Hybrid Poly(hydroxy urethane)s: Folded-Sheet Morphology and Thermoreversible Adhesion

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ABSTRACT: Hybrid poly(hydroxy urethane)s (PHUs) are synthesized by copolymerizing aromatic/alicyclic cyclic carbonates with a polyether amine via addition polymerization. They result into polymers with an average molecular weight of 10 kDa and exhibit solubility in common organic solvents. The hybrid PHUs display Tgs up to 18 °C. PHUs are enriched with multiple H-bonded interactions and they are assessed using temperature-dependent 1H NMR and Fourier-transform infrared studies. PHUs possess folded-sheet morphology with nanogap between folds and nanowidth between chains. The secondary interactions bestow thermoreversible property to PHUs, and they display good adhesion to both polar (Al–Al) and nonpolar (HDPE–HDPE) substrates. Hybrid PHUs show improved optical transparency compared to homo PHUs. The PHUs are thermally stable up to 250 °C.

1. INTRODUCTION

Polyurethanes are versatile polymers; they find various applications from cushions, beds, and biomedical devices to high-tech aerospace needs.1–3 According to 2016 database, an average of 18 metric ton per year is the global demand for polyurethanes. Although huge application exists, their synthesis is nongreen due to the use of harmful aromatic or aliphatic isocyanates. The isocyanates are extremely harmful to human health and environment, continuous exposure to which results in severe lung irritation, occupational asthma, contact dermatitis, etc. The International Agency for Research on Cancer has classified 2,4-toludenediisocyanate as a possible human carcinogen. Recently, polyurethanes derived from nonisocyanate route (polyhydroxy urethanes-PHUs) have been emerged as a potential area of research.4–7 Polyyhydroxy urethanes (PHUs) can be synthesized by different routes: the mainly employed routes are (i) trans-urethiniization between bicarbamate and a diol, (ii) aziridine copolymerization with CO2, and (iii) ring-opening polyaddition between a bicyclic carbonate and a diamine. Among these methods, the most employed and studied is the third one because it is highly economical from the industrial point of view and carries a green aspect too. The synthesis of bicyclic carbonate from bisepoxy and CO2 is an important reaction strategy since it helps in the chemical fixation of CO2. On the other hand, global warming is ballooning as a big threat, where CO2 is the main culprit (carbon dioxide evolved from various human-intervened processes).8,9 Avoiding isocyanate chemistry and employing CO2 gas in the chemical transformation route to obtain polyurethane is a useful and interesting approach. Reports point out that if CO2 is used for PHU synthesis and considering overall consumption of PHU, CO2 emission can be reduced by 120 million tons per year. Step-growth polyaddition of cyclic carbonates to di/multiamines is a viable and notable technique to produce poly(hydroxy urethane)s (PHUs). The cyclic carbonate monomers are synthesized by chemical insertion of CO2 into naturally abundant (soybean oil, epoxidized fatty acid diesters, vegetable oils, lignin, etc.) or synthetically (methyl-9-decenolate,5-(2-propenyl)-1,3-dioxan-2-one, 4-(3-propenyl)-1,3-dioxan-2-one, 6-methyl-1,3,5-diazocan-2-one) made epoxide-containing molecules.10–24 Although thermoplastic, thermosts, and elastomers are synthesized based on PHU, smart properties are rarely achieved on PHUs.

Recent studies focus mainly to understand polymer synthesis and properties of resultant PHU polymers.25–42 (Figure 1). In 2018, two interesting works were reported with fascinating reworkable properties on PHUs.44,45 PHU-containing acetal group undergoes acid-catalyzed reversibility in solvents.33,44 By using cystamine as comonomer, reprocessable PHUs were achieved at 150 °C.45 The work features the retrieval of original cross-link density after reprocessing the PHU.
PHUs with smart properties are essential for challenging applications in various sectors. In the present work, a novel thermoreversible nonisocyanate hybrid PHU was presented. Combinations of aromatic- and alicyclic-based cyclic carbonates were polymerized together with a suitable amine to result folded-sheet superstructures. H-bonding and self-assembly of polar/nonpolar PHU chains in hybrid PHUs were investigated by temperature-dependent $^{1}$H NMR and Fourier-transform infrared (FTIR) techniques. Morphological changes of PHUs were studied by temperature-controlled polarized light microscopy (PLM) and by field emission scanning electron microscope (FESEM). Reworkable adhesive properties of PHUs were evaluated on both polar and nonpolar substrates. Additionally, reversibility of superstructures in PHUs was confirmed by temperature-dependent spectral and PLM studies.

