

Influence of Hydrogen Bonding on the Temperature-Accelerated Hydrolysis of Silicone Based Polyetherurethane

He-Cheng Wu^a, Shu-Ren Shao^a, Shuo-Hong Dong^a, Ao Wang^a, Zhen Li^{a*}, Xiang-Long Han^b, Feng Luo^a, Jie-Hua Li^a, Dai-Guo Zhao^c, Wan-Ling Lan^c, and Hong Tan^{a*}

^a College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Med-X Center for Materials, Sichuan University, Chengdu 610065, China

^b State Key Laboratory of Oral Diseases, National Clinical Research Center for Oral Diseases, West China Hospital of Stomatology, Sichuan University, Chengdu 610041, China

^c Sichuan Institute for Food and Drug Control, Chengdu 611731, China

Electronic Supplementary Information

Abstract Temperature-accelerated *in vitro* degradation was established to estimate the longevity of polyurethane applied for long-term implantation. However, the prediction did not correlate well with the data from clinical explants and the rationality of accelerated *in vitro* test is still in a controversial due to the deviation. To improve the accuracy of the *in vitro* prediction, the influence of hydrogen bonding (HB) on the accelerated hydrolysis of silicone based polyetherurethanes (SPEUs) extended with three side chains. Combining the temperature-controlled FTIR and the physical properties after temperature-accelerated *in vitro* degradation, it was demonstrated that side chain could increase the degree of hydrogen bond dissociation at higher temperature, resulting in the decrease of the calculated activation energy (E_a) of hydrolysis. At low temperatures, changes in surface morphology and molar mass of PEUs are minimal and HB are less easily dissociated, which had barely impact on the hydrolysis resistance. It was proposed that the E_a will not be impacted and that the accuracy of prediction will be increased if the acceleration temperature is lower than 70 °C and HB change is less than 15%.

Keywords Polyether urethane; Polydimethylsiloxane; Activation energy; Hydrogen bonding; Hydrolysis resistance

Citation: Wu, H. C.; Shao, S. R.; Dong, S. H.; Wang, A.; Li, Z.; Han, X. L.; Luo, F.; Li, J. H.; Zhao, D. G.; Lan, W. L.; Tan, H. Influence of hydrogen bonding on the temperature-accelerated hydrolysis of silicone based polyetherurethane. *Chinese J. Polym. Sci.* 2023, 41, 1230–1237.

INTRODUCTION

Thermoplastic segmented polyetherurethanes (PEUs) have a wide range of applications in long-term implantation, such as pacemakers, defibrillators, and heart valves.^[1–3] As the advancement of medical technology, the increase in average life expectancy demands a high precision predictions of service life. The strict criteria ISO 10993 standard prefers to real-time tests before the decision making. However, some biostable materials (e.g., silicone based PEUs, SPEUs) can be used *in vivo* for over ten years, in which period the running of the experiment requires careful controls and experimental variation is increased.^[4,5] The material development cycle is also greatly prolonged as a result, which makes it challenging to provide timely materials to address pertinent demands.^[4]

Recently, some efforts were made to estimate the long-term biostability of silicone-based TPU such as PurSil and

Elast-Eon by accelerated *in vitro* test.^[6,7] Chaffin *et al.* evaluated the hydrolytic stability of E2A (Elast-Eon 2A) and P35 (PurSil 35) *via* temperature-accelerated *in vitro* hydrolysis. At temperatures ranging from 37 °C to 85 °C, the PEUs were incubated in deoxygenated phosphate buffered saline (PBS) water for up to 52 weeks. Hydrolysis activation energy (E_a) was calculated by Arrhenius equation, and it was found that E_a of SPEU is significantly lower than that of PEU. Runt *et al.* claimed that the phase separation structure of the polyurethane differs dramatically at 85 °C compared to 35 °C, which meant the temporal temperature superposition (TTS) was not suitable for segmental copolymer like polyurethane.^[5,8] More notably, in a 10 year follow-up study, the decrease in molecular weight was mainly in the first two years, while the molecular weight remained stable after five years.^[5,9]

The rationality of accelerated *in vitro* test is in a controversial. To the best of our knowledge, a critical factor hydrogen bonds (HB) has been overlooked in previous studies on the stability of SPEUs. HB has been demonstrated to have a large effect on the hydrolytic stability of polyurethanes, that hydrogen-bonded carbamate exhibited better resistance to hydrolysis.^[10–13] The hydrolysis would be accelerated at higher tem-

* Corresponding authors, E-mail: zhenli@scu.edu.cn (Z.L.)

E-mail: hongtan@scu.edu.cn (H.T.)

Received November 28, 2022; Accepted January 31, 2023; Published online March 10, 2023

perature (e.g., 85 °C) as more HBs are dissociated.^[14] The deviation of the prediction from the E_a is aroused given that the real implantation temperature is 37 °C that the hard segments are more closely packed with strong HB.

In order to prove this hypothesis, several SPEUs with different microstructural organization and hydrogen bonding degree were investigated in temperature-accelerated *in vitro* hydrolysis. Here, we characterized HB and the microphase separation structure using FTIR and DSC. Tensile testing, GPC and SEM were used to monitor the deterioration behavior. Combining the results of HB changes and hydrolytic stability we are trying to find appropriate conditions for accelerated hydrolysis.

