



Biobased reprocessable polyisobutylene - polyurethane networks

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Received: 20 April 2023 / Accepted: 24 July 2023 / Published online: 27 July 2023
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Abstract

A synthetic strategy for the preparation of novel and reprocessable biobased polyisobutylene (PIB) – polyurethane (PU) network with soybean oil (SBO) derivative was reported. For this purpose, SBO triglycerides were converted to a polyol with primary hydroxyl functionalities via UV activated thiol-ene chemistry. Optimization of grafting of hydroxyl groups was performed by varying the process parameters such as ratios of both initiator and thiol to double bond as well as the irradiation time. SBO/PIB based PU network (X-SBO/PIB-PU) was then prepared by successful integration of the SBO based polyol to PIB-PU formulation as a co-polyol. The resultant network formed a nearly optically clear film which can be swollen in good solvent. Selective cleavage of the ester bonds by acid catalyzed hydrolysis was found to be an efficient way to solubilize the network by enabling the recovery of polyurethane segments with carboxylic acid functionalities. Thermal, mechanical and microstructural characterization data confirmed that hydrolysis of the network can be conducted without disturbing the polyurethane structures with high mechanical and thermal stability. It has been suggested that hydrolyzed X-SBO/PIB-PU (H-SBO/PIB-PU) with polar functional groups can then be used as building block in the development of polymer conjugates formulated with rigid polymers and nanocomposites.

Keywords Soybean oil · Thiol-ene reaction · Polyisobutylene · Polyurethane · Network · Hydrolysis

Introduction

Polyurethanes (PUs) are distinguished from other classes of polymer by their unique segmented block copolymer structure that originated from hard urethane and soft polyol segments [1]. As a result of their distinguished mechanical properties and biocompatibility, PUs are preferred polymers for medical devices. Current biomedical applications of PU are catheters, blood oxygenators, stents, cardiac valves, dialysis devices, dressings, adhesives, drug delivery devices, tissue engineering, pacemaker, and coatings for breast implants [2–4]. Major handicap of PUs is the lability of inherent urethane linkages to hydrolysis and oxidation. Besides that, the common soft segments like polyethers, polyesters, polycarbonates and polydimethylsiloxanes are also reported to suffer from hydrolytic and oxidative deterioration, and hence

these PUs are not able to maintain their superior mechanical properties for long term medical applications [5–7]. It has been reported that although polyurethanes exhibited appropriate mechanical properties for heart valve function, the biological instability of earlier generations put limitations to cardiac applications [7]. Therefore achieving mechanical durability and biostability at the same time is an overarching objective of the researchers.

Polyisobutylene (PIB), on the other hand, is a valuable polymer with outstanding oxidative-hydrolytic-chemical stability, gas impermeability and biocompatibility [8]. PIB is used broadly in areas where environmental and chemical stability, gas impermeability and high damping characteristics are required, such as tire inner liners (i.e., halogenated butyl rubbers), vibration proof materials and engine mounts, as well as in biomaterial applications e.g., TAXUS coronary stent coating [9, 10]. In this context, PIB based PUs have been realized as unique materials that would embody the superior properties of individual polymers; that is, exceptional inertness, chemical and biostability of PIB and high strength of segmented thermoplastic PUs [8]. Recently, Naficy et al. presented an excellent review on advancements in polyurethane heart valve replacements

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(HVRs) by addressing the shortcomings of earlier generation of polyurethane HVRs [7]. They pointed out to PIB based polyurethanes in their future perspectives as a potential material having robust performance, calcification resistance, relatively low protein adsorption—particularly the ones with some PTMO co-soft segments and high hydrolytic stability than polyether urethanes and ureas, polycarbonate urethanes and polysiloxane urethanes [7]. Moreover, even only 70% PIB based PUs without any PTMO co-soft segment with considerably high mechanical strength, hydrolytic-oxidative stability [11–13], calcification resistivity [14], biocompatibility [15] as well as impressive fatigue resistance were recently reported as a superior alternative to conventional TPUs for a synthetic heart valve application [3].

On the other hand, while fossil based starting materials of polyurethanes in biomedical applications are improving, renewable contents seem to be necessary for most of them in order to have a certificate and increase their 0.1% market share [16]. Production of bio-based polyurethanes and their hybrids with petroleum based polyols are thought to be one of the most important issues also for the protection of global environment [17]. Although there has been a considerable research effort on synthesis and characterization of segmented polyurethanes from renewable polyols and diisocyanates [17–19], studies on their hybrids with polyisobutylene based polyol are not included in the literature yet.

In current study it is aimed to develop a synthetic approach for the preparation of a novel bio-based PIB-PU with a soybean oil derivative, X-SBO/PIB-PU. The important milestones of the study are (a) to convert SBO triglycerides to a polyol with primary hydroxyl functionalities via UV activated thiole-ene chemistry, (b) to optimize the grafting efficiency, (c) to synthesize novel X-SBO/PIB-PU. A short strategy were also proposed to make the resultant networks reprocessible by selective hydrolysis of network moieties which can be resulting in a soyben oil based PIB-PU having valuable polar sites for their further blends and composites forms.

Materials and methods

Materials

Hydroxyl telechelic PIB (OHTPIB, $M_{n,NMR}$ = 4418 g/mol) was synthesized as described previously [20]. Dibutyltin dilaurate (DBTDL), 2-mercaptoethanol, diethyl ether (DEE), hydrochloric acid (HCl, 37%), calcium hydride (CaH_2), sodium bicarbonate ($NaHCO_3$) and sodium sulfate (Na_2SO_4) were purchased from Merck and used as received. Dichloromethane (DCM) and tetrahydrofuran (THF) obtained from Merck were refluxed and distilled over CaH_2 . 1,4-butanediol (BDO) was purchased from Merck,

dried over Na metal, and distilled under reduced pressure. 4,4'-Methylenebis(phenyl isocyanate) (MDI) obtained from Across was distilled under reduced pressure ($\sim 150^\circ C$ at 10^{-2} mmHg) and stored under N_2 atmosphere in the refrigerator. 2,2-dimethoxy-2-phenylacetophenone (DMPA) purchased from Across was used without further purification.

SBO was purchased from a local grocery shop and used after purification. Following extraction with water, the organic phase was dried over Na_2SO_4 , purified by activated carbon, dissolved in toluene, and filtered through a fine-sintered glass. Following the complete removal of water using a Dean-Stark trap, toluene was evaporated on a rotary evaporator, and the oil was dried on the high vacuum line.

Synthesis of SBO based polyol

In a typical UV light activated thiol-ene addition reaction, SBO (5.00 g, 5.81 mmol triglyceride), 2-mercaptoethanol (2.75 g, 35.2 mmol, thiol/double bond = 1.44) and DMPA (1.19 g, 4.65 mmol, DMPA/double bond = 0.19) were weighed into a vial and dissolved in 6 ml DCM. The vial was sealed, purged with N_2 and placed into the UV chamber. After irradiation at 11 mW/cm^2 for 4 h at room temperature, the content was dissolved in DEE and extracted with water. The organic phase was dried over Na_2SO_4 , filtered through a sintered glass and the solvent was evaporated on the rotary evaporator. Finally, the modified oil was dried on the high vacuum line to remove any leftover solvent.

Synthesis of PIB-PU

PIB-PU ($M_{n,SEC}$ = 80500 g/mol and MWD = 2.05) was also synthesized according the previous procedure for control purpose [3].

Synthesis of X-SBO/PIB-PU

OHTPIB (0.931 g, 0.211 mmol), SBO polyol (0.118 g, 0.105 mmol) and MDI (0.352 g 1.41 mmol) were weighed into a dried reactor equipped with a condenser. The mixture was degassed on the high vacuum line, charged with N_2 , and dissolved in 4 ml dry THF. Prepolymerization reaction was carried out at $65^\circ C$ for 1 h upon addition of 0.5 ml of 1.84 mg/ml catalyst solution into the reactor. BDO (0.0982 g, 1.09 mmol) dissolved in 3 ml dry THF was transferred to the reactor via steel capillary under N_2 pressure. Two minutes after transferring BDO solution, the polymer was cast into a 7×7 cm glass mold. THF was evaporated slowly at room temperature for 6 days. The film was further dried in vacuum oven at $60^\circ C$ for 20 h and annealed at $80^\circ C$ for 1 h.

