Universal TA instrument (UK). For this analysis, films were cut into small pieces and about 10–15 mg of sample was taken in the crucible and heated at a constant rate of 10°C min⁻¹ in a nitrogen atmosphere from 25 to 600°C with a continuous N₂ flow at a rate of 30 mL min⁻¹. The DSC Q100 Universal instrument is used for the DSC analysis of the samples. The viscoelastic behavior of the synthesized HBPU films in nitrogen atmosphere was analyzed with DMTA IV instrument (Rheometric Scientific, USA) in a tensile mode at a frequency of 1 Hz and a heating rate of 3°C min⁻¹. The sample dimension was 15 × 10 × 0.15 mm³ and the temperature range used was from –40 to 180°C. The energy dissipated due to vibration was measured from the respective *E'* curve at lower temperature zone. The UTM study of free film of coatings was done with AGS-0kNG, SHIMADZU, system connected with AUTOGRAPH controller/measurement unit using dumbbell shape specimen having 5 cm length. The two ends of the sample were taped with cello tap for better clamping during the experiment. Three samples were tested for each formulation and the average was taken as the value for tensile strength measurement.

Synthesis of isopropylidene-2,2-bis(methoxyl) propionic acid (compound 1)

To a stirred solution of bis-MPA (10 g, 74.5 mmol) in 100 mL dichloromethane, was added 2,2-dimethoxypropane (50 mL) and CSA (cat.) under Nitrogen atmosphere at room temperature. The reaction mixture was stirred for 6 h. Then the reaction mixture was quenched with saturated sodium bicarbonate solution (aq.). The two layers were separated and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined dichloromethane fraction was dried over anhydrous Na₂SO₄. The dichloromethane was evaporated in rotavapour. The compound 1 (9.54 g) obtained as white crystals.



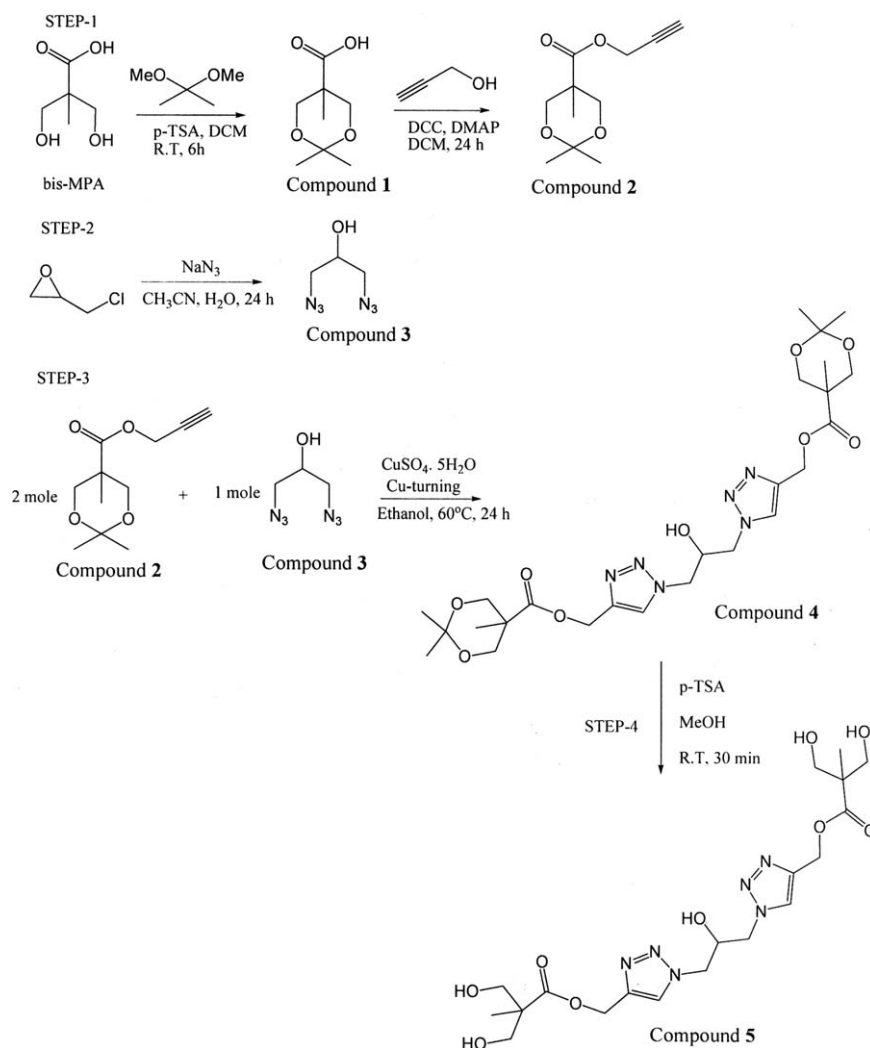
Scheme 1 The total reaction path showing the different steps involved in the synthesis of pentol chain extender by click chemistry.

Yield: 74%. IR (neat, cm^{-1}): 3458–3100 (—OH acid), 2879–2991 (—CH str), 1714 (—C=O acid), 1080 ($\nu_{\text{C-O-C}}$ ether), 828 ($\delta_{\text{C-H}}$ out of plane). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 9.02 (bs, 1H), 4.13 (d, $J = 11.33$ Hz, 2H), 3.58 (d, $J = 11.33$ Hz, 2H), 1.40 (d, $J = 6.79$ Hz, 6H), 1.23 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) 180.1, 96.6, 66.2, 43, 24, 19.2; ESIMS: m/z 197 ($\text{M}+\text{Na}$) $^+$.