MATERIALS AND METHODS

Materials

Both hydroxybutyl-terminated polydimethylsiloxane (PDMS, $M_w=2000$) and poly(tetramethylene oxide) (PTMO, $M_w=1000$) were bought from Degussa in Germany and PTG in Korea, respectively. 1,4-Butanediol (BDO) was acquired from Chron Chemicals in Chengdu, China, while 4,4'-methylenediphenyl diisocyanate (MDI) was provided by Wanhua Chemical Group in Yantai, China. 1,2-Octanediol (HDO, $M_w=146$) was bought from HX-R in Chengdu, China. 2-Ethyl-2-((3-(1,3,3,3-tetramethyl-1-((trimethylsilyl)oxy)-1-disiloxanyl)propoxy)methyl)-1,3-propanediol (SDO, $M_w=396$) and 1-((2,2,3,3,4,4,5,5-octafluoropentyl)oxy)ethane-1,2-diol (FDO, $M_w=306$) were synthesized and purified in our laboratory.^[15,16]

General Characterization

Bruker 400 MHz Avance III HD magnet is used to performed proton Nuclear Magnetic Resonance (NMR) spectroscopy. To dissolve the samples, *N,N'*-dimethylformamide-*d*₇ (DMF-*d*₇) was used. Temperature-controlled Fourier transform infrared spectroscopy (FTIR) spectra of polyurethane membranes were carried out using a Nico-iS50 FTIR instrument with INSTEC Cooling/Heating stage. The testing scope was ranging from 3800 cm⁻¹ to 650 cm⁻¹ with 24 times for each sample, and the film ramped up to 170 °C with a rate of 5 °C/min. Peaks in carbonyl region were fitted with Gaussian-Lorentzian functions. Gel permeation chromatography (GPC) was carried out using a Waters-1515, USA, using two columns in series with a DMF/LiBr solution at a flow velocity of 1.0 mL/min under 40 °C. The polymethyl methacrylate (PMMA) standard was used as the calibration standard.

Synthesis of Polyurethanes

Bulk polymerization was used to synthesize the polyurethane copolymers. In a nutshell, PTMO and PDMS were directly weighed in the three-necked flask and dewatered under vacuum for two hours at 100 °C. Dangling side chain was added and blended while the macrodiol were cooled to 55 °C. Consistently cooling to 40 °C, adding weighed MDI melt precisely and trace organic bismuth to further the reaction, and maintaining a temperature of 70 °C for 40 min allowed the mixture to react. BDO was added after the prepolymer had been cooled to 50 °C, which was followed by velocity mixing before being put into a Teflon plate. In the next 6 h, the mixture was baked at 100 °C to continue the polymerization process. Table

S1 (in the electronic supplementary information, ESI) provides synthetic recipes and molar mass of samples.

Samples

The obtained material was made into 0.3 mm thick sheets by thermo-compression molding. The sheets were annealed at 85 °C for 4 h to eliminate the effect of thermal history. Polyurethanes are identified as *ix*PEU, where *i* indicates the kind of functional chains (10% of the molar ratio in chain extenders) and *x* indicates that PDMS-diol was used as the 2nd macrodiol, respectively. FSPEU, HSPEU and SSPEU use FDO, HDO and SDO as the 2nd chain extender, respectively (Scheme S1 in ESI).

Thermal Analysis

TA DSC250 was used to perform differential scanning calorimetry (DSC). Following is a description of the DSC method: Samples equilibrated at -90 °C for 3 min, before ramping up to 230 °C at a rate of 10 °C/min.

Tensile Testing

A universal tensile tester from Dongguan Lixian Instrument, China was used to measure the mechanical properties, and the tensile speed used was 500 mm/min. Before testing, samples were kept in an incubator at 23 °C for two days.

Scanning Electron Microscopy (SEM)

Nova Nano SEM450, Field emission scanning electron microscope (FESEM) was used to evaluate the surface morphology of specimen. Before the test, the surface of films was washed three times with alternating water and ethanol.

Small Angle X-ray Scattering (SAXS)

Xeuss 2.0, Xenocs, France with a Cu K X-ray radiation source ($\lambda=0.154$ nm) and semiconductor detector, Pilatus 100 K, DECTRIS, Switzerland is used to test the phase structure. There was a 2.5 m gap between the samples and the detector. The samples were developed onto film with an exposure time of 5 min in a vacuum atmosphere at ambient temperature.

Hydrolysis Production Characterization

High performance liquid chromatography-mass spectrometry (HPLC-MS) was used to quantify the hydrolysis of urethane linkages for water phase. More detailed method is exhibited in ESI.

In vitro Hydrolysis

The samples were hydrolysed in PBS at 40, 55 and 85 °C for 1 year, with buffer changes every two weeks. PBS was deoxygenated by bubbling nitrogen continuously. The samples were periodically taken out of the aging conditions, cleaned with ultrapure water, and then vacuum-dried for three days at 50 °C.