Acid catalyzed hydrolysis of X-SBO/PIB-PU

Acid catalyzed hydrolysis reaction was carried out in a manner similar to that described by Murgasova et al. and Chapman [21, 22]. 1.22 g of PU film was refluxed in HCl (0.25 M, 12.2 mmol) in 48.9 ml THF/water mixture (92% THF by volume) at 70 °C for 48 h. Following the evaporation of the solvent, the hydrolysis product was dissolved in CHCl_3 , washed with 1% NaHCO_3 solution and then with water. The organic phase was then dried over MgSO_4 and filtered. The solvent was then evaporated on the rotary evaporator. Finally, the product was solvent cast from THF into a glass mold, air dried for 6 days and vacuum dried for 20 h at 40 °C.

Characterization

UV light-initiated reactions were carried out in a UV chamber equipped with an air circulating fan and low-pressure mercury-vapor fluorescent lamps with an emission maximum at 365 nm. The intensity of light was measured between 8–13 mW/cm² by using UVA/B Light Meter.

¹H NMR spectra were obtained using a Varian Gemini 400 MHz in CDCl_3 (δ CDCl_3 : 7.26 ppm) or pyridine (δ pyridine-*d*₅: 7.22, 7.58 and 8.74 ppm).

The molecular weight distributions of the polymers were determined by Size Exclusion Chromatography (SEC) at 30 °C using Waters Isocratic HPLC Pump with Waters 2414 Refractive Index Detector and four Waters 4.6 × 300 mm Styragel columns HR 3, HR 4, HR 4E and HR 5E. Distilled THF was used as the mobile phase at a flow rate of 0.35 mL/min. Polystyrene standards ranging from 400 to 2.5×10^6 g/mol were used for calibration. Samples were injected using 100 μL Hamilton syringe.

FTIR spectra were collected using a Thermo Scientific Nicolet 380 FTIR spectrometer with a smart orbit diamond ATR accessory. 32 scans for each sample with a resolution of 4 cm⁻¹ were run in the frequency range of 500–4000 cm⁻¹. Spectral analysis was done using EZ-Omnice software.

Swelling measurement of dried film of the network was performed in THF at room temperature by determining deformations resulting from linear swelling ratio [23]. Lengths of the swollen films were measured using a traveling microscope at regular time intervals until equilibrium swelling was reached. The linear swelling ratio (λ) was calculated as the ratio of the length of swollen film, L , divided by the dry length of the film before immersion in THF, L_0 [23].

$$\lambda = \frac{L}{L_0}$$

Differential Scanning Calorimetric (DSC) measurements were done with a DSC instrument (TA Q200) under

N_2 atmosphere. The tests were carried out in a temperature range of -90–230 °C at a heating rate of 10 °C/min.

X-ray diffraction (XRD) analyses of the cast films ($1.5 \times 1.5 \text{ cm}^2$) were conducted on Rigaku D/Max-Ultimat diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) as the X-ray source, operating at 40 kV and 40 mA. XRD patterns were recorded from 3° to 70° (2 θ) with a scanning rate of 2°/min. Thermogravimetric analyses (TGA) of the samples were performed with a Seiko TG/DTA 6300 instrument in a temperature range of 20–600 °C at 10 °C/min heating rate under N_2 .

Stress-strain traces were recorded on a Zwick/Roell Universal Testing Instrument with a 1 kN load cell. Strips ($50 \times 5 \times 0.3 \text{ mm}$) were cut from solvent cast films and tested to failure at a drawing rate of 50 mm/min at room temperature [24].

Results and discussion

Synthesis and characterization of SBO based polyol

Considering the polyol is the main constituent of polyurethanes, a great deal of research has been done to functionalize vegetable oil fatty chains with hydroxyl groups in order to increase the bio-content of PUs [25–32]. Commercial ones mostly depend on the epoxidation-ring opening strategy resulting in polyols with secondary hydroxyl groups which do not contribute to urethane formation effectively [29, 30]. Hydroformylation and ozonolysis reactions are other strategies focusing on the functionalization of double bonds of fatty acid chains with primary hydroxyl groups via the intermediacy of an aldehyde but particularly the former one requires the use of expensive Rh catalyst for quantitative conversion. In the ozonolysis strategy, on the other hand, lower molecular weight polyol with less than three terminal hydroxyl groups can be achieved for oils with saturated fatty acid chains [29, 30]. In spite of this, these methods proceed over two step mechanism. Therefore, radical addition of hydroxyl functional thiols to olefinic unsaturations, has emerged as a prominent alternative to the abovementioned strategies because thiol-ene reaction is one step reaction and allows preparation of polyols with primary hydroxyl functionalities under mild reaction conditions [33–42].

SBO polyols by UV induced thiol-ene addition of 2-mercaptoethanol onto triglycerides were synthesized under N_2 using DMPA as the photo initiator in DCM as shown in Scheme 1.

The effects of reaction parameters such as ratios of DMPA to double bond and thiol to double bond as well as irradiation time on the reaction efficiency were studied. For this purpose, 0.48 and 0.19 equiv. DMPA and 1.44 and 1.01 equiv. thiol with respect to double bond were studied at 8–13 mW/cm² irradiation intensity for 1–4 h reaction time as summarized in Table 1.

Scheme 1 UV initiated thiol-ene addition of 2-mercaptoethanol onto triglycerides

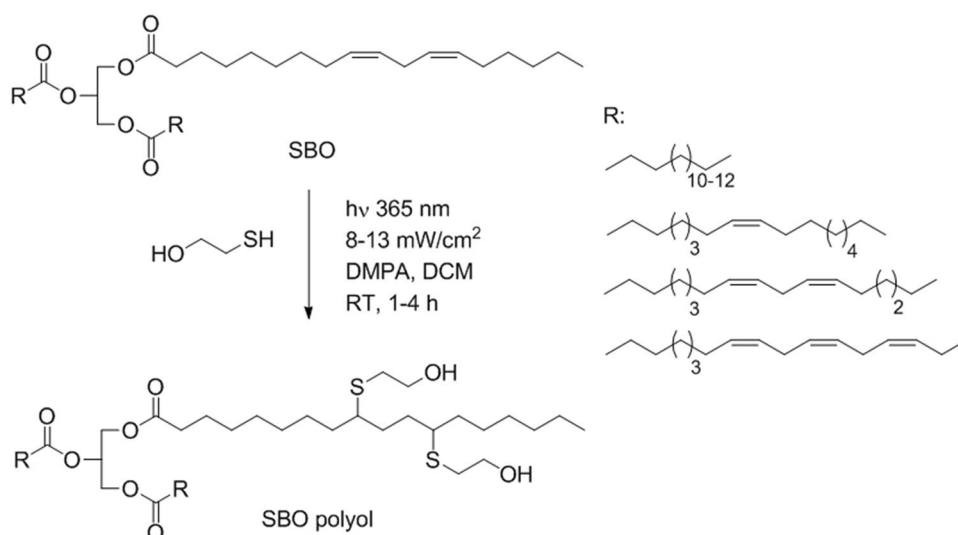


Figure 1 shows ^1H NMR spectra of the purified SBO and the polyol obtained under the reaction conditions of 0.48 equiv. DMPA, 1.44 equiv. thiol at 13 mW/cm^2 for 4h. In the spectrum of SBO, the integral of the peak at 5.33 ppm ($-\text{CH}=\text{CH}-$) indicates about 4.2 double bonds per triglyceride and the peak centered at 5.25 ppm is due to the glycerol unit ($-\text{CH}_2-\text{CH}-\text{CH}_2-$) [43]. In the spectrum of the SBO polyol, the absence of the peaks at 5.33 ($-\text{CH}=\text{CH}-$), 2.03 ($-\text{CH}_2-\text{CH}=\text{CH}_2$) and 2.76 ppm ($=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$) belonging to the unsaturations indicated an almost complete conversion of double bonds ($\sim 98\%$). Besides, the appearance of the peak at 2.6 ppm corresponding to the thioether group ($-\text{CH}-\text{S}-$) proves addition of 2-mercaptoethanol onto the double bonds and its integral indicates $\sim 92\%$ grafting efficiency. The peaks at 2.7 ($-\text{S}-\text{CH}_2-$) and 3.7 ppm ($-\text{CH}_2-\text{OH}$) are due to the protons of the grafted 2-mercaptoethanol.