Synthesis of 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid prop-2-ynyl ester (compound 2)

To a stirred solution of the acetone protected acid compound 1 (8.28 g, 47.5 mmole) in dry DCM, the propargyl alcohol (4.22 mL, 73 mmole) was added slowly

at room temperature in nitrogen atmosphere. After complete addition of propargyl alcohol the mixture was stirred for another 30 min at 0°C, then DCC (11.78 g, 57 mmol) was added with catalytic amount of DMAP. After addition of DCC (11.78 g, 57 mmol), white precipitate of dicyclohexylurea as by product was formed. The reaction was continued for 24 h in nitrogen atmosphere. The white precipitate was filtered off and the solvent was removed by reduced pressure. The pure compound 2 was isolated by column chromatography technique (silica gel 60–120 mesh, stationary phase) using 5% ethyl acetate in hexane. The compound 2 showed single spot in 20% ethyl acetate in hexane by thin layer chromatography at 0.4 R_f . The product (6.32 g) obtained as a light greenish viscous liquid.



Scheme 2 The reaction path showing the synthesis of the final HBPUU coating based on the pentol chain extender.

Yield: 71%. IR (neat, cm^{-1}): 3273 ($\nu_{\text{C-H}}$), 2925–2854 ($\nu_{\text{-CH}_3}$), 2120 ($\nu_{\text{-C}\equiv\text{C}}$), 1740 ($\nu_{\text{-C=O}}$), 1082 ($\nu_{\text{C-O-C}}$ ether), 831 ($\delta_{\text{C-H}}$ out of plane). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 4.70 (s, 2H), 4.16 (d, $J = 11.33$ Hz, 2H), 3.61 (d, $J = 11.33$ Hz, 2H), 2.43 (s, 1H), 1.40 (ds, $J = 7.55$ Hz, 6H), 1.23 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) 172.5, 97.4, 74.6, 65.1, 51.6, 41.2, 23.6, 17.9; ESIMS: m/z 235 ($\text{M}+\text{Na}$) $^+$.

Synthesis of 1,3-diazido propan-2-ol (compound 3)

To a stirred solution of Epichlorohydrin (5.93 mL, 1 equiv) in a mixture of acetonitrile and water (70 : 30) was added sodium azide (12.3 g, 2.5 equiv) slowly at room temperature and the mixture was refluxed at 90°C for overnight. Then the solvent acetonitrile was removed under reduced pressure and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulphate. The pure compound 3 (6.1 g) was obtained after removing the solvent under reduced

pressure was a transparent viscous liquid. The compound shows single spot in 30% ethyl acetate in hexane by thin layer chromatography at 0.6 R_f .

Yield: 90%. IR (neat, cm^{-1}): 3413 ($\nu_{\text{-OH}}$), 2104 ($\nu_{\text{-CH}_2\text{-N}_3}$), 1278 ($\delta_{\text{-OH}}$). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) 3.89 (qt, 1H), 3.38 (d, $J = 5.28$ Hz, 4H), 2.75 (s, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) 70.78, 54.98; ESIMS: m/z 165 ($\text{M}+\text{Na}$) $^+$.

Click reaction between the acetylene and azide compounds (compound 4)

The azide compound 3 (3.93 g, 0.7 equiv) and alkyne compound 2 (8.46 g, 1.4 equiv) were taken in ethanol solvent in a single neck round bottom flask. To this mixture 3 mL of saturated $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution and a pinch of Cu-turning were added. The reaction mixture was heated at 60°C for 48 h with continuous stirring. After the reaction was over, the reaction mixture was filtered off by filter paper to remove solid residues. The solvent was removed under the reduced pressure and then crude mixture was

TABLE I
The Characteristic Spectral Data of Various Synthesized Intermediate Compound

Compound Nos.	Different characteristic peaks			
	¹ H-NMR (ppm)	¹³ C-NMR (ppm)	FTIR (cm ⁻¹)	ESI-mass
Compound 1	δ 9.02 (bs,1H), carboxylic acid proton. δ 4.13 (d, 2H), δ 3.58 (d,2H), δ 1.40 (d,6H), δ 1.23 (s, 3H),	δ 180.1, δ 96.6, δ 66.2, δ 19.2.	ν _{O-H,acid} at 2879–2991 ν _{C=O} acid at 1714 ν _{C-O-C} ether at 1080 ν _{CH} at 2879–2991	(M+Na)peak at m/z 197
Compound 2	δ 4.70 (s, 2H), δ 4.16 (d, 2H), δ 3.61 (d,2H), δ 2.43 (s,1H), Acetylene proton, δ 1.40 (ds,6H), δ 1.23 (s, 3H).	δ 172.5, δ 97.4, δ 95.5, δ 74.6, δ 65.1, δ 51.6, δ 41.2, δ 23.6, δ 17.9.	ν _{EC-H} at 3273, ν _{C≡C} at 2120, ν _{-CH₃} , 2925–2854, ν _{C=O} 1740 1080, ν _{C-O-C} ether at 828	(M+Na) Peak at m/z 235
Compound 3	δ 3.89 (qt,1H), δ 3.38 (d, 4H),CH ₂ -N ₃ δ 2.75(s,1H),alcoholic proton.	δ 70.78, δ 54.98.	ν _{-OH} at 3413, ν _{-CH₂-N₃} at 2104.	(M+Na) peak at m/z 165
Compound 4	δ 7.7 (s, 2H), δ 5.2 (s, 4H), δ 4.2 (bs, 1H), δ 4.4 (m, 4H), δ 3.59 (d, 4H), δ 3.39 (m, 1H), δ 1.13 (m,12H), δ 1.11 (s, 6H).	δ174, δ125, δ96, δ69, δ65, δ57, δ53, δ41, δ25, δ18.	Absence of acetylene peak 3200 cm ⁻¹ and azide peak at 2100 cm ⁻¹ but the presence of the ν _{-OH} at 3389 cm ⁻¹ , ν _{C-H} (triazole) at 1659.29 cm ⁻¹ confirms the reaction	(M+Na) peak at m/z 589
Compound 5	δ 7.8 (s, 2H), δ 5.6 (bs,5H), δ 4.6(s, 4H), δ 4.4 (m, 4H), δ 3.3(m,9H), δ 1.3 (s, 6H),	δ174, δ125, δ96, δ69, δ65,	Absence of acetylene peak at 3200 and azide peak at 2100 ν _{-OH} at 3389, ν _{C-H} (triazole)at 1570	