RESULTS AND DISCUSSION

Molar Mass Change

Accelerated testing is a crucial method for characterize hydrolysis since the accompanying reaction kinetics can be easily observed through variations in the polymer molar mass (M_n) over time. Figs. 1(a)–1(e) depict the relative molecular weight of polyurethane as a function of temperature and time. All polyurethane after hydrolysis showed a little drop in M_n at 40 °C and a mild loss at 55 °C, while there was a significant decrease

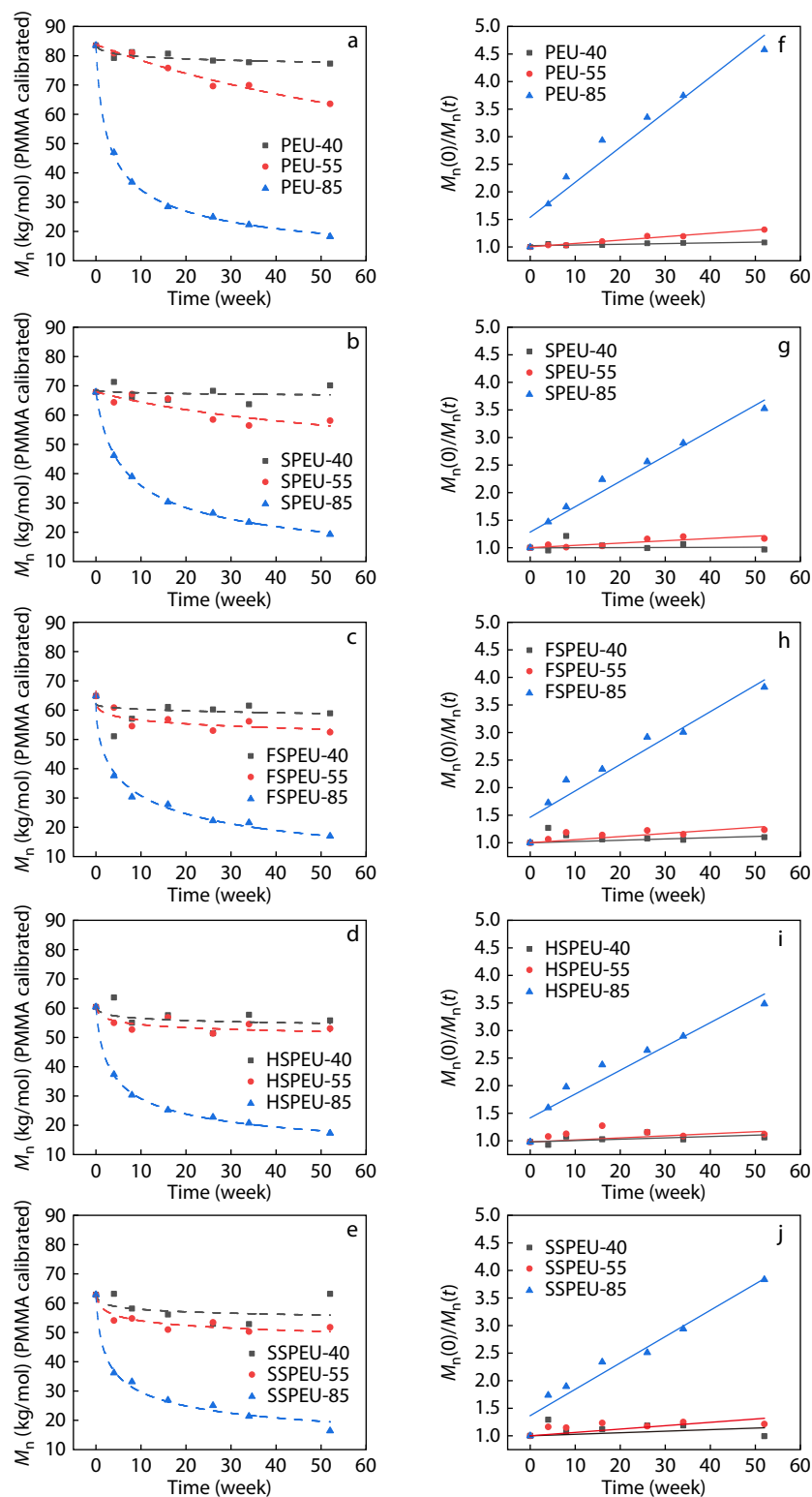


Fig. 1 Molecular weights change of *ix*PEU with temperature and time (a–e), $M_n(0)/M_n(t)$ versus time for *ix*PEU (f–j). * $M_n(0)$ is the initial molecular weight and $M_n(t)$ is molecular weight at each degradation time point.

at 85 °C. Among the *ix*PEUs hydrolysis at 55 °C, the M_n of PEU and SPEU were gradually reduced over time. M_n of *i*SPEUs exhibited rapid decrease at first 8 weeks and no discernible change were observed since then. At 85 °C, *i*SPEUs and SPEU

showed comparable loss of M_n (~70%–75%) in contrast to PEU displaying more (~80%) M_n loss.

The correlation between the rate of chain scission and E_a of hydrolysis has been described in various studies, where the

dependency of M_n reduction as a function of time can be explained by Eq. (1) underneath the assumption that basic biomolecular reaction between a hydrolysis sensitive group (Hyd) and H_2O follows pseudo-zero-order kinetics:^[6,17]

$$\frac{M_n(0)}{M_n(t)} = \frac{2k'}{[TG]_0}t + 1 \quad (1)$$

where symbol $[TG]_0$ is the content of the initial Terminal group. Besides, rate of the chemical reaction of polyurethane were shown in Figs. 1(f)–1(j). From the slopes at 40 °C, there was no difference in hydrolytic stability. However, due to the slope at 85 °C, the SPEUs own better degradation resistance.