Figure 2 shows the ^1H NMR spectra of the polyols obtained from the set of reactions summarized in Table 1. One of the variables having a prominent effect on the reaction efficiency is the irradiation time. The integrals of the peaks at 2.6 ppm representing the proton attached to the carbon adjacent to the newly formed thioether moiety

increase with increasing irradiation time, which is followed by a decrease and disappearance of above mentioned peaks at 5.3 ppm and 2.0 ppm. An almost complete consumption of the double bonds (SBO polyol exp. 7) was observed for 4h irradiation. The ^1H NMR spectra with peak integrals are also presented in Supplementary Material File (Figs. S1–S6).

The conversions of double bonds and the grafting efficiencies were calculated by the ratio of the integrals of the peaks at 5.3 and 2.6 ppm, respectively, to the number of double bonds which is calculated to be 4.2 for the pristine SBO. As shown in Fig. 3, for the reactions with the same mole ratios of DMPA/double bond, higher percentages of thiol-ene coupling were achieved when their thiol/double bond mole ratios were 1.44 (SBO polyol exp. 6 and 7). Also, among the reactions with the same mole ratios of thiol/double bond, higher percentages of thiol-ene coupling were obtained when their DMPA/double bond mole ratios were 0.48 (SBO polyol exp. 5 and 7). Under the given reaction conditions, the highest thiol-ene coupling was obtained for the reaction with thiol/DMPA/double bond ratio of 1.44/0.48/1 and at 4 h irradiation.

Table 1 Reaction conditions for the synthesis of SBO based polyol

Exp.	SBO (mmol)	Thiol (mmol)	DMPA (mmol)	Solvent (DCM) (ml)	DMPA/ene mol ratio	Thiol/ene mol ratio	Reaction time (h)	UV intensity (mW cm^{-2})
1	0.23	0.99	0.43	0.25	0.48	1.01	1	8
2	0.23	0.99	0.19	0.25	0.19	1.01	2	9
3	0.23	0.99	0.43	0.25	0.48	1.01	2	9
4	0.23	0.99	0.19	0.25	0.19	1.01	4	9
5	0.23	0.99	0.43	0.25	0.48	1.01	4	13
6	5.81	35.2	4.65	6.00	0.19	1.44	4	11
7	0.23	1.40	0.43	0.25	0.48	1.44	4	13

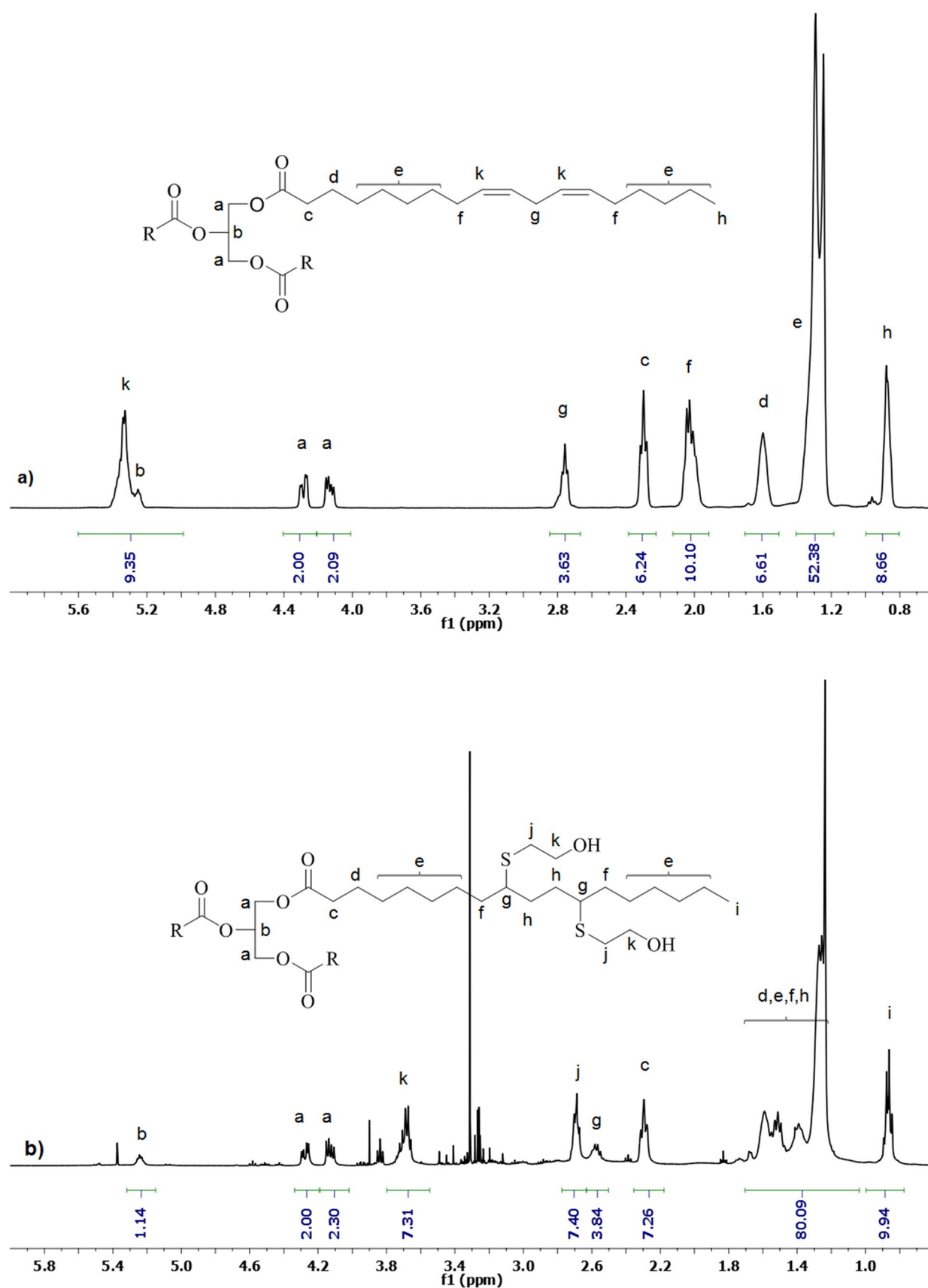
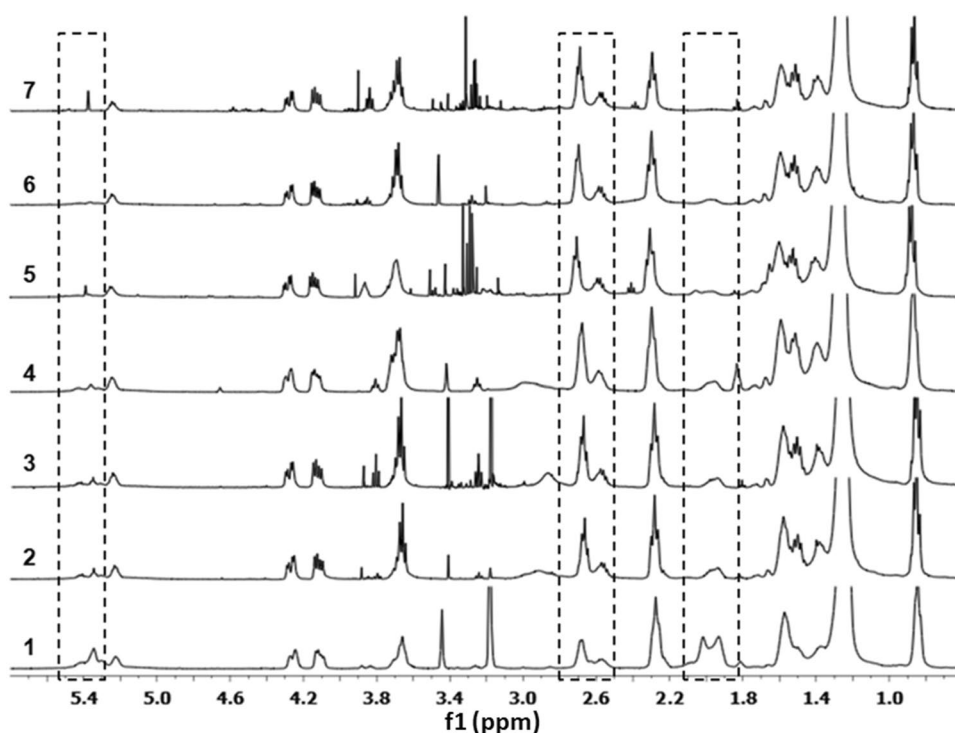


Fig. 1 ^1H NMR spectra of (a) SBO and (b) SBO polyol (exp. 7 in Table 1)

Fig. 2 ^1H NMR spectra of the SBO polyols for different irradiation time and thiol/DMPA/double bond ratios (The numbers 1–7 represent the experiments given in Table 1)



Thiol-ene coupling was also confirmed by FTIR technique. Figure 4 shows the spectra of pristine SBO and SBO polyol (thiol/DMPA/double bond = 1.44/0.19/1, 4h, 81.3% grafting efficiency, 81.7% double bond conversion).