purified by column chromatography technique by using 50% ethyl acetate in hexane as mobile phase. The obtained compound 4 (4.9 g) gives single spot in pure ethyl acetate at 0.3 *R_f*.

Yield: 40%: IR (neat, cm⁻¹): 3389 (ν_{-OH}), 1659 (ν_{triazole}), 1278 (δ_{-OH}). ¹H-NMR (300 MHz, CDCl₃): δ 7.7 (s, 2H), 5.2 (s, 4H), 4.4 (m, 4H), 4.1 (d, 4H), 3.59 (d, 4H), 3.39 (m, 1H), 1.13 (m,12H),1.11 (s, 6H); ¹³C-NMR (75 MHz, CDCl₃): δ (ppm) 174.058, 125.35, 96.121, 69.181, 65.952, 57.894, 53.792, 41.922, 25.456, 18.32; ESIMS: m/z 589 (M+Na)⁺.

Deprotection of the click chain extender (compound 5)

The compound 4 (4.9 g, 8.6 mmole) was taken in 20 mL of methanol solvent and a catalytic amount of *p*-TSA was added at 0 °C. The resulting mixture was stirred for 2.5 h under N₂ atmosphere. After completion of the reaction (monitored by TLC), the *p*-TSA was neutralized by adding solid NaHCO₃ followed

by filtration through sintered funnel under vacume. Then the excess solvent was removed under the reduced pressure and the crude reaction mixture

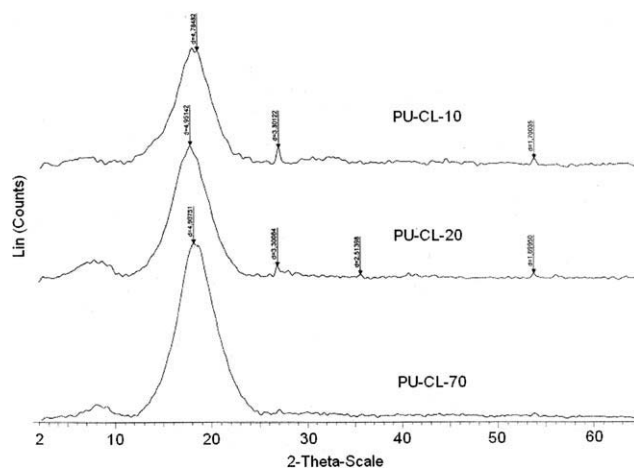


Figure 1 The representative XRD spectrum of PU-CL-10, PU-CL-20 and PU-CL-70 cured films.