The temperature dependence of k is obtained by Eq. (2) using the Arrhenius equation.

$$\ln k' = \ln(A[Hyd]_0[H_2O]_0) - E_a/RT \quad (2)$$

Eq. (1) can be further transformed as

$$\ln(\text{slop}) = \ln(k'M_n(0)\rho^{-1}) = \ln k' + \ln(M_n(0)\rho^{-1}) \quad (3)$$

By plotting the logarithm of the slope in Figs. 1(f)–1(j) versus the accelerate temperature derivative (Fig. S1 in ESI). The E_a for all samples can be obtained from the slop in Fig. S1 (in ESI) and are summarized in Table 1. And they fall within the published range of 23–115 kJ/mol for the hydrolysis activation energy of polyurethane.^[6,7,17–19] E_a for PEU and SPEU are similar (~100 kJ/mol), SPEU even higher than PEU. To our surprise, side-chain modified SPEUs only achieve 2/3 to 1/2 of

Table 1 Hydrolysis activation energy of ixPEU series.

Samples	E_a (kJ/mol)
PEU	83.82
SPEU	107.49
FSPEU	65.33
HSPEU	60.91
SSPEU	58.79

the PEU or SPEU's E_a . It seems that SSPEU has the worst hydrolytic stability.

Surface Morphology

The surface morphology hydrolyzed for up to 52 weeks at 85 °C is exhibited in Fig. 2. After 26 weeks, no evidence of hydrolysis was observed in the surface of all the samples at any accelerate condition except HSPEU. Two months later, SPEU and SSPEU exhibited intact surface, while others show the signs of hydrolysis with tiny pits. After one year, expanded shallow pits and fissures were detected surface of all samples.

Fig. 3 displays the surface appearance of ixPEU which incubated in 40 and 55 °C for a year. The specimen in the 40 °C PBS solution did not exhibit surface morphological changes and showed intact surfaces without any surface damage. Intact surface was only observed in SPEU and SSPEU after hydrolyzed at 55 °C, while holes and cracks developed in other PEUs.

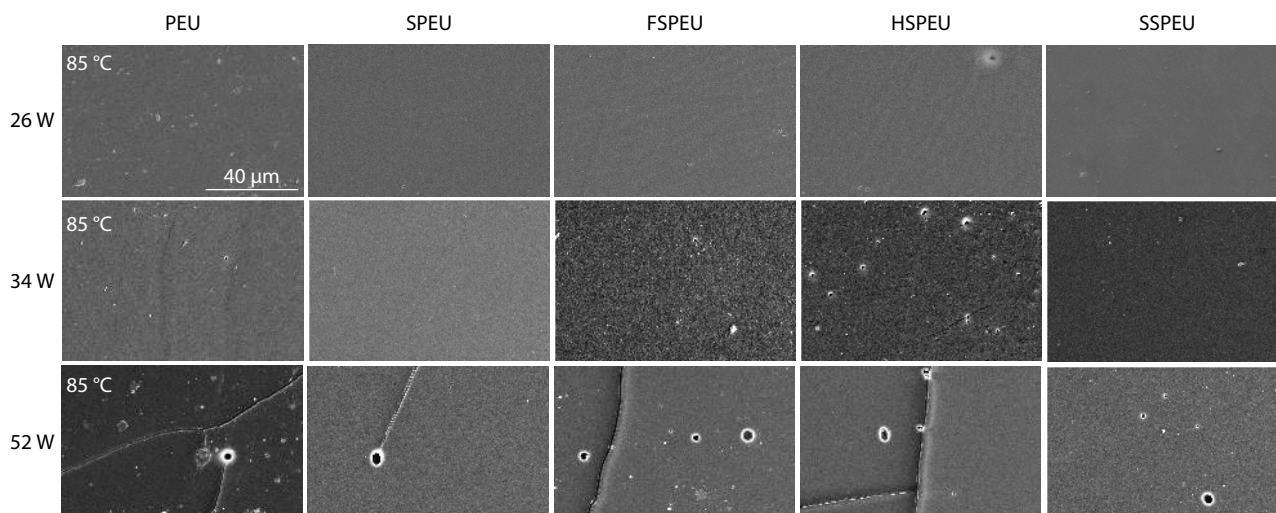


Fig. 2 SEM images of ixPEU hydrolyzed at 85 °C in different time points.

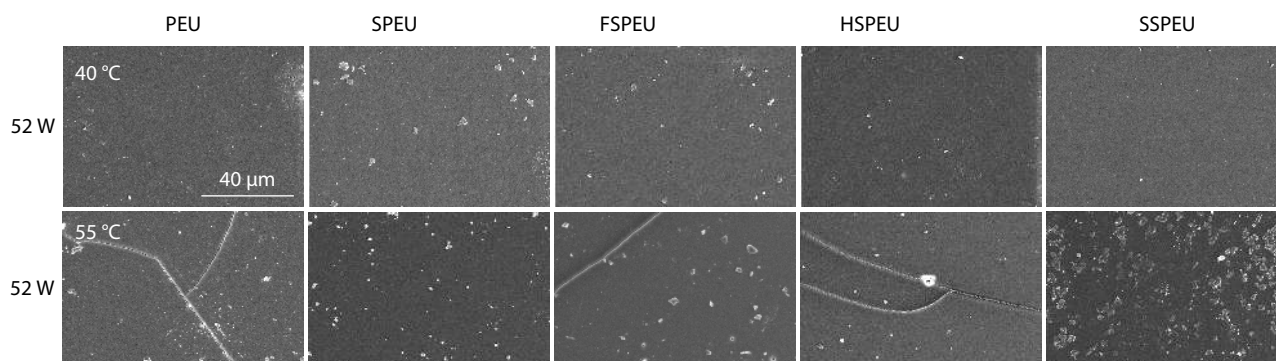


Fig. 3 SEM images of ixPEU after hydrolyzed at low temperature for 1 year.