The characteristic absorption bands of inherent functional groups of triglycerides, that is olefinic unsaturations and ester groups, can be easily detected. The bands associated with the internal double bonds appearing at 3008 and 1654 cm^{-1} were due to C–H stretching and weak C=C stretching vibrations of cis H–C=C–H, respectively [44]. C–H bending vibrations of cis double bonds also appeared as weak bands at 1418, 1397 and 913 cm^{-1} , those of trans double bonds appeared at 987 and 967 cm^{-1} [45, 46]. Absorptions

associated with the ester groups appeared at 1742 cm^{-1} due to strong C=O stretching vibrations and in the region 1300–1000 cm^{-1} due to C–O stretching vibrations [44–46].

After thiol-ene coupling reaction, the appearance of a broad band centered at 3430 cm^{-1} due to hydrogen bonded OH stretching vibrations, and a new distinctive peak observed at 1043 cm^{-1} due to CO stretching of primary alcohol proved the addition of 2-mercaptoethanol.

Synthesis and characterization of X-SBO/PIB-PU

Scheme 2 outlines the strategies for the preparation of the PU network by the use of both PIB and SBO polyols, conventional diisocyanate (MDI) and chain extender (BDO) as well as for the acid catalyzed hydrolysis of the products.

Due to multiple primary hydroxides of SBO polyol, the polyurethane formation resulted in a network film. Both insolubility of the network and almost 2.2 equilibrium swelling ratio in good solvent THF (Fig. 5) confirmed the crosslinked nature of X-SBO/PIB-PU.

The optical clarities of X-SBO/PIB-PU and H-SBO/PIB-PU films are also compared with a typical PIB-PU film in Fig. 6. As compared with an optically clear PIB based PU (Fig. 6a), slight scattering dependent haziness in X-SBO/PIB-PU film (Fig. 6b) can be attributed to the network junction based optical imperfections.

X-SBO/PIB-PU was also characterized by FTIR technique (Fig. 7). X-SBO/PIB-PU spectrum exhibits all characteristic absorption bands of urethane groups, PIB soft

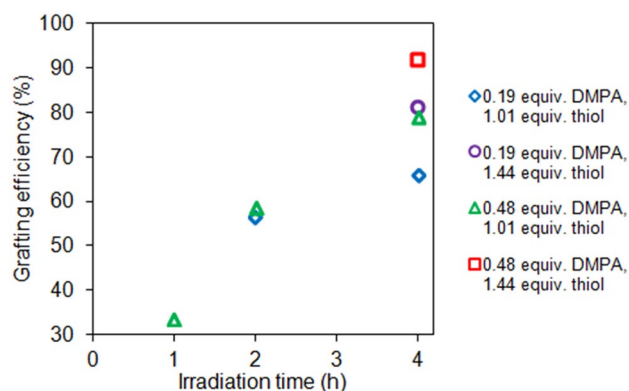
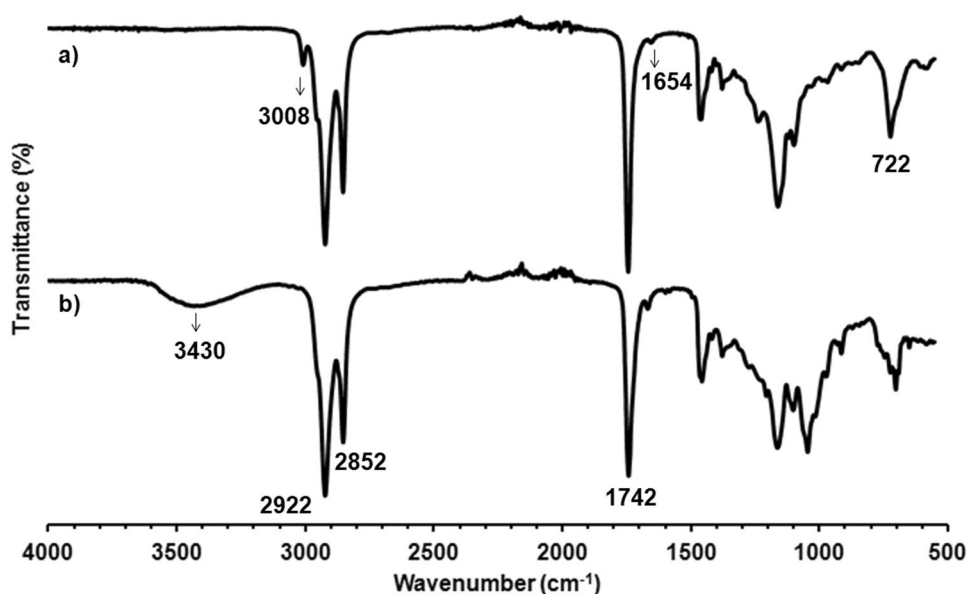


Fig. 3 Grafting efficiencies for the photoinitiated addition of 2-mercaptoethanol onto SBO for different ratio of DMPA/ene and thiol/ene

Fig. 4 FTIR spectra of (a) SBO and (b) SBO polyol



segment, and triglycerides. At 3324 cm^{-1} , hydrogen bonded N–H stretching vibrations of urethane groups appeared as a medium band, whereas a weak shoulder at 3440 cm^{-1} assigned to free N–H groups is barely visible. In the region of $1760\text{--}1650\text{ cm}^{-1}$, the carbonyl stretching peaks of ester and urethane groups combined and appeared as a broad band with a maxima and shoulder at 1700 and 1733 cm^{-1} , respectively, representing the hydrogen bonded and free carbonyl groups [47]. The presence of above mentioned relatively weak stretching bands for both free N–H groups and carbonyl groups indicates that most of the carbonyl groups are apparently hydrogen bonded.

Other peaks of urethane groups were observed at 1596 cm^{-1} due to the C=C stretching vibrations of the aromatic rings and at 1529 , 1310 cm^{-1} (Fig. 7) due to the overlapping N–H bending and C–N stretching vibrations [47]. In the region $1280\text{--}1000\text{ cm}^{-1}$, the strong absorption centered at 1226 cm^{-1} was assigned to the overlapping vibrations of N–H bending and C–N stretching of the urethane groups and C–H bending of the methylene groups of the PIB backbone. The shoulder near 1250 cm^{-1} and the peak at 1080 cm^{-1} appeared due to C–O–C stretching vibrations of urethanes [47]. The absorption peaks typical of PIB soft segment were observed at 2949 and 2892 cm^{-1} due to strong C–H stretching vibrations. The peak at 1470 cm^{-1} corresponded to C–H bending, and the peaks at 1388 and 1365 cm^{-1} were due to CH_3 swing of the methyl groups [48, 49].