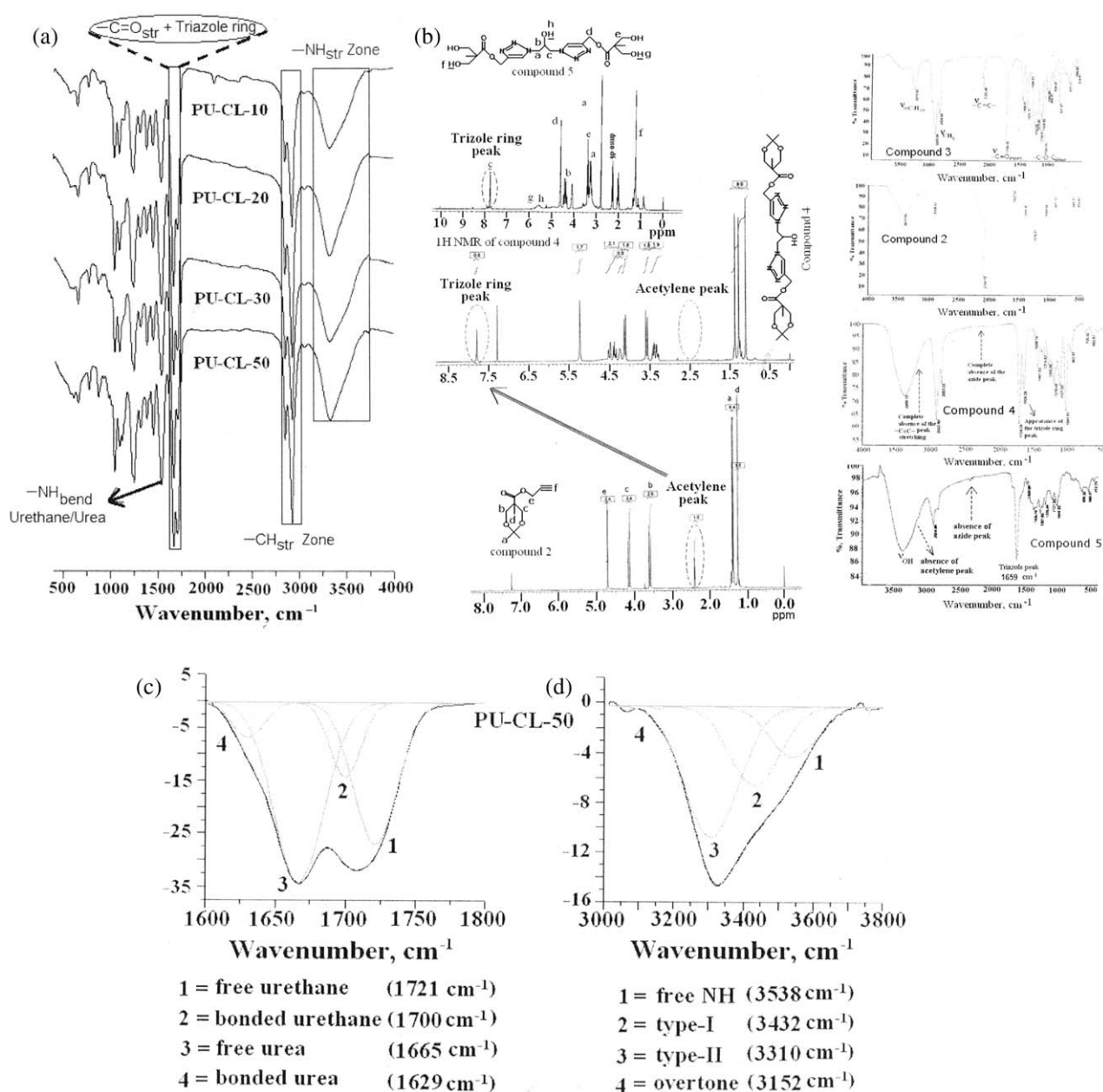


Figure 2 (a) The representative FTIR spectrum of the different HBPUU cured films on KBr disc in the zone 400–4000 cm^{-1} . (b) Confirmation of click reaction by ^1H NMR and FTIR spectroscopy. (c,d) Representative peak deconvolution of the (c) -C=O , zone and (d) -NH zone, for the sample PU-CL-50.

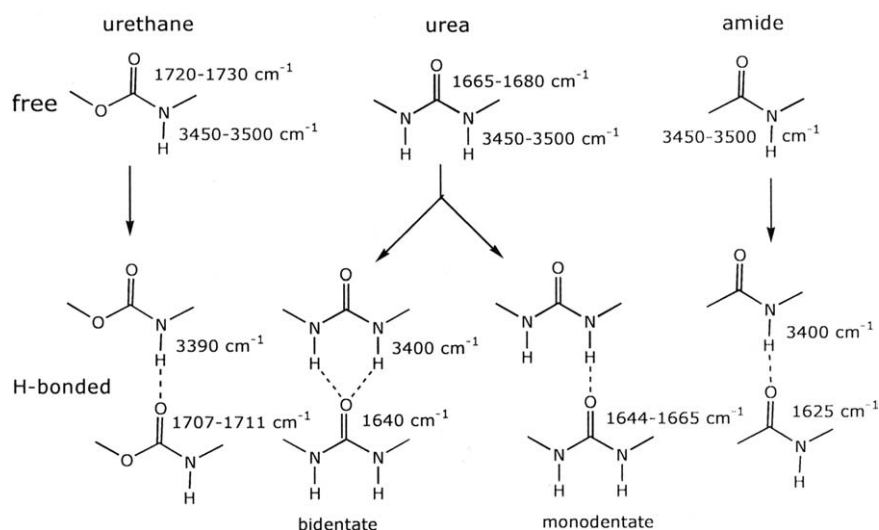
was purified through column chromatography by eluting with pure ethyl acetate to obtain the compound 5 (2.5 g). The resulting product is a light green viscous liquid.

Yield: 60%: IR (neat, cm^{-1}): 3413 ($\nu_{\text{-OH}}$), 1278 ($\nu_{\text{-OH}}$). ^1H -NMR (300 MHz, CDCl_3): δ (ppm) 7.4 (s, 1H), 5.2 (bs, 2H), 4.3 (s, 2H), 4.2 (m, 2H), 3.2 (m, 4H), 1.11 (s, 6H).

The presence of different resonance peaks in ^1H -, ^{13}C -NMR, and ESI-mass given in Table I, confirms the formation of the intermediate compounds during the pentol chain extender synthesis.

Preparation of NCO terminated prepolymer and HBPUU coatings

The synthesis of the first generation hyperbranched polyester polyol (HBP-G1) and the corresponding NCO terminated polyurethane prepolymer was synthesized earlier.^{13–19} The extra NCO content of the prepolymer resin was determined by standard dibutylamine titration method. The synthesized resin was divided into five equal parts. The 10, 20, 30, 50, and 70% of the excess NCO was chain extended with the pentol chain extender. The different HBPUU coating films were casted on a tin foil



Scheme 3 The different types of possible hydrogen bonding in case of urethane, urea and amide structures.

supported over a glass plate by a manual driven square applicator after mixing the pentol chain extender to the prepolymer resin with one drop of DBTL as catalyst and Tagastab as surfactant. The chain extended HBPUU films were moisture cured at 30°C and laboratory humidity condition for about 25 days. The supported films were extracted after amalgamation and cleaning.