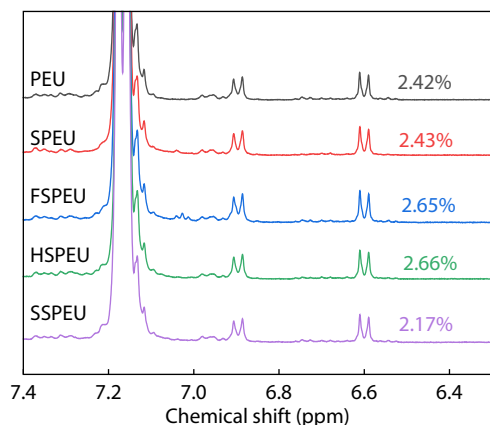


Fig. 4 Degradation product detected in 85 °C hydrolyzed specimen by ^1H -NMR.

Cleavage of Urethane Linkage

The mechanism of urethane linkage cleavage was exhibited in Fig. S2 (in ESI), and the process is divided into two steps. Firstly, urethane link was attacked by H_2O to produce a single NH terminated molecular chain, then the neighboring urethane link is further broken to generate a 4,4'-methylene diamine (MDA) which is prone to be liberated into the water. ^1H -NMR were adopted to characterize hydrolyzed specimen in order to have a clear view on first step of the urethane linkage cleavage. Resonate at 6.80 and 6.60 ppm in the NMR spectra are attributed to protons on the phenyl ring next to amino.^[7,16] The fraction of urethane oxidation was calculated by dividing the peak at 6.60 ppm (protons ortho to the amino the phenyl rings) over the sum of peaks at 7.17 and 6.60 ppm (all the aromatic protons). As revealed in Fig. 4, the incorporation of SDO displayed minimal chain scission of carbamate groups while FDO and HDO seems to enhance the hydrolysis rate. The MDA

produced in second step of cleavage was characterized by HPLC-MS. The weight percentage MDA was obtained by multiplying the MDA concentration by the volume of degradation fluid and normalizing it to the total sample mass. As shown in Table S2 (in ESI) after hydrolyzed for 52 weeks at 85 °C, the weight percentage of SSPEU MDA was similar to that of PEU and SPEU, while HSPEU and FSPEU produced more.

It is evident from the characterization of hard segment hydrolysis behavior and surface appearance that SSPEU has comparable hydrolytic resistance with SPEU and PEU. However, the addition of HDO and FDO reduced the hydrolytic resistance of SPEUs at high temperature. Unexpectedly, the outcomes of surface morphology and rate of hard segment degradation diverge significantly from the activation energy of hydrolysis. The conflict appeared between hydrolysis activation energy and stability.

Transition of Microstructural Organization

The activation energy calculation described above was based on the principle of time-temperature equivalence, where the fundamental presumption was that temperature was the only variable changes during the experiment and all constituents of the polymer responded similarly to temperature changes.^[6] Recent study has confirmed that high temperature-accelerated hydrolysis causes severe transition in microstructure, which would not occur at body temperature and resulted in inaccurate activation energy calculated from TTS.^[5]

In the present study, structural alterations were monitored throughout the degradation period of *ix*PEUs. The glass transition of soft segment ($T_{g,s}$) can reflect the microphase structure of PEU. When $T_{g,s}$ more closer to the neat PTMO, the more separated microstructure was formed. For *ix*PEUs hydrolyzed at 40 °C, the $T_{g,s}$ decreased rapidly and then stabilized (Fig. 5). Combining the results of GPC that little difference in M_n after hydrolyzed for 52 weeks, it was indicated that