2. RESULTS AND DISCUSSION

The compositions of PHUs are given in Table 1. The chemical structure of monomers is shown in Figure 2. After the polymerization, all samples exhibited two peaks corresponding to $-\text{CO}$ groups. One was observed at 1702 cm$^{-1}$ and the other at 1798 cm$^{-1}$ (Figure 4a). The former peak is attributed to $-\text{CO}$ peak of urethane linkage, and the latter one is ascribed to the $-\text{CO}$ group of unreacted carbonate group. Characteristic signal of the $-\text{CO}$ group confirmed the formation of PHU, which is evident from FTIR spectra. A typical drawback of all PHUs is that polymerization will be stopped after attaining a certain molecular weight. Further polymer chain growth will be very difficult (due to steric and electronic reasons). The present samples were subsequently analyzed for average molecular weight by gel permeation chromatography (GPC). It is noted that reasonably high molecular weight was achieved by polymerization. The independent PHUs (BACY 10 and BACY 01) and hybrid PHUs (BACY 73, BACY 55, and BACY 37) attained a molecular weight of about 10 kDa (Table S1). From GPC results, it is clearly observed that these PHUs have relatively significant molecular weight to exhibit polymer properties. This study further confirms that no reduction in average molecular weight occurred in hybrid PHUs vis-a-vis independent PHUs. The chain structures of homo (Figure S1) and hybrid PHUs (Figure 3) are given.

Nonisocyanate polyurethanes (NIPUs) were synthesized by curing of limonene dicarbonate with Priamine 1074, which gave a molecular weight ($M_n$) of 4300 g/mol. Studies on the curing of diglyceroldicarbonate (DGC) with isoiodide diamine resulted in PHUs with $M_n = 4900$ g/mol. A bisfuranic hydroxy urethane monomer was synthesized and polymerized with a poly(propylene oxide)-bismaleimide to yield an NIPU with a molecular weight of 4300 g/mol. Ricinoleic acid-derived primary amide was oxidized in situ to isocyanate intermediate by an organic oxidant iodosobenzene, which subsequently self-condensed resulting in PHUs with $M_n = 1300$ g/mol. Studies are available where PHUs of higher $M_n$ (>5000 g/mol) were reported via different methods. PHUs of higher molecular weight (9200–13 500 g/mol) were produced by the reaction of diglyceroldicarbonate (DGC) with different amines such as butane-1,4-diamine (BDA), pentane-1,5-diamine, nonane-1,9-diamine, and dimerized fatty acid diamine. Terephthallic biscyclo carbonate with amines (jeffamine D2000/1,4-butanediol (BDA)) in different ratios yielded thermoplastic nonisocyanate polyurethane with $M_n$ ranging from 9850 to 10 750 g/mol. Hence, PHUs...
achieved in the above possess reasonably high molecular weight (~10 kDa).