RESULTS AND DISCUSSION

XRD analysis

Figure 1, shows the X-ray diffractograms of different pentol chain extender-based HBPU coating films. The X-ray diffractograms of these samples show, a broad intense reflection peak at 2θ range of 10–22° and the peak intensity (degree of crystallinity) increases with increasing the amount of pentol chain extender content. This effect is might be due to the better phase compatibility of the pentol chain extender with the PU polymer matrix through hydrogen bondings.¹³

FTIR analysis of the HBPUU coatings

Figure 2(a), shows the representative overlapped FTIR spectra of different HBPUU cured film on KBr disc in the range 400–4000 cm^{-1} . The presence of triazole ring peak at 1659 cm^{-1} and the absence of free -NCO peak at 2270 cm^{-1} in all the HBPUU cured samples indicates the incorporation of pentol chain extender into the polymer back bone and complete moisture curing of the HBPUU coatings respectively.^{12,20} The observed absorption bands (cm^{-1}) at 3200–3700 (-NH stretch), 2800–3000 (-CH stretch consisting of asymmetric -CH_3 stretch at 2957, asymmetric -CH_2 stretch at 2920, symmetric

-CH_3 stretch at 2872 and symmetric -CH_2 stretch at 2851 cm^{-1}), 1600–1800 (-C=O stretching of amide I), 1500–1600 (amide II, stretch consisting of a mixture of peaks $\delta_{\text{N-H}}$, $\nu_{\text{C-N}}$, and $\nu_{\text{C-C}}$),²¹ 1659 (aromatic triazole ring stretching), 1394 (δ_{CH_2} symm/assym), 1215–1350 cm^{-1} (amide III consisting of $\nu_{\text{C-N}}$, -NH bending and $\text{C-C}\alpha$), 1254 (δ_{OH} free), 766 (amide IV due to -NH out of plane vibration) and 720 (-CH_2 rocking) indicates the formation of HBPUU coatings. The conformation of the acetylene azide click reaction was identified by the completely disappearance of acetylene (2.4 ppm and 3273 cm^{-1}) and azide (2104 cm^{-1}) peaks and appearance of new aromatic triazole peaks (7.7 ppm, 1659 cm^{-1}) in the ^1H - and FTIR spectra of compound 4 [see the Fig. 2(b)]. In order to understand the effect of pentol chain extender on the phase mixing behavior of different HBPUU coatings, we have deconvoluted the -C=O and -NH stretching zones of different coating samples and a representative sample (PU-CL-50) is shown in Figure 2(c,d). The -C=O , zone deconvolution result [shown in Fig. 2(c)] for the above representative sample shows four deconvoluted peaks at peak values 1720–1725, 1700–1710, 1660–1670, and 1630–1640 cm^{-1} , due to the free urethane, bonded urethane, free urea and bonded urea groups respectively.^{22,23} The fraction of free and hydrogen bonded -C=O , can be calculated by comparing the peak areas of these four peaks and the obtained data (Table not shown) suggest that the peak contribution for the hydrogen bonded -C=O , from urea as well as urethane groups was highest for the sample PU-CL-70 and lowest for PU-CL-10. In a similar way, the -NH zone deconvolution shown in Figure 1(d), also indicates four deconvoluted bands at 3538, 3432, 3310, and 3152 cm^{-1} , and were assigned to free -NH , hydrogen bonded -NH (Type I) [NH-O=C-], hydrogen bonded -NH (Type II)

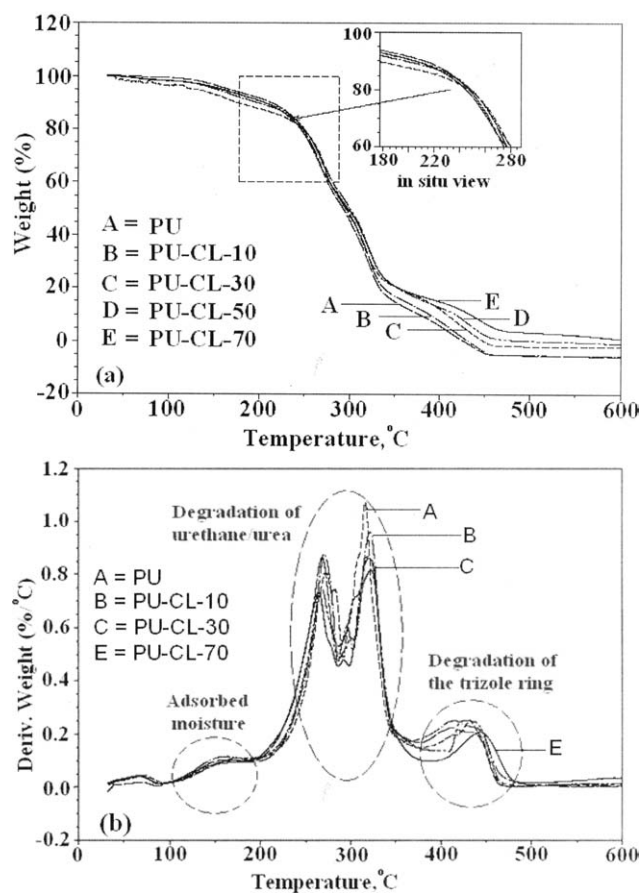


Figure 3 (a) The TGA thermograms of different HBPUU coatings such as (A) PU, (B) PU-CL-10, (C) PU-CL-30, (D) PU-CL-50 and (E) PU-CL-70. (b) The DTG thermograms of different HBPUU coatings such as (A) PU, (B) PU-CL-10, (C) PU-CL-30, and (E) PU-CL-70.