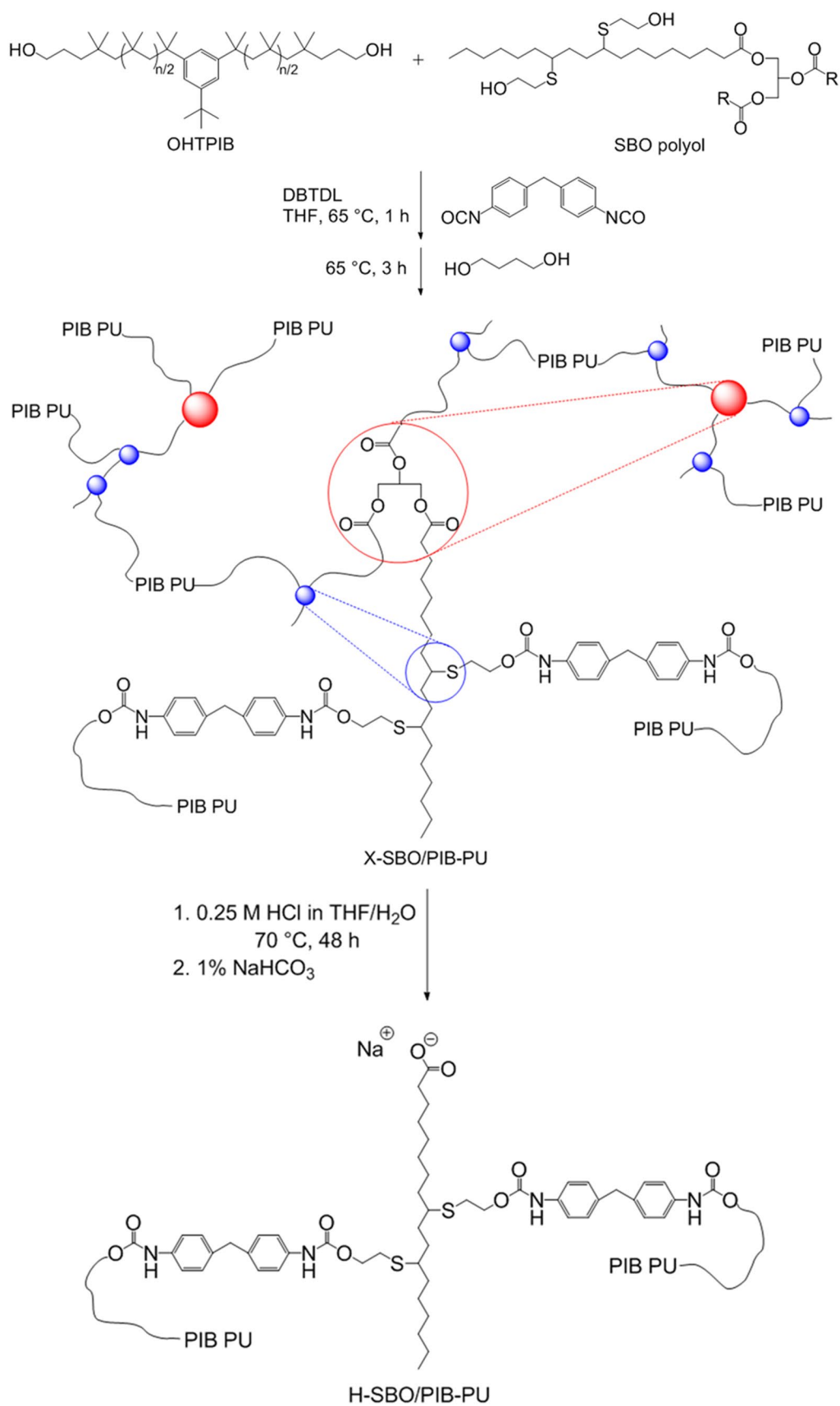
Acid catalyzed hydrolysis of X-SBO/PIB-PU

X-SBO/PIB-PU contains functional groups that have different hydrolytic stabilities, i.e., urethanes and ester moieties

coming from the SBO triglycerides (Scheme 2). In literature, selective hydrolysis has been widely applied to characterize the soft and hard phases of PUs [21, 22]. The preferential cleavage of the ester bonds stems from the higher reactivity of the ester bonds when compared to the ether and urethane bonds under acid/alkaline hydrolysis conditions. Chapman et al. proposed that acid hydrolysis selectively cleaves polyester soft blocks of polyester based PUs and leave the hard blocks unharmed [22]. This methodology allowed study of the hard segment length distribution by MALDI, SEC, and IR analyses [21]. In light of this information, acid catalyzed hydrolysis of the X-SBO/PIB-PU film was conducted for selective cleavage of the ester bonds enabling recovery of PIB polyurethane segments with carboxylic acid functionalities (Scheme 2).

Figures 8 and 9 show the ^1H NMR and FTIR spectra of the selective acid catalyzed hydrolysis product, H-SBO/PIB-PU.

The peaks associated with the urethane linkages appeared at 4.23 and 4.35 ppm due to $-\text{CH}_2-\text{O}-$ protons of BDO (peak c) and OHTPIB (peak b), respectively, and at 10.64 ppm due to $-\text{NH}$ protons (peak h) [50]. The peaks related to SBO polyol appeared at 2.81 ppm corresponding to tertiary $-\text{CH}-\text{S}-$ protons (peak i), at 2.97 ppm due to $-\text{S}-\text{CH}_2-$ protons (peak k), and 4.54 ppm due to $-\text{CH}_2-\text{O}-$ protons (peak l) confirming the incorporation of SBO polyol in the PU structure. Meanwhile, the absence of the peaks associated with the glycerol moiety of the triglycerides (peaks a and b in Fig. 1) proved the preferential cleavage of the more labile ester linkages leaving the urethane bonds intact. The aromatic protons of MDI (peaks d and f) and the cationic initiator (peak e) appeared between 7.90 and 7.30 ppm , while the methylene protons between the aromatic rings of MDI appeared at 3.94 ppm (peak a).



Scheme 2 Synthesis of X-SBO/PIB-PU followed by acid catalyzed hydrolysis

Fig. 5 Linear swelling ratio vs swelling time for X-SBO/PIB-PU

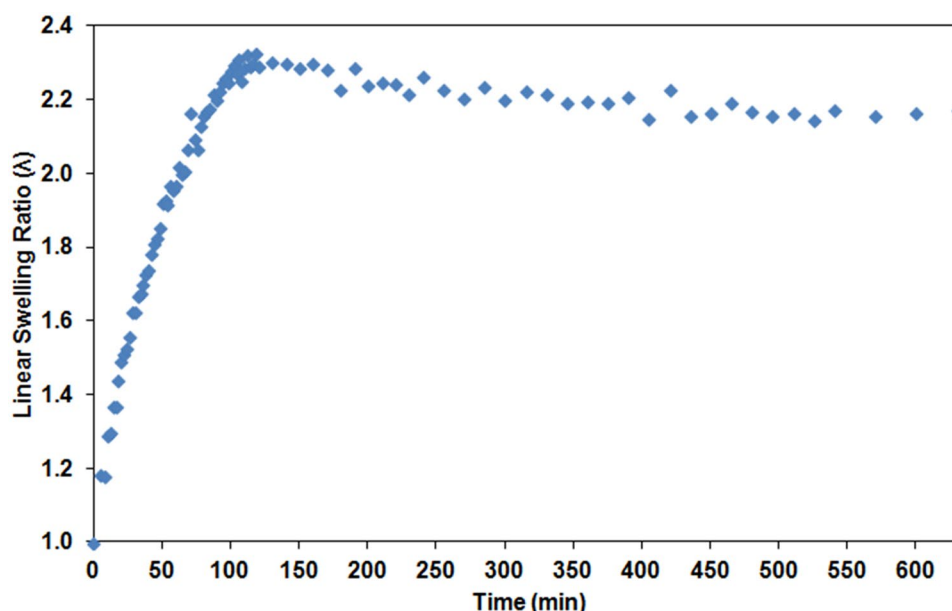


Table 2 depicts the SEC traces of the OHTPIB and H-SBO/PIB-PU. Almost two times higher number average molecular weight (M_n) and broader molecular weight distribution (MWD) than that of OHTPIB for H-SOB/PIB-PU can be accepted as another proof of preservation of the urethane linkages during hydrolysis [21, 22].

FTIR spectra of the network and the hydrolysis product are given in Fig. 9. SBO related methylene stretching vibrations that can be seen at 2922 and 2852 cm^{-1} in Fig. 4, shifted slightly and appeared at 2918 and 2850 cm^{-1} in the spectrum of the hydrolysis product. This proves that, after acid hydrolysis, the fatty acyl chains of the SBO polyol are still present in the structure of the PU through the urethane linkages. Moreover, the soluble and solvent castable

hydrolysis product leading to a clear film without haziness (Fig. 6c) can be accepted as an indication of the successful cleavage of the ester bonds of the SBO polyol at the network junctions. Besides, an increase in breath of hydrogen bonded NH at 3324 cm^{-1} suggests the formation of additional hydrogen bonds between acidic end groups of the fatty acyl chains in hydrolyzed product and urethane moiety [51].