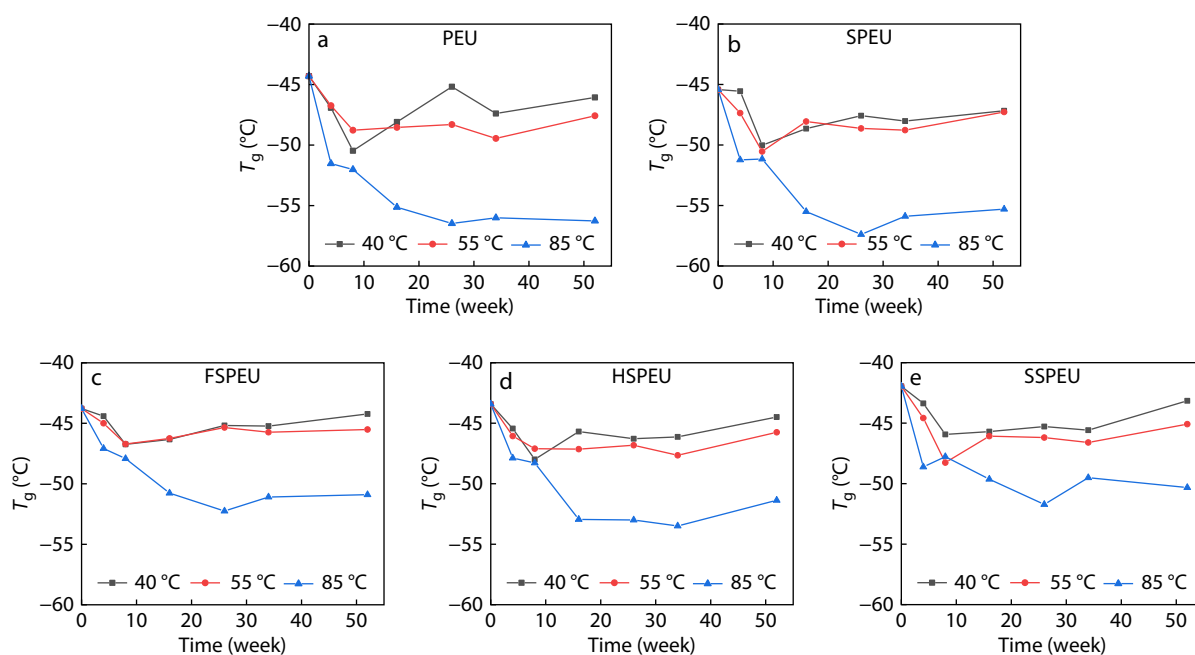


Fig. 5 Changes in glass transition temperature (T_g) of soft segments in *ix*PEU during hydrolysis.

the transition of microstructure was due to annealing effect. As the results, the ultimate tensile strength (UTS) of *ix*PEU, was improved after hydrolyzation (Figs. S4 and S5 in ESI).^[20–22] The similar phenomenon was observed in hydrolysis at 55 °C. The shift of $T_{g,s}$ was mainly happened at first 8 weeks, although there was slightly decrease in M_n . It was suggested that the phase transition occurred at 55 °C have little influence at E_a calculation of *ix*PEU.

Things are different when hydrolysis at 85 °C, that $T_{g,s}$ declined almost continuously in the first 16 weeks. On the one hand, the decrease of $T_{g,s}$ can be attributed to annealing of *ix*PEU. On the other hand, the non-hydrogen bonded and weakly hydrogen bonded carbamates located in the intermediate phase region are more likely to hydrolysis, resulting in a decrease in the attachment between the soft and hard segments.^[11,23] Due to the cleavage of urethane linkage, mobility of soft segment increased, which will also lead to the decline of $T_{g,s}$. At the same time, the shift of scattering peak in SAXS, increase in the proportion of hydrogen-bonded carbonyl as well as melting point in DSC proved that the increase of microphase separation was led by hydrolyzed at 85 °C (Figs. S3, S6 and S7 in ESI).^[5] Thus, it was suggested that the microphase transition observed by SAXS during the high-temperature hydrolysis was caused by degradation of SPEUs and it was not the factor that leading the deviation in the calculation of E_a .

Temperature-controlled FTIR

As discussed in the introduction, HB is considered to be a critical factor that determined the hydrolytic stability of PEUs. the impact of temperature on the hydrogen bonding was illustrated in Fig. 6. At lower temperatures, spectra show a significant band at 1703 cm^{-1} , whose absorbance gradually decent with the increase of temperature. The band attributed to non-bonded carbonyl absorbance, which was previously at 1733 cm^{-1} , red-

shifted to a little higher wavenumber, and the absorbance rises with rising temperature.^[24,25]

In order to provide a clear perspective of hydrogen bonding changes, the carbonyl region was divided into three parts: the strongly hydrogen-bonded region ($\sim 1703 \text{ cm}^{-1}$), the weakly hydrogen-bonded region ($\sim 1715 \text{ cm}^{-1}$), and the non-hydrogen-bonded region ($\sim 1735 \text{ cm}^{-1}$).^[15,24,26] The proportional distributions of the three different types of carbonyl groups are shown in Fig. 7. When the temperature was raised from 40 °C to 85 °C, the proportion of strong HB of SPEU dropped less than the rest of specimen, by only 10%. As described above, SPEU hold the higher calculated E_a and showed no sign of degradation after 52 weeks of hydrolyzed at 55 °C (Fig. 3), indicating a high consistency between E_a and degradation rate. As the side chain structure breaks the aggregation structure of the hard segment, the dissociation of strong HB in *is*SPEU is significantly severer by up to $\sim 20\%$, and the E_a is low. In our prior study, it has been proved that side-chain can break the aggregation of hard segment, resulting a poor hydrolysis resistance at high temperatures.^[16] It can be told from Fig. 7 and Table 1 that the more decrease in strong HB, the lower E_a we can obtained from the calculation. Combining the results of hard segment hydrolysis behavior characterization and surface appearance, HSPEU and FSPEU are less hydrolytic stable. For SSPUE, although the calculated E_a is low, it shown the comparable hydrolytic stability with SPEU. It has been proved in our previous study that SDO could increase the compatibility between phases and enhance the oxidation stability of Silicon-based polyetherurethane.^[15] In this work, the special microstructural organization brought by SDO also prevents the hydrolysis of hard segments.