[$-\text{NH}-\text{O}-\text{C}-\text{ester}$] and overtone due to Fermi resonance respectively. The peak contribution from Types I and II hydrogen bonding for the representative sample PU-CL-50 suggests that, the amount of phase mixing was higher compared to phase separation [see the peak area at 3310 and 3432 cm^{-1} in Fig. 2(d)]. This behavior is due to the more interaction between the hydroxyl groups of the pentol chain extender and NCO groups of the prepolymer (shown in Scheme 3), which disrupts the phase separation phenomenon and thus decreases the hard

phase formation in the PU matrix. The disruption of the phase separation phenomenon with increasing the chain extender content, is due to the rigid geometry of the triazole moiety-based pentol chain extender which constrains the $-\text{NH}$ groups of the hard segments in the reacting PU polymer, to form hydrogen bondings with the other hard segment $-\text{C}=\text{O}$ groups [i.e., $\text{NH}-\text{O}=\text{C}-$ (Type I)]. Thus there is a more possibility of formation of phase mixing (Type II) structures with increasing the pentol chain extender content [i.e., $-\text{NH}-\text{O}-\text{C}-\text{ester}$ (Type II)]. The similar behavior is also observed in case of the ZnO nanoparticles-based PU coatings earlier reported.²⁴

TGA/DSC analysis

The representative TGA and DTG curves of different HBPUU coatings with increasing the pentol chain extender content is shown in Figure 3(a,b), respectively. The DTG curve clearly indicates a three-step degradation profile with a initial decomposition temperature around 250°C. The smaller weight loss temperature around 150°C is might be due to the evaporation of absorbed moisture in the coating films. The TGA data as reported in Table II, suggests that the onset temperature (T_{10N}), 10% weight loss temperature (T_{d10}), and 50% weight loss temperature (T_{d50}), all increases with increase the pentol chain extender content in the coating formulation. This result indicates good compatibility between the polymer and pentol chain extender through hydrogen bondings. For instance, the T_{10N} and wt % remaining at 350°C for the samples, PU, PU-CL-10, and PU-CL-30 are 235.7, 248.5, 253.8°C, and 17.0, 18.2, 20.8%, respectively. The similar behavior is also observed for the other HBPUU coatings. The above trend is due to the formation of more number of hydrogen bonded urethane/urea structures at higher chain extender containing coatings. The more the hydrogen bonding the more is the crosslink density, which brings the polymer backbones closer and thus reduces the molecular mobility, and increases the thermal stability and glass transition temperature (T_g).²⁵ DSC results of different HBPUU coatings with increasing the chain extender content was shown in

TABLE II
The Thermal Stability Data of Different HBPUU Coatings

Sample code	Onset decomposition temperature (T_{10N}) in °C	10%, wt loss temperature in (T_{d10}) (°C)	50%, wt loss temperature in (T_{d50}) (°C)	% wt remaining at 350°C	T_g , in (°C) from DSC
PU	235.7	200.9	298.5	17.0	58
PU-CL-10	248.5	203.7	297.5	18.2	61
PU-CL-20	251.2	174.4	296.6	20.7	62
PU-CL-30	253.8	196.2	295.7	20.8	65
PU-CL-50	254.0	200.5	300.4	21.6	67
PU-CL-70	235.5	204.7	302.8	21.8	73

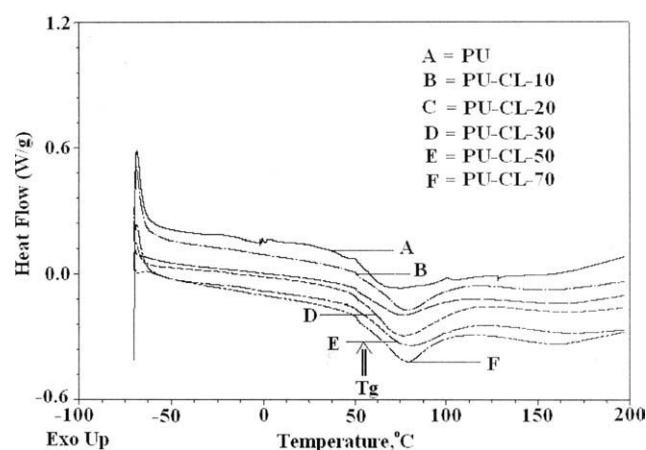


Figure 4 The DSC thermograms of the different HBPUU coatings such as (A) PU, (B) PU-CL-10, (C) PU-CL-20, (D) PU-CL-30, (E) PU-CL-50, and (F) PU-CL-70.

Figure 4, whereas the T_g data are given in the Table II. All the coating samples having T_g ranging between 55 and 75°C and the value increase with increasing the pentol chain extender content. The obtained data suggests that the base polymer is having T_g at 58°C whereas, the other samples possess higher T_g than the base polymer. This result is might be due to the higher structural rigidity of the triazole moiety-based pentol chain extender, which forms urethane linkages with the prepolymers. Once this type of structure is formed the hydrogen bonding interaction between the hard/hard segment decreases [$-\text{O}-\text{CO}-\text{NH}-\text{O}=\text{C}-\text{O}-\text{NH}$, (phase separation)]. This phenomenon is might be due the rigid geometry of the click chain extender, which constrains the adjacent $-\text{NH}$, groups to form hydrogen bonds with the other urethane/urea $-\text{C}=\text{O}$, groups. Thus, the number of hard phase formation decreases and storage modulus decreases (observed in DMTA analysis), but the T_g value increases (observed in DSC analysis) because of the restricted chain mobility due to hydrogen bonding. The similar behavior is also observed by Zheng et al.,²⁶ for ZnO nanoparticle-based polyurethane systems.