In the next step, solubilities of hybrid PHUs were evaluated in both polar and nonpolar solvents (Table S2). The hybrid PHU (and independent aromatic/aliphatic PHUs) exhibited good solubility in ethanol, acetone, ethylacetate, and dimethyl sulfoxide. All samples were soluble in a time of 1 h at room temperature in the above-mentioned solvents. This indicates that the polymer chains were entangled sufficiently but not cross-linked. This is a positive signature that the PHUs can be used for further reaction or processing of new materials. To understand the segmental motions of PHUs, they were subjected to differential scanning calorimetric (DSC) studies in inert atmosphere. The $T_g$s of PHUs increased with the incorporation of aromatic-rich segments. The $T_g$s of BACY 10 (aromatic moiety alone) and BACY 01 (aliphatic moiety alone) were only about 5 °C, as determined from DSC profiles (Figure S2). However, with the addition of BACC into CYCC, $T_g$s were enhanced up to 18 °C, as seen in BACY 55. In BACY 73, $T_g$ was reduced to 12 °C. Generally, no increase in $T_g$ was expected in hybrid PHUs unless otherwise secondary forces exist.

The homo PHUs possess almost same molecular weights and $T_g$s ($T_g$s of homo PHU derived from BACC and CYCC are only ca. 5 °C). The increase in $T_g$ in hybrid PHUs is attributed to enhanced interactions between polymer chains. The secondary interactions such as H-bonding may play a crucial role in determining the thermal properties and morphology (vide infra). Further, single $T_g$s of hybrid PHUs confirm the formation of single polymeric chain made up of both aromatic and aliphatic segments. In another way, the polymerization occurred in a hybrid manner and no independent PHU exists in the copolymer. This is the rationale for the absence of two $T_g$s and the presence of a single $T_g$ in hybrid PHUs. Additionally, PHUs were subjected to softening point evaluation since no melting endotherm was observed in DSC. All of the PHUs exhibited a softening tendency at about 80−100 °C, and the softening temperature was not sharp but wide (Figure S3). This is a very significant information that hybrid PHUs cannot flow (do not show melting endotherm in DSC too), but restricted chain movement is possible. This restriction is ascribed to the secondary interactions, which can give temperature-dependent polymer properties.

The synergetic effect observed in $T_g$ is attributed to increased polymer chain interactions present in hybrid PHU or increased chain rigidity. In addition, the absence of sharp-melting-point endotherm in DSC indicates the absence of long-range order in PHUs. Further, X-ray diffraction patterns imply the amorphous nature of hybrid PHUs (Figure S4). All of these evidences lead to the thought that increased segmental stability is due to ordered regions, which exist locally via H-bonds. H-bonding is possible between secondary and primary hydroxyl groups or −NH of urethane groups or −CO groups. In the first step of understanding H-bonding present in PHUs, $^1$H NMR investigation was carried (Figure 4b). Since the hybrid PHUs flow at 80−100 °C, a temperature regime of 30−90 °C was considered under the assumption that this regime will be the most suitable range for H-bonding studies. The signals corresponding to −NH (6.9 ppm) of urethane shifted to upfield with increase in temperature and finally returned to original position when cooled to 30 °C. To corroborate this observation, signals at 3.6 ppm (−OH groups) also tracked such that they got shifted in the same fashion to the upfield and reached back to the original position by cooling to 30 °C (Figure 4b). This is a clear indication that primary or secondary −OH groups and −NH of urethane are involved in H-bonding. However, the −CO group of urethane is a very strong H-bond acceptor that can definitely participate in H-bonding. The participation of −CO groups in H-bonding was investigated by variable-temperature FTIR spectroscopy.