Figure 10 shows DSC heating traces of PIB-PU and X-SBO/PIB-PU. The thermograms exhibited a prominent glass transition temperature (T_g) of PIB soft phase and a melting endotherm (T_m) due to the crystalline hard phase, indicating microphase separated morphology of the polyurethanes. Both PIB-PU and the network showed an almost similar soft phase related T_g at $\sim -59^\circ\text{C}$. However, the presence

Fig. 6 Comparisons of optical clarities of the (a) PIB-PU, (b) X-SBO/PIB-PU, and (c) H-SBO/PIB-PU films

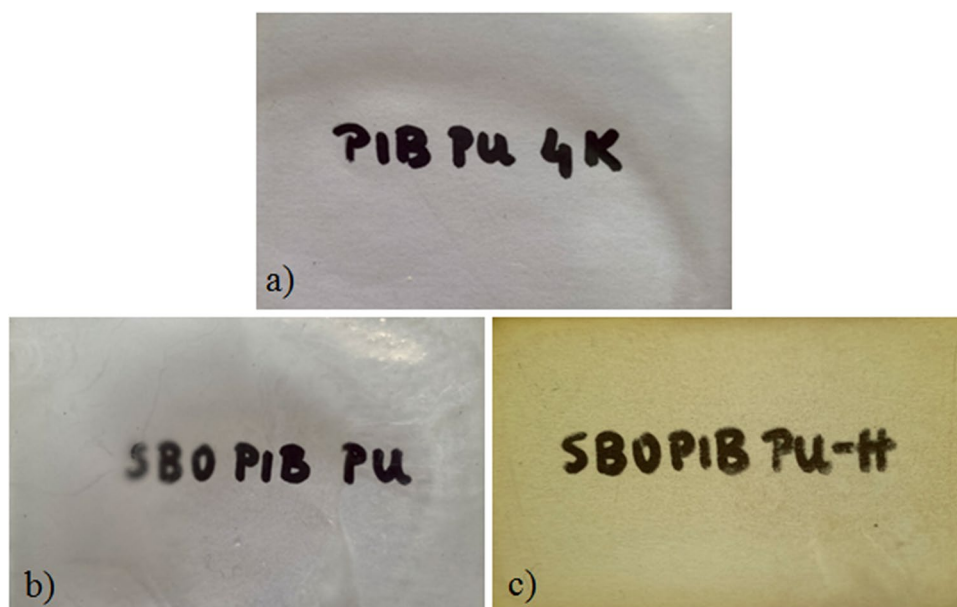
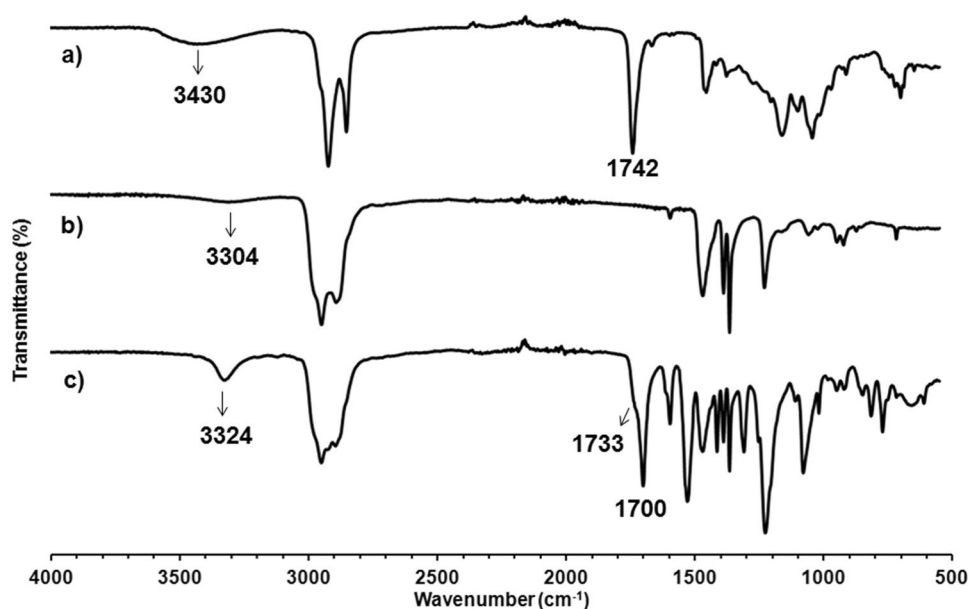


Fig. 7 FTIR spectra of (a) SBO polyol, (b) OHTPIB, and (c) X-SBO/PIB-PU



of crosslink moieties had a pronounced influence on the higher temperature transitions of the hard phase. Similar results were reported by elsewhere and correlated well with

data from dynamic mechanical thermal analysis (DMTA) measurements [52]. The shift of characteristic T_m peak of PIB-PU from 203 °C to 189 °C with much smaller peak

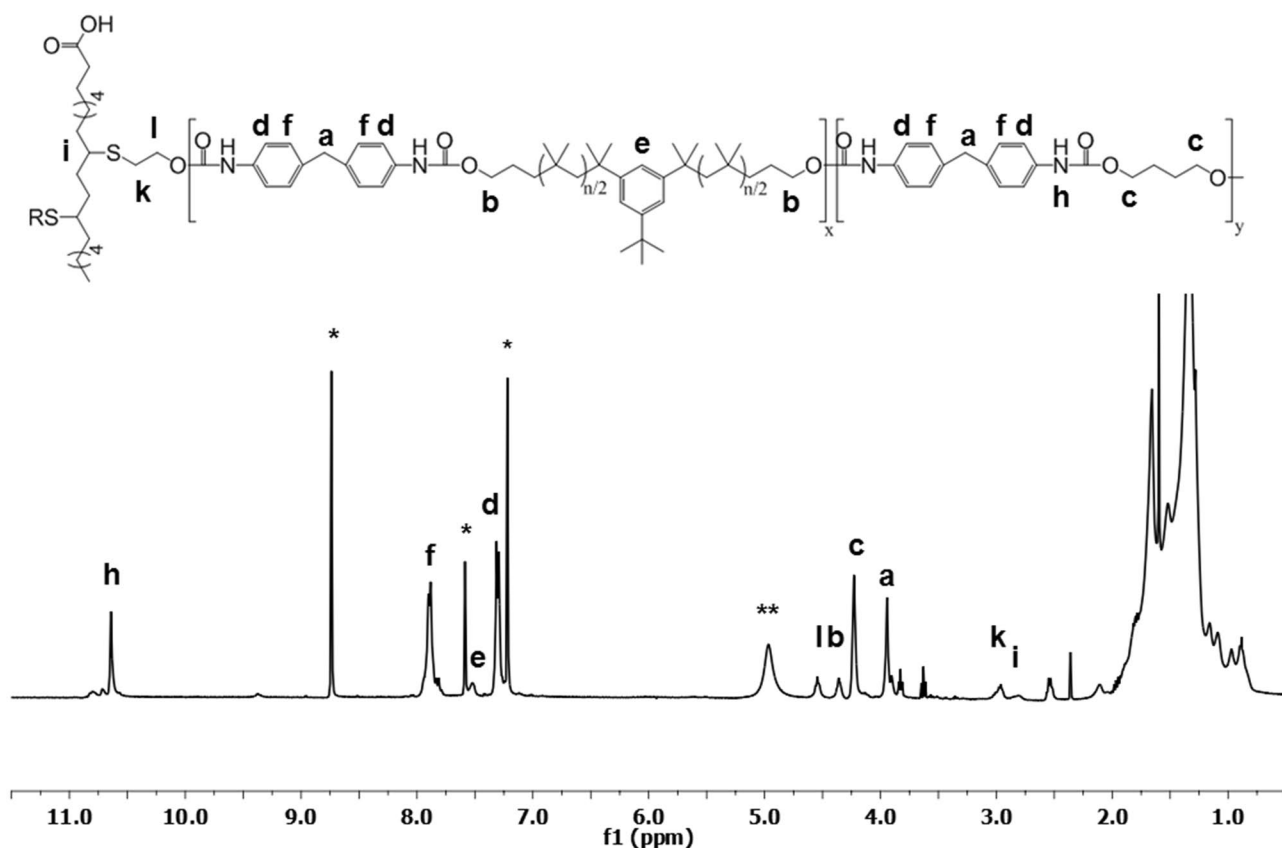
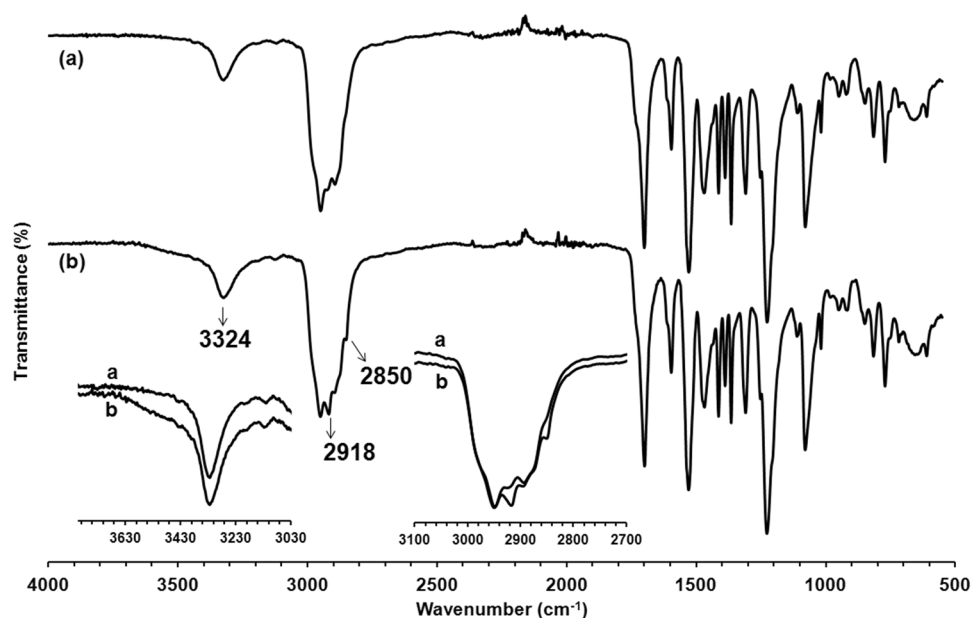