DMTA and UTM analysis

Viscoelastic behavior of different pentol chain extender-based HBPUU coatings were studied by DMTA instrument. The E' and $\tan \delta$ vs. temp. curve of one representative HBPUU coating film PU-CL-30 is shown in Figure 5(a), while the overlapped E' vs. temp. curves of all coating samples are shown in Figure 5(b). The DMTA data of the different HBPUU coatings are given (Table III). The obtained result suggests that the storage modulus decreases and glass transition temperature (T_g) increases regularly with the loading of pentol chain extender. For

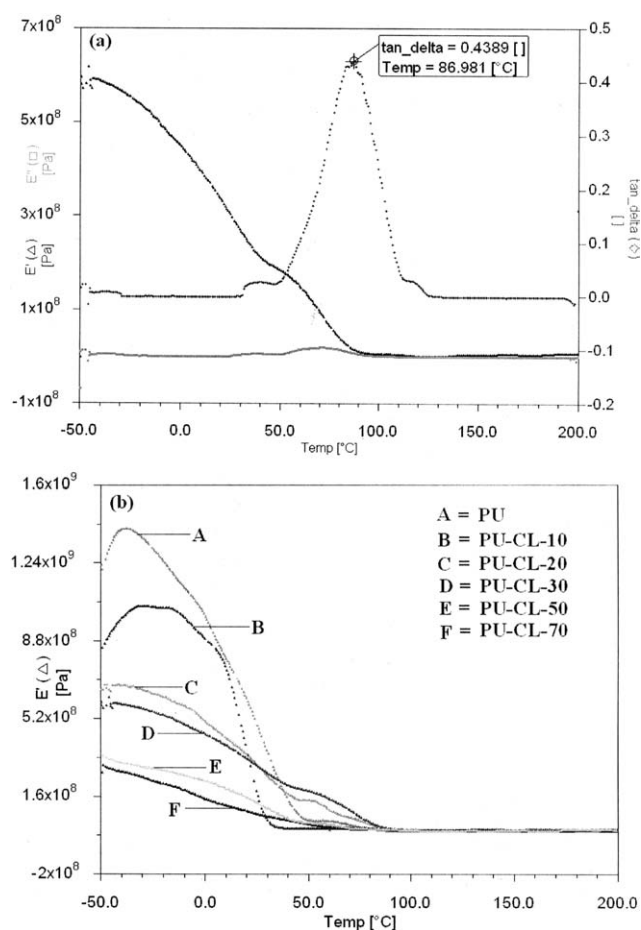
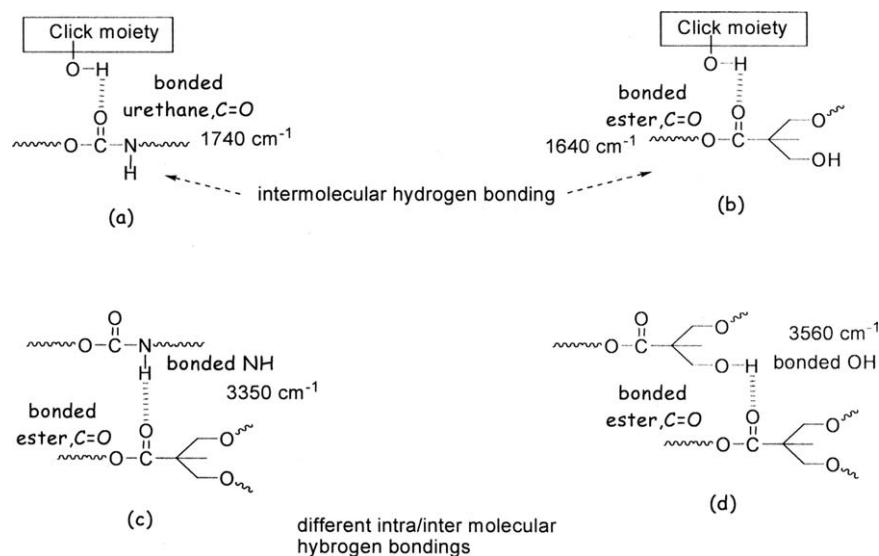


Figure 5 (a) The representative DMTA profile of E' and E'' vs. temp. profile of PU-CL-30 coating. (b) The overlapped DMTA profile of E' vs. temp. curves of different HBPUU coatings along with the pure polymer.

instance the T_g and E' values for the samples PU, PU-CL-10, PU-CL-20, and PU-CL-30 are 73.6, 75.2, 77.7, 86.9°C and 1.4×10^9 , 1.0×10^9 , 5.7×10^8 , 3.0×10^8 [Pa], respectively. This behavior might be due to the interaction between the surface hydroxyl groups of the click chain extender and PU prepolymer (shown in Schemes 3 Scheme 4), which disrupts the phase separation phenomenon, and thus decreases the hard phase formation in the PU matrix, which thus decrease the storage modulus. The disruption

TABLE III
The Mechanical Property Data Obtained from DMTA and UTM Instrument of Different HBPUU Coatings

Sample code	E' at -40°C in (Pa)	T_g in ($^\circ\text{C}$)	Tensile strength in (MPa)
PU	1.4×10^9	73.6	27.6
PU-CL-10	1.0×10^9	75.2	43.6
PU-CL-20	5.7×10^8	77.7	40.7
PU-CL-30	3.0×10^8	86.9	31.2
PU-CL-50	1.6×10^8	–	31.0
PU-CL-70	2.3×10^8	–	24.7



Scheme 4 The different types of possible hydrogen bonding present in the pure polymer and click chain extender-based HBPUU coatings.

of the phase separation phenomenon with increasing the click chain extender content, is might be due to the highly symmetry and structural rigidity of the click-based chain extender, which constrains the $-\text{NH}$ groups of the hard urethane segments in the reacting prepolymer to form hydrogen bonds with the other hard segment $-\text{C}=\text{O}$, groups [i.e., $-\text{NH}\cdots\text{O}=\text{C}-$ (Type I)]. Thus there is a more possibility of formation of phase mixing structures with increasing the chain extender content [i.e., $-\text{NH}\cdots\text{O}-\text{C}-\text{ester}$ (Type II)]. But, the increase in the glass transition temperature is due to the restricted chain mobility because of the Type II hydrogen bonding. The similar type of result is also observed earlier by Zheng et al., and Mishra et al., in case of different PU/ZnO hybrids.^{24,26} The tensile behavior of different click-based HBPUU coatings studied by UTM instrument and the data are reported (Table III). This data suggest that the tensile modulus follows the similar trend as that of the DMTA for the different click pentol chain extender-based coatings (see the tensile modulus data from Table III).