The BACY 55 PHU was heated from 30 to 100 °C and FTIR spectra were recorded at 30, 60, 90, and 100 °C and after cooling to 30 °C (Figure 5a). Notable spectral shifts were observed, which provided valuable insights into the H-bonded interactions. Four distinct spectral regions were focused for explaining the ordered/disordered carbonyl H-bonding. Generally, in polyureas, the ordered H-bonded domain appears below 1650 cm$^{-1}$ (due to bifurcated H-bonding), whereas polyurethanes exhibit still higher frequency of about 1711 cm$^{-1}$.52 The present system consists of −CO, −OH, and −NH groups (multiple H-bond donors and acceptors). The region corresponding to 1697−1705 cm$^{-1}$ is attributed to H-bonded C=O in ordered domain. Two peaks were present in the FTIR spectra (at 30 °C and also when cooled to 30 °C) of PHU, one oriented at 1697 cm$^{-1}$ and the other at 1705 cm$^{-1}$. These regions are related to ordered domains. It is to be noted that these H-bonded ordered domains observed at 1697 and 1705 cm$^{-1}$ were always present at all temperatures studied. This is a clear observation that, ordering due to H-bonding is not fully vanished with increase in temperature (i.e., there is a high possibility of breaking of H-bonds with rise in temperature). It means that H-bonds break and form with...
other available H-bonding sites with increasing temperature. This is possible because vast H-bonding groups are present in PHUs. With increase in temperature, new peaks were noted at 1716 and 1722 cm$^{-1}$. We assume the peak observed at 1716 cm$^{-1}$ is associated with disordered domain since the intensity of that peak increases drastically with increase in temperature (see the peak at 100 °C and the peak at 1716 cm$^{-1}$ evolved significantly at 100 °C). At 30 °C, the peaks at 1716 and 1722 cm$^{-1}$ were absent or merged with each other. The inference is that more ordering occurred at 30 °C and degree of ordering changed with increase in temperature. But complete absence of ordered domain is not possible since multiple H-bonding occurs in hybrid PHUs. Due to this, PHU exhibits restricted flow at higher temperature (softening only). Additionally, −OH and −NH groups were examined in FTIR spectra. The −NH or OH peaks were oriented about 3400 cm$^{-1}$ at 30 °C, which moved to higher frequency (ca. 3450 cm$^{-1}$) on progressive heating. When cooled to 30 °C, the peak was returned to 3400 cm$^{-1}$ range due to the formation of H-bonding. The increased frequency peak with increase in temperature is due to the breaking of H-bonds. This study reveals the participation of −OH and −NH groups toward hydrogen bonding along with −CO groups in PHUs.

A next interesting aspect is whether hybrid nature of PHU has any impact on H-bonding or ordering phenomenon. To see that, BACY 10 and BACY 01 (both are homo PHUs) were subjected to temperature-variable FTIR studies (Figure S5) as carried out for BACY 55. On studying the FTIR spectra of BACY 01, the region of −C=O group gave a peak with wide distribution at 1740–1650 cm$^{-1}$. On heating, peaks were evolved in both higher and lower frequencies but less intense (at 100 °C). This is due to lesser degree of H-bonding in BACY 01. To corroborate the low level of H-bonding in BACY 01, −NH/−OH region was examined and found that no significant change was noted in the peak position. Peaks at 30 °C and 100 °C exhibited wide distribution, and this wide peak was oriented near to 3450 cm$^{-1}$ (however, intensity increased considerably at 100 °C). Surprisingly, no significant peak change was noted in the −CO and −OH/NH region of BACY 10 with increase in temperature. The FTIR studies reveal the

Figure 5. (a) Changes in the spectral peaks of FTIR upon heating from 30 to 100 °C and on cooling to 30 °C, with (A) showing changes in −CO bonding and (B) showing changes in −NH/OH groups in PHUs. (b) Possible chain structure of hybrid PHUs showing secondary interactions.
prominence of H-bonding in hybrid PHU compared to homo PHUs. This enhanced H-bonding can offer special properties and enhanced mechanical features to hybrid PHUs. This observation is further confirmed by rheological studies. The hybrid PHU (BACY 55) was subjected to heating (50−150 °C) and cooling back to 50 °C in a rotational rheometer (plate−plate assembly) where the polymer completely regained the original viscosity (Figure S6). The heating/cooling cycle was repeated and no appreciable change in viscosity was observed. This repeatability implies the reassembly of PHUs where H-bonded domains play a crucial role. Possible H-bonding interactions (representative structures) are shown in Figure 5b.