Fig. 8 ^1H NMR spectrum of H-SBO/PIB-PU in pyridine- d_5 (*pyridine- d_5 , ** water)

Fig. 9 FTIR spectra of (a) X-SBO/PIB-PU and (b) H-SBO/PIB-PU. Inserts show the enlarged peak areas from the spectra



area for the network suggesting the decreasing hard phase crystallinity due to the presence of large network moieties. Multiple endotherms appeared between 30–100 °C may be attributed to presence of different regions relaxing in a broad temperature range. These regions are most probably due to different sized crosslinks and their nonhomogeneous distributions in the network structure [53].

After the acid catalyzed selective hydrolysis reaction, the resulting structure still keeps the characteristic multiple thermal transitions of X-SBO/PIB-PU. The appearance of a melting endotherm at lower temperature (~180 °C), on the other hand, is most probably due to the extra ionic and hydrogen bonding type interactions which may cause to a further disturbance of crystallinity.

Figure 11 depicts XRD traces of PIB-PU, X-SBO/PIB-PU and H-SBO/PIB-PU and Table 3 tabulates the XRD data. XRD analyses yield typical and similar results of polyurethanes having SBO, PIB, MDI, and BDO. It is known that a broader peak at ~14° is due to lateral self-organization of hard domains, the shoulder at ~20° is mainly due to lateral distances between molten aliphatic chains, and the broader low intensity signal in the 30–50°

range is due to second-order distances [51]. Gradual decreasing intensity of the peak at ~14° suggests low self-organization of hard and soft domains due to formation of different sized crosslinks and intense interactions particularly after hydrolysis. Similar trend was also observed by Hu et al. in their studies with carboxylated polyurethanes [54]. In contrast to the broader, less intense peaks of X-SBO/PIB-PU typical of random low periodicity crystals, PIB-PU shows a narrower XRD peak indicating larger crystallites [51]. The disturbance of chain alignment/crystallinity is also in a good agreement with DSC results (Fig. 10).

Figure 12 gives both TG and DTG thermograms of the synthesized polyurethanes.

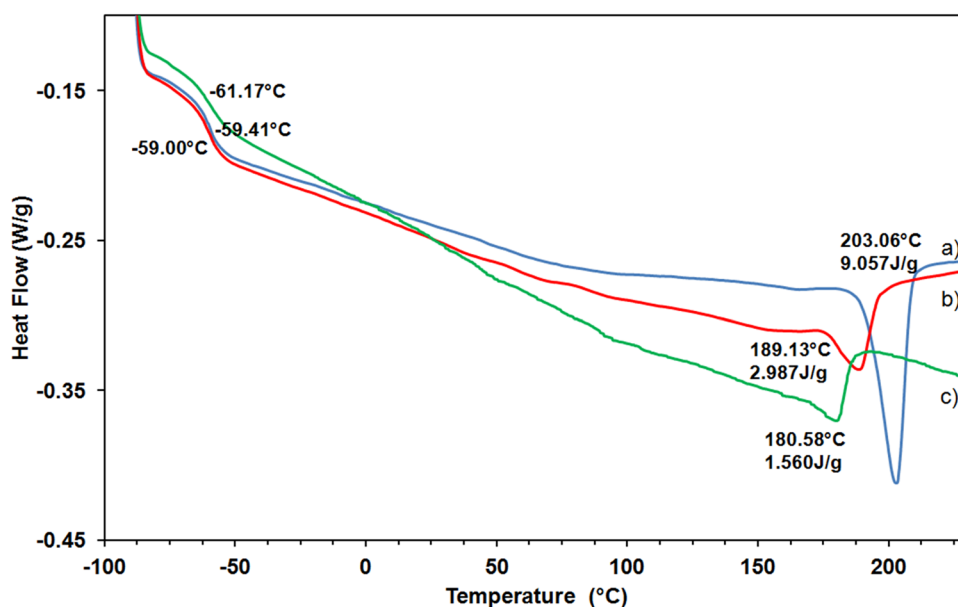
The typical peaks at 326 and 418 °C of PIB-PU are associated with degradation of the hard polyurethane and the soft PIB phase, respectively [51]. Hard phase degradations in X-SBO/PIB-PU and H-SBO/PIB-PU shifted to lower temperatures, 321 and 319 °C, respectively. This result can be ascribed to the presence of network junctions and intense interactions after their hydrolysis causing a gradual disturbance of the crystallinity which is in consistent with XRD and DSC data. In contrast, soft phase degradation shifted to higher temperatures from 415 °C to 430 °C in network structure by staying almost constant after hydrolysis. Evidently, network formation increases thermal stability of soft phase by almost 15 °C as pointed out by Wilkie et al. [55] in their study reporting the correlation between cross linking and thermal stability.

Mechanical strengths of the synthesized polyurethanes are given in Fig. 13. As compared to PIB-PU, higher stiffness

Table 2 Molecular Weight Characterization data for OHTPIB and H-SBO/PIB-PU

Samples	$M_{n,SEC}$ (g/mol)	MWD (M_w/M_n)
OHTPIB	4800	1.14
H-SBO/PIB-PU	11500	1.75

Fig. 10 DSC thermogram of (a) PIB-PU (blue line), (b) X-SBO/PIB-PU (red line), and (c) H-SBO/PIB-PU (green line)



(elastic modulus) and lower extension in SBO based PU can be attributed to the high degree of crosslinking.

It also seems that hydrolysis resulted in reduced mechanical strength and toughness as well as extensibility in certain amount, this can be driven by decreasing in molecular weight and molecular weight distributions of PIB-PU as well as lowering in hard domain periodicity and domain size. Almost 30% increase in elastic modulus for H-SBO/PIB-PU, on the other hand, can be explained by initial resistance to deformation due to the additional ionic and hydrogen bonding type interactions after acid catalyzed hydrolysis [56].