CONCLUSIONS

In this study different HBPUU coatings were prepared through molecular engineering of hyper-branched polyester and by using diisocyanate and pentol chain extender. For this initially, the pentol chain extender was synthesized by using azide-acetylene reaction and later on this pentol chain extender was incorporated into the polymer backbone by chain extension process. The structure property relation of different HBPUU coating films were

analyzed by FTIR peak deconvolution technique using Gaussian curve fitting procedure while, their viscoelastic and thermo-mechanical properties were measured by DMTA, TGA, DSC, and UTM instruments. The FTIR peak deconvolution result suggests that the amount of phase mixing increases with increasing the pentol chain extender content in the coating formulation. TGA data indicates higher thermal stability and char residue value for the higher pentol chain extender containing HBPUU coatings, and this is due to the good compatibility between the polymer and pentol chain extender through hydrogen bonding and also due to the presence of nitrogen containing heterocyclic rings in the polymer backbone. DSC result suggests that all the coating samples having T_g ranging between 55 and 75°C and the value increase with increasing the content of the click-based pentol chain extender in the final coating formulation. This result is due to the restricted chain mobility, because of the formation of the interlocking structures, through Type-II hydrogen bonding as well as due to the rigid conformational structure of the pentol chainextender. The DMTA and UTM result suggests that the storage and tensile modulus decreases and T_g increases with the loading of the click-based pentol chain extender. On the basis of the combined study it can be concluded that the integration of branched polymer architecture and rigid pentol chainextender can result coatings with better thermal stability, higher glass transition temperature and good flexibility.

References

1. Kim, Y. H. *J Polym Sci Part A Polym Chem* 1998, 36, 1685.
2. Voit, B. *J Polym Sci Part A Polym Chem* 2000, 38, 2505.

3. Malmstrom, E.; Hult, A. *Macromolecules* 1996, 29, 1222.
4. Malmstrom, E.; Johansson, M.; Hult, A. *Macromolecules* 1995, 28, 1698.
5. Nishikubo, T.; Kudo, H.; Maruyama, K. *Polym Adv Technol* 2009, 20, 529.
6. Hawker, C. J.; Wooley, K. L. *Science* 2005, 309, 1200.
7. Wan, L.; Luo, Y.; Xue, L.; Tian, J.; Hu, Y.; Qi, H.; Shen, X.; Huang, F.; Lei, Du.; Chen, X. *J Appl Polym Sci* 2007, 104, 1038.
8. Reed, R., Jr.; Ridgecrest, C. A. U.S. Pat. 6,103,029 (2000).
9. Tian, J.; Wan, L.; Huang, J.; Hu, Y.; Huang, F.; Du, L. *Polym Adv Technol* 2007, 18, 556.
10. Wan, L.; Tian, J.; Huang, J.; Hu, Y.; Huang, F.; Du, L. *J Macromol Sci Part A Pure Appl Chem* 2007, 44, 175.
11. Malkov, G. V.; Shastin, A. V.; Estrin, Y. I.; Badamshina, E. R.; Mikhailov, Y. M. *Propellants Explos Pyrotech* 2008, 33, 431.
12. Rana, S.; Lee, S. Y.; Cho, J. W. *Polym Bull* 2010, 64, 401.
13. Mishra, A. K.; Narayan, R.; Aminabhavi, T. M.; Pradhan, S. K.; Raju, K. V. S. N. *J Appl Polym Sci*, DOI 10.1002/app.34970.
14. Goswami, A.; Singh, A. K. *React Funct Polym* 2004, 61, 255.
15. Raghu, A. V.; Gadaginamath, G. S.; Jawalkar, S. S.; Halligudi, S. B.; Aminabhavi, T. M. *J Polym Sci Part A Polym Chem* 2006, 44, 6032.
16. Raghu, A. V.; Gadaginamath, G. S.; Mathew, N. T.; Halligudi, S. B.; Aminabhavi, T. M. *React Funct Polym* 2007, 67, 503.
17. Raghu, A. V.; Gadaginamath, G. S.; Priya, M.; Seema, P.; Jeong, H. M.; Aminabhavi, T. M. *J Appl Polym Sci* 2008, 110, 2315.
18. Raghu, A. V.; Gadaginamath, G. S.; Aminabhavi, T. M. *J Appl Polym Sci* 2005, 98, 2236.
19. Reddy, K. R.; Raghu, A. V.; Jeong, H. M. *Polym Bull* 2008, 60, 609.
20. Riva, R.; Schmeits, S.; Stoffelbach, F.; Jerome, C.; Jerome, R.; Lecomte, P. *Chem Commun* 2005, 42, 5334.
21. Diaz, D. D.; Punna, S.; Holzer, P.; McPherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. *J Polym Sci Part A Polym Chem* 2004, 42, 4392.
22. Jena, K. K.; Mishra, A. K.; Raju, K. V. S. N. *J Appl Polym Sci* 2008, 110, 4022.
23. Lee, H. S.; Wang, Y. K.; Romanova, V.; Begishev, V.; Karmannov, V.; Kondyurin, A.; Maitz, M. F. *J Raman Spectrosc* 2002, 33, 769.
24. Mishra, A. K.; Mishra, R. S.; Raju, K. V. S. N. *Prog Org Coat* 2010, 67, 405.
25. Dutta, S.; Karak, N. *Polym Int* 2006, 55, 49.
26. Zheng, J.; Ozisik, R.; Siegel, R. W. *Polymer* 2005, 46, 10873.