To study the self-assembly behavior and differentiate assembly pattern due to the incorporation of aromatic/aliphatic units in the polymer chain, FESEM of each composition was imaged. It is evident from the images that aliphatic PHU (BACY 01) and aromatic PHU (BACY 10) feature a smooth surface with folded-sheet morphology (Figure 6). The layer thickness is in the order of 500 nm. This morphology is attributed to multiple hydrogen bonding reported elsewhere.52 It is well established that H-bonding can give different orientations. By comparing the folded structures of BACY 10 and BACY 01, BACY 10 possessed a closely aligned sheet structure, whereas BACY 01 exhibited less folding. On the other way, folding density is higher for BACY 10, which may be due to the additional π−π interaction (due to aromatic nature) in association with H-bonding. When aliphatic content was incorporated via tandem polymerization of BACC and CYCC (i.e., BACY 73), folded sheets become closer and roughness was introduced. In the hybrid BACY 55, the folded-sheet...
formation was intensified and folding density was high compared to other hybrids. The highly populated sheet formation was composition-dependent, and surface revealed rough morphology. When the hybrid became aliphatic-rich (BACY 37), close alignment of polymer chains was difficult due to lack of secondary interactions, which finally gave folded sheets similar to BACY 10 and BACY 01 PHUs. As a single T_g was observed for hybrid PHUs (BACY 37, BACY 55, and BACY 73), it is concluded that a single polymer matrix exists in hybrid where aliphatic or aromatic backbones are competing each other to self-assemble in the hybrid polymer due to their thermodynamically incompatible nature.

When assessed the width of folds and gap between folds, interesting observations were noted (Figure S7). In both BACY 10 and BACY 01 (nonhybrid PHUs), widths of folds were in micron level, but in hybrid PHUs, widths were reduced to nano-level. In BACY 55 (Figure 6C inset), the widths of folds were <200 nm. In addition, we have tried to obtain the gap between folds, which were also in the range of 100–200 nm in BACY 55 PHU. In other hybrids BACY 37 and BACY 73, the fold gaps were in the range of 500–700 nm. This unraveled that, hybrid PHUs were aligned closer or self-assembled more vis-à-vis independent PHUs.

To observe the material features and behavior toward polarized light at different temperatures, PLM on samples of all PHUs were studied (magnification: 40×). Irrespective of the composition, all exhibited a melting feature at 80–100 °C (Figure 7). With increase in temperature, a kind of melting phenomenon occurred and folded chains were diffused to some extent. It is interesting that the folded chain structure is slightly diffused only under polarized light (no complete melting), which implies the restricted flow of the hybrid PHUs. It is to be perceived that the morphology is maintained at softening temperature also as evidenced in PLM studies. In the cooling of PHU, the folded morphology was regained. To understand the evolution of ordering in PHUs, BACY 55 was heated to 100 °C and allowed to cool to 30 °C slowly and the images were captured in the dark field. Interestingly, we could see the formation of ribbonlike structures. This is nothing but folded surfaces due to multiple H-bonding interactions in PHUs. These ribbonlike structures will assemble to form a weblike structure, as observed from PLM images (Figure 7). The folded chains are clearly visible in FESEM images also.

In the next step, the application potentials of the synthesized homo and hybrid PHUs were explored by evaluation of adhesive strength. Two different substrates were taken for the determination of lap shear strength, viz., Al–Al (high-surface-energy polar substrates) and HDPE–HDPE (low-surface-energy nonpolar substrates). The aromatic homo PHU BACY 10 achieved an adhesive strength of 9 MPa, whereas that of homo PHU BACY 01 recorded a lower value of 6 MPa. By increasing the aromatic content, the adhesive strength reduced to 5.0–7.5 MPa in the case of Al–Al substrates. When the substrates are HDPE, the adhesive strengths of both homo PHUs are about 1 MPa. Surprisingly, the adhesion was improved and doubled to 2 MPa in PHU hybrids. This is attributed to the balanced behavior of hybrid PHUs with polar and nonpolar counterparts. Hence, the hybrid methodology adopted in this work is able to provide reasonable adhesion between nonpolar substrates. Since hybrid PHUs exhibit restricted flow at elevated temperature, they were tested for thermoreversible adhesion. To prove the efficiency of the material for repeated use (thermoreversible adhesion), the bonded substrates were heated to 100 °C and kept at this temperature for 0.5 h to allow the breaking of noncovalent interactions. Then, the substrates were debonded manually. The PHU-containing substrates were bonded again at 100 °C and cooled to 30 °C. These coupons were tested for adhesive strength evaluation, and it was found that there is no considerable degradation in the adhesive strength in the case of both Al–Al and HDPE–HDPE substrates (Figure 8). These results demonstrate that the noncovalent interactions can lead to the reversal of adhesive property and the hybrid PHUs reported in this work are reworkable by heating.