Therefore, the calculated E_a obtained *via* accelerated hydrolysis is inconsistent with the actual value if rapid dissociation of HB occurred at a high temperature. E_a of PEU calcu-

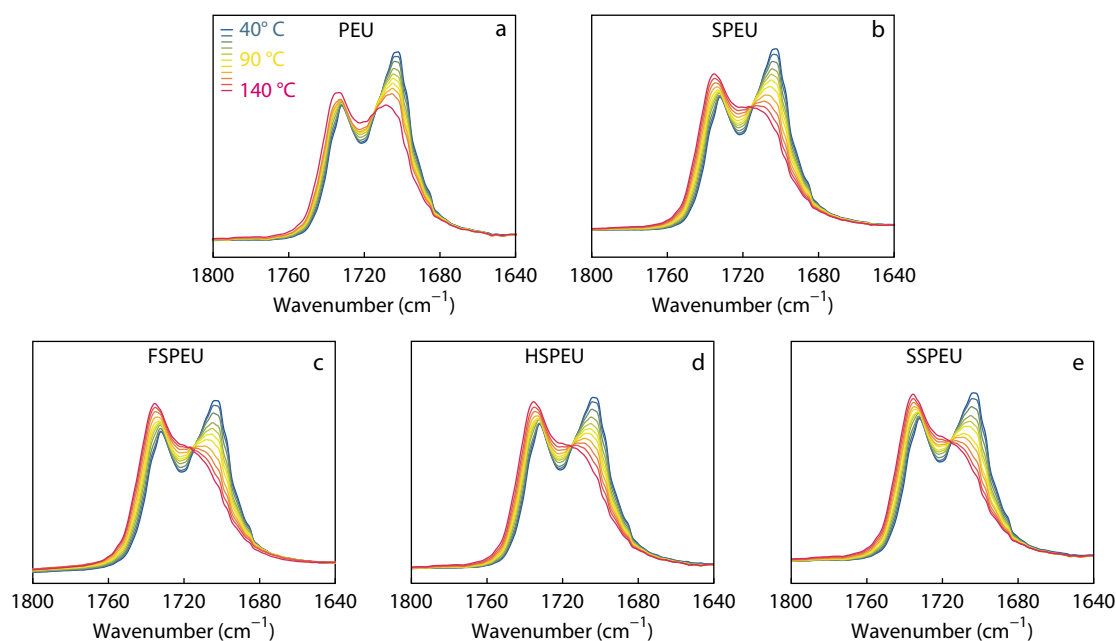


Fig. 6 FTIR spectra from 1800 cm^{-1} to 1640 cm^{-1} as a function of temperature for *ix*PEU.

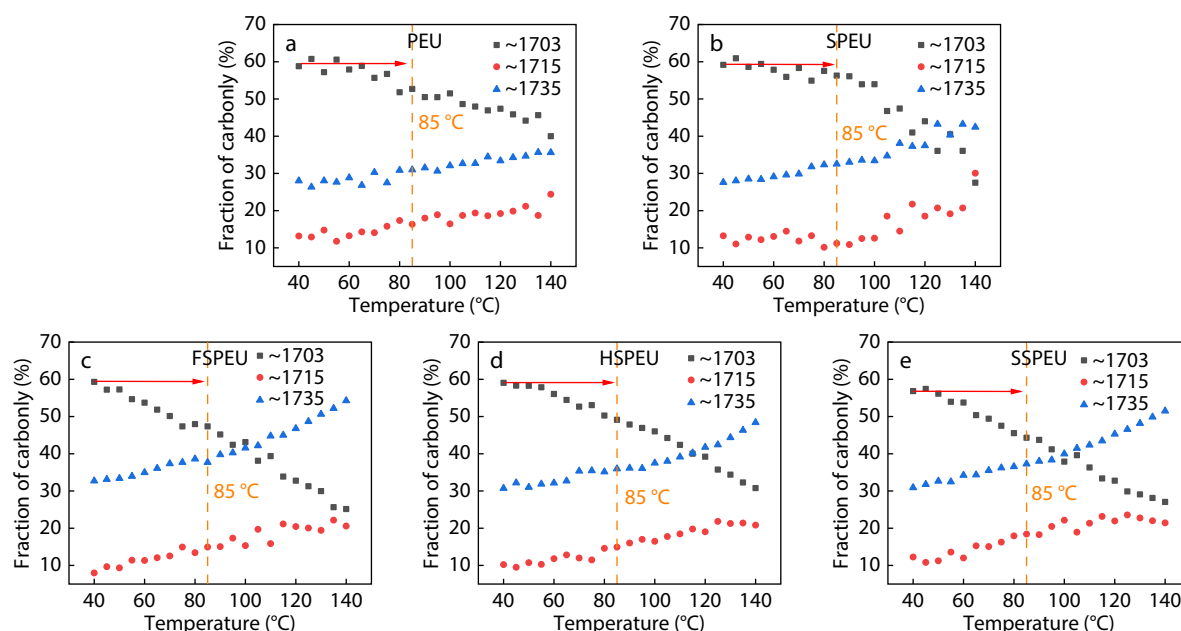


Fig. 7 The fractions of non-bonded (blue), loosely hydrogen-bonded (red) and strongly hydrogen-bonded (black) urethane carbonyl groups for *ix*PEU in the temperature range from 40 °C to 140 °C.

lated in our work is more in line with the actual clinical results.^[4] In order to calculate E_a and predict material life more precisely, it is essential to prevent the influence of rapid drop in HB at high-temperature accelerated hydrolysis. Ideally, the change in HB should be less than 15% and the accelerated temperature should not exceed 70 °C according to HB transition of SSPEU and PEU. Meanwhile, M_n not changes significantly when hydrolysis is carried out at low temperature (Fig. 1),^[4] so a longer degradation time is also required.