Table 3 XRD data for PUs

Samples	2 θ (°)	d(Å)	Area	FWHM ^a
PIB-PU	14.63	6.05	8825	0.81
	17.76	4.99	72	0.10
	21.24	4.18	516	0.08
X-SBO/PIB-PU	14.89	5.94	6562	0.69
	18.05	4.90	1945	0.49
	22.61	3.93	2540	0.46
H-SBO/PIB-PU	14.63	6.05	7055	0.67
	15.39	5.75	2689	0.32
	17.44	5.08	4549	0.53
	31.76	2.81	1043	0.15

^aFull Width Half Maximum as a measure of breath of peak

Fig. 11 XRD traces of (a) PIB-PU (blue line), (b) X-SBO/PIB-PU (red line), and (c) H-SBO/PIB-PU (green line)

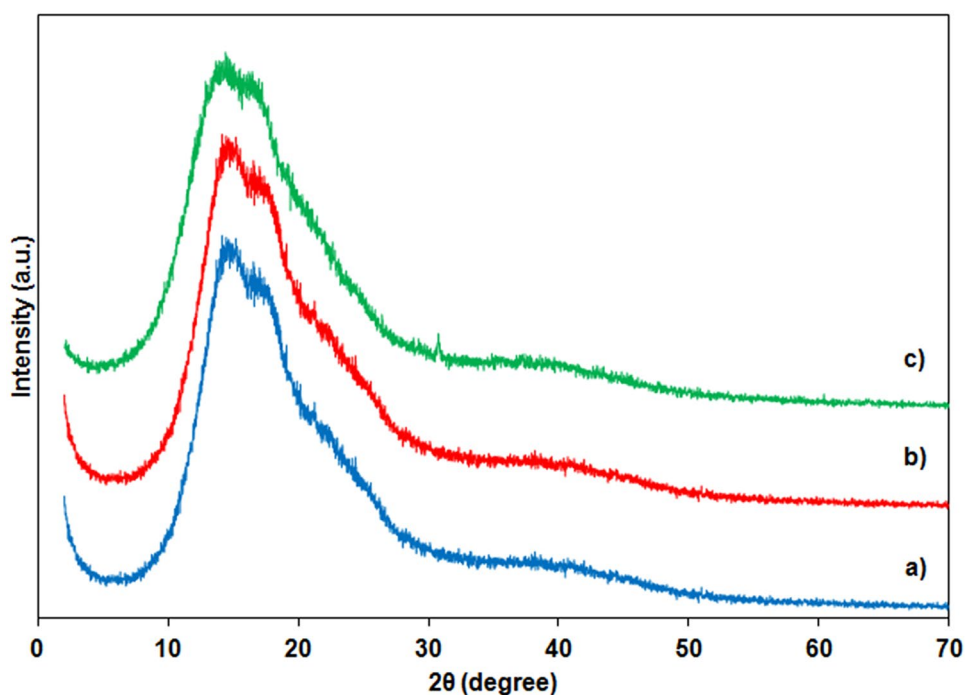


Fig. 12 TG and DTG curves of (a) PIB-PU (blue line), (b) X-SBO/PIB-PU (red line), and (c) H-SBO/PIB-PU (green line)

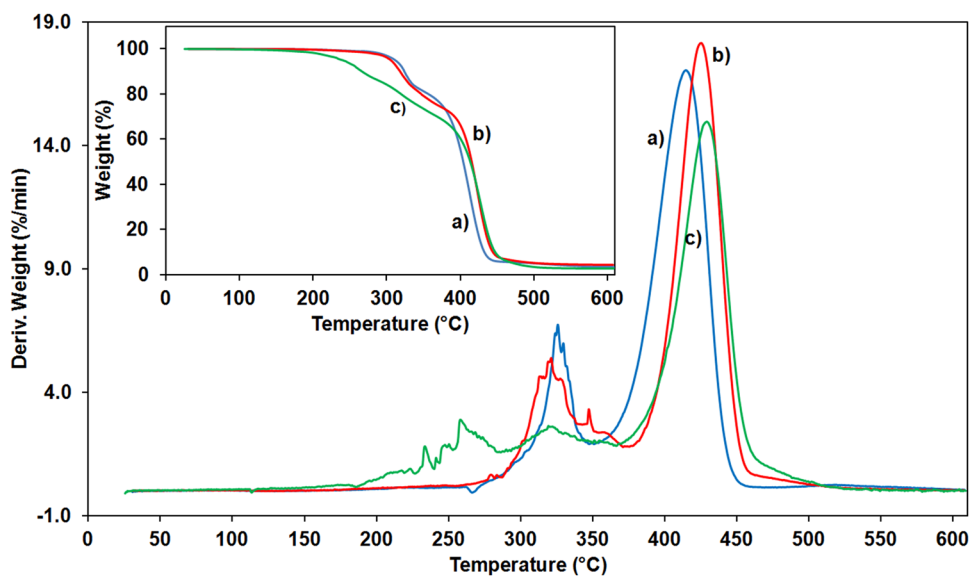
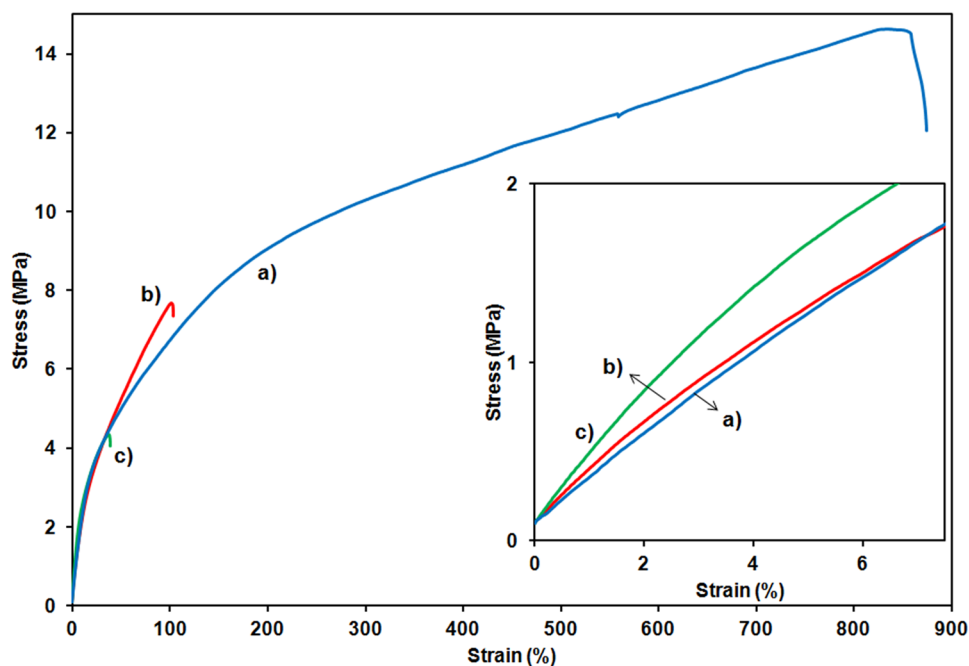


Fig. 13 Stress-strain curves of (a) PIB-PU (blue line), (b) X-SBO/PIB-PU (red line), and (c) H-SBO/PIB-PU (green line)



Conclusion

Novel biobased X-SBO/PIB-PU was successfully prepared with SBO. SBO was first efficiently decorated with primary hydroxyl groups and integrated to PIB based polyurethane formation as a co-polyol. Network characterization data confirmed the crosslinked structure. Subsequent acid catalyzed hydrolysis of resultant X-SBO/PIB-PU film selectively cleaved the ester bonds by enabling the recovery of

soluble SBO/PIB based polyurethane segments without disturbing the original polyurethane structure.

It has been suggested that after selective acid hydrolysis of network moieties, carboxylic acid based extra active polar site equipped PIB based polyurethane may then serve as a versatile platform for the synthesis of further novel blend or nanocomposites of biobased PIB-PU materials.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10965-023-03715-5>.

Funding The authors thank Bogazici University Research Foundation Projects (project 11763) for financial support.

Data availability The data that supports the findings of this study are available from the corresponding author upon the reasonable request.

Declarations

Conflict of interests The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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