The hybrid nature of PHU gives good adhesive strength on both polar and nonpolar substrates. The polar nature of aromatic-based PHU (BACY 10) and alicyclic-based PHU was tested by contact angle measurement. BACY 10 (aromatic PHU) and BACY 01 (alicyclic nonpolar) exhibited contact angles of 65 and 80°, respectively. This clearly substantiates that BACY 10 is polar in nature and BACY 01 is nonpolar in nature. By combining these chemical structures, the hybrid PHUs are able to adhere to both polar and nonpolar substrates effectively, as the hybrid structure comprises both aromatic and alicyclic PHU backbones.

To physically observe the weight-holding property of PHUs, a 1 kg weight was hung on the PHU-bonded Al coupons (after thermal bonding and debonding) and the adhesive was found to be capable of withstanding this weight for 24 h (Figure S8). Additionally, the suitability of PHUs for pressure-sensitive adhesive applications was investigated. Peel strength evaluation was conducted on polyaniline–polymide film substrates, and the values are in the range of 1–1.5 kg/cm. Meanwhile, BACY 55 could not be tested successfully due to failure of polyaniline substrate. It indicates that the peel strength of BACY 55 is higher than 1.5 kg/cm. Previously, trimethylolpropane triscarbonate and poly(propylene oxide) bis carbonate hybrid system were polymerized using an amine (EDR 148-PEA MW 148 g/mol), which resulted in a low adhesive strength (LS) of about 0.05 MPa between wood substrates. In another study, same hybrid system was cured with 1,3-cyclohexanediis-
polyurethanes. The hybrid networks are resistant to moisture allowing water molecules to attach easily. This indicates the decomposition of urethane bridge. It is the recorded on a Bruker Avance spectrometer (300 MHz) with an increasing aromatic content in hybrid PHU, which was achieved in the 400—800 nm visible range. This is one of the useful attributes with other features of PHUs described above. Thermogravimetric analyses (TGA) of the homo and hybrid networks were assessed by TGA under N2 atmosphere from 30 to 500 °C (Figure S10). All PHUs exhibited Tg% in the 245—250 °C range (temperature at which 5% weight loss), which indicates the decomposition of urethane bridge. It is the first decomposition pattern typically observed for conventional polyurethanes. The hybrid networks are resistant to moisture as noted by the absence of considerable weight loss below 100 °C in TGA profiles due to multiple H-bonding, which may not allow water molecules to attach easily.

3. CONCLUSIONS

In the present contribution, hybrid poly(hydroxy urethane)s were synthesized by mixed cyclic carbonate-amine polymerization. Aromatic- and aliphatic-based cyclic carbonates were synthesized using epoxy-CO2 reaction under pressure. By increasing the aromatic content in hybrid PHU, Tg% enhanced to 10 °C, which is attributed to multiple noncovalent interactions. Signature peaks contributing to H-bonding (between −CO and OH/NH) were tracked and identified by temperature-dependent FTIR. Participation of −OH and NH groups in H-bonding with −CO was detailed further by temperature-dependent NMR. The PHUs featured folded-sheet morphology, and the folds became closer with equal concentration of aromatic/aliphatic content in PHU. Growth of folded-sheet morphology was very vivid in PLM images, which were traced by cooling down the PHU. Since PHUs displayed restricted flow, they possessed excellent thermoreversible adhesion with good bonding to both polar (Al−Al: 5—9 MPa) and nonpolar (HDPE−HDPE: 1.5—2.0 MPa) substrates. PHUs are thermally stable up to 250 °C. Here, we demonstrate a green synthetic route to obtain hybrid PHUs with thermoreversible adhesion features.

4. MATERIALS AND METHODS

4.1. Materials. Diglycidyl ether bisphenol A monomer (DGEBA, EpoBase 123, 99.9%, Fine Finish Organics Pvt. Ltd., Maharashtra, India), Araldite CY230 (Huntsman India Pvt. Ltd.), benzyl triethyl ammonium chloride (BTAC, Spectrochem Pvt. Ltd., Mumbai), N-methyl-2-pyrrolidone (99.5%, Sigma-Aldrich, Germany), CO2 (99.9%, Cheers India gas suppliers, India), poly(propylene glycol) bis (2-amino propyl ether) (PEA, average Mw = 400 g/mole) (Sigma-Aldrich, Germany), and Araldite HY960 (Huntsman India Pvt. Ltd.) were used as received.

4.2. Characterization Techniques. FTIR spectra were recorded using a Nicolet iS50 FTIR spectrometer in a frequency range of 4000—500 cm−1. The sample was mixed with KBr powder and pelletized. This pellet was used for recording FTIR spectra. The NMR studies (1H NMR) were recorded on a Bruker Avance spectrometer (300 MHz) with tetramethylsilane as the internal standard. For variable-temperature experiment, the sample solution prepared in CDCl3 was taken in the NMR tube. The machine was programmed in such a way that NMR tube was heated from 300 to 370 K and back to 300 K. The samples were equilibrated at the specified temperature for 5 min before acquisition. The acquisition took 1 h for completion. Waters 600 GPC equipped with Waters 2414 refractive index detector was engaged for determining average molecular weight and distribution. Tetrahydrofuran was used as eluent and the instrument was calibrated using polystyrene as standard. A TA Instruments model 2920 modulated DSC was employed for differential scanning calorimetry (DSC) investigations (heating rate of 10 °C/min under N2). In all of the above tests, microgram-level samples were used. Rheological observations were carried out on TA Instruments model DHR-3 using 25 mm parallel-plate assembly at 1 Hz frequency and at a controlled strain of 0.01%. The surface morphological features of hybrid PHU samples were examined using a Hitachi SU6600 scanning electron microscope at an accelerating voltage of 5 KV. Thin layer of PHUs prepared in acetone was deposited over carbon tape, and gold coating was given by sputtering using SCD 500 Sputter Coater (BAL-TEC AG, Liechtenstein) prior to the analysis. Polarized light microscopy (PLM) studies were conducted on Olympus BX51 microscope. A thin layer of PHU was coated over a glass slide, and imaging was carried out at a magnification of 40x. Static water contact angle of PHUs was measured by sessile drop method in an automated goniometer (Data Physics model OCA-20). Instron UTM 5569 Microtest model EM2/S0/FR was employed for the determination of adhesive strength (Lap Shear Strength) of PHU samples. The selected substrates for the study were aluminum—aluminum (Al−Al) and high-density polyethylene—high-density polyethylene (HDPE−HDPE) (substrate dimension: 100 × 25 mm). Lap shear strength was evaluated by ASTM D 1002 standard (crosshead speed of 50 mm/min was used for testing). The substrates to be bonded were thoroughly etched with chromic acid and dried at 70—80 °C. The dried substrates were used for bonding. The adhesive was mixed with amine/catalyst, applied on the substrate, and the substrates were bonded tightly by Teflon tape for 24 h. These bonded coupons were used for LSS evaluation at 25—28 °C. Peel strength of PHUs was tested according to ASTM D 1876. Polyimide films were cut according to ASTM standard and bonded with the adhesive. The 90° peel test was used for evaluating the peel strength. Instron UTM 5569 Microtest model EM2/S0/FR was employed for the determination of peel strength of the bonded film. A simultaneous DTA−TGA instrument model SDT-2960 was used for thermogravimetric analysis (TGA) (heating rate, 10 °C/min under N2).

4.3. Synthesis of Cyclic Carbonates and Homo/Hybrid PHUs. Prior to the synthesis of hybrid PHUs, aromatic (BACC) and aliphatic (CYCC) cyclic carbonates were synthesized from their respective epoxy functional monomers (Figure 2). Synthesis of aromatic-based cyclic carbonate (BACC, starting monomer: diglycidyl ether bisphenol A) is given below. The epoxy monomer was reacted with CO2 at 12 bar pressure at a temperature of 100 °C (no solvent was used). The reaction was performed in an autoclave made of stainless steel with a capacity of 500 mL and that can withstand a maximum pressure of 100 bar. The reactants were magnetically stirred and was connected with a pressure gauge.
for monitoring the inside pressure. Here, 20 g of DGEBA was used for the synthesis of cyclic carbonate. Benzyl triethyl ammonium chloride (BTAC, 3% by weight) was used as phase-transfer catalyst. When the pressure inside the autoclave (monitored with digital pressure gauge) attained a constant pressure, reaction was stopped (ca. 16 h). The conversion to BACC was confirmed by FTIR spectroscopy (Figure S11), where the intense peak at 1798 cm⁻¹ was noted, which is ascribed to the peak corresponding to ≈CO of cyclic carbonate monomer. The epoxy content of BACC was almost equal to 0 eq/kg, which underlined the complete conversion of epoxy to cyclic carbonate group. Aliphatic cyclic carbonate (CYCC) was synthesized employing the same strategy of CO₂ insertion into the epoxy ring (12 bar pressure at 100 °C for 16 h) in the presence of BTAC as catalyst (no solvent was used). The conversion was confirmed by FTIR spectroscopy (Figure S12). The presence of CC ring at 1798 cm⁻¹ and the absence of peak of epoxy group in the resultant product indicate the insertion of CO₂. Further, epoxy content of CYCC was ≈0 g/equivalent KOH, which implies the complete conversion of epoxy ring to cyclic carbonate.

Initially, homo PHUs were synthesized. BACC was reacted with PEA-400 by applying a progressive heating profile (100 °C/2 h and 150 °C/2 h) to obtain homo PHU (BACY 10). Similarly, CYCC was polymerized with PEA-400, which gave homo PHU (BACY 01). Hybrid poly(hydroxy urethane)s were synthesized by copolymerizing BACC and CYCC monomers in different molar ratios with PEA-400. In all polymerization attempts, an amidoamine (Aradur HY960) was used as catalyst. In the hybrid synthesis, the monomers BACC, CYCC, and PEA-400 were mixed by magnetic stirring for 1 h. Then, the mixture was maintained at ambient temperature for 15–17 h. In the second step, the mixture was heated at 100 °C for 2 h and finally at 150 °C for 2 h to complete the polymerization. The copolymerized samples were subjected to FTIR and GPC studies.

**ASSOCIATED CONTENT**

1. **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00789.

Chain structure of individual PHUs; DSC profile of homo and hybrid polyhydroxy urethanes; softening point observed for different PHUs from differential scanning calorimetry; X-ray diffraction patterns of PHUs; temperature-dependent FTIR spectra of homo PHUs BACY 01 and BACY 10; complex viscosity with heating and cooling for BACY 55; SEM images of PHUs focusing on the width of folded chains; physical strength evaluation by hanging weight; transparency of PHUs in the visible region obtained from solid-state UV–visible spectroscopy; thermogravimetric profiles of (polyhydroxy urethane)s; FTIR spectra of BACC and CYCC; and molecular weight of poly(hydroxy urethane)s by GPC and solubility of hybrid PHUs in different protic and aprotic solvents (PDF)

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**Notes**

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