CONCLUSIONS

In the present study, the stability of five polyurethanes was investigated by *in vitro* accelerated hydrolysis and the hydrogen bonding behavior of polyurethanes at different temperatures was studied by temperature-controlled FTIR. The results of hard segments degradation behavior as well as the surface morphology revealed that SSPEU has comparable stability with SPEU, while its E_a is significantly reduced. The side chain modification makes the hydrogen bonding of silicone containing polyurethanes more sensitive to temperature changes, resulting in reduced hydrolytic stability at high temperatures and leading to a bias in the E_a calculations. Accelerated hydrolysis investigations ought to be carried out at temperatures lower than 70 °C with longer hydrolysis time in order to achieve more precise activation energy and lifespan predictions.

Conflict of Interests

Hong Tan is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-2957-8>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51973134), the State Key Research Development Program of China (No. 2020YFC1107000), the NSAF (No. U1930204) and Interdisciplinary Innovation Projects of West China Hospital of Stomatology Sichuan University (No. RD-03-202001). We thank Chenxu Tian from the College of Polymer Science and Engineering of Sichuan University for her help in the measurement of SEM.

REFERENCES

- Tian, C. X.; Zhang, T.; Song, Y. Q.; Ming, H.; Liu, P. Q.; Jiang, M. J.; Luo, F.; Li, J. H.; Tan, H.; Fu, Q. Elaborating polyurethane pillow soft mat on polypropylene monofilament surface with stepwise surface treatments. *Chinese J. Polym. Sci.* **2022**, *40*, 1389–1401.
- Dandeniya, L. S.; Adhikari, R.; Bown, M.; Shanks, R.; Adhikari, B.; Easton, C. D.; Gengenbach, T. R.; Cookson, D.; Gunatillake, P. A. Morphology and surface properties of high strength siloxane poly(urethane-urea)s developed for heart valve application. *J. Biomed. Mater. Res. B* **2019**, *107*, 112–121.
- Stokes, K.; Cobian, K. Polyether polyurethanes for implantable pacemaker leads. *Biomaterials* **1982**, *3*, 225–231.
- Chaffin, K. A. Longevity expectations for polymers in medical devices demand new approaches to evaluating their biostability. *ACS Macro. Lett.* **2020**, *9*, 1793–1798.
- Padsalgikar, A.; Cosgriff-Hernandez, E.; Gallagher, G.; Touchet, T.; Jacob, C.; Mellin, L.; Norlin-Weissenrieder, A.; Runt, J. Limitations

- of predicting in vivo biostability of multiphase polyurethane elastomers using temperature-accelerated degradation testing. *J. Biomed. Mater. Res. B* **2015**, *103*, 159–168.
- 6 Chaffin, K. A.; Buckalew, A. J.; Schley, J. L.; Chen, X.; Jolly, M.; Alkatout, J. A.; Miller, J. P.; Untereker, D. F.; Hillmyer, M. A.; Bates, F. S. Influence of water on the structure and properties of PDMS-containing multiblock polyurethanes. *Macromolecules* **2012**, *45*, 9110–9120.
 - 7 Chaffin, K. A.; Chen, X.; McNamara, L.; Bates, F. S.; Hillmyer, M. A. Polyether urethane hydrolytic stability after exposure to deoxygenated water. *Macromolecules* **2014**, *47*, 5220–5226.
 - 8 Hernandez, R.; Weksler, J.; Padsalgikar, A.; Choi, T.; Angelo, E.; Lin, J. S.; Xu, L. C.; Siedlecki, C. A.; Runt, J. A comparison of phase organization of model segmented polyurethanes with different intersegment compatibilities. *Macromolecules* **2008**, *41*, 9767–9776.
 - 9 Kleemann, T.; Nonnenmacher, F.; Strauss, M.; Kouraki, K.; Werner, N.; Fendt, A.; Zahn, R. Long-term performance and lead failure analysis of the Durata defibrillation lead compared to its previous model, the recalled Riata defibrillation lead. *J. Cardiovasc. Electrophysiol.* **2019**, *30*, 2012–2019.
 - 10 Gunatillake, P. A.; Dandeniyage, L. S.; Adhikari, R.; Bown, M.; Shanks, R.; Adhikari, B. Advancements in the development of biostable polyurethanes. *Polym. Rev.* **2019**, *59*, 391–417.
 - 11 Rueda, L.; Fernandez d'Arlas, B.; Corcuera, M. A.; Eceiza, A. Biostability of polyurethanes. Study from the viewpoint of microphase separated structure. *Polym. Degrad. Stabil.* **2014**, *108*, 195–200.
 - 12 Hergenrother, R. W.; Wabers, H. D.; Cooper, S. L. Effect of hard segment chemistry and strain on the stability of polyurethanes: in vivo biostability. *Biomaterials* **1993**, *14*, 449–458.
 - 13 Liu, W. K.; Zhao, Y.; Wang, R.; Luo, F.; Li, J. S.; Li, J. H.; Tan, H. Effect of chain extender on hydrogen bond and microphase structure of biodegradable thermoplastic polyurethanes. *Chinese J. Polym. Sci.* **2018**, *36*, 514–520.
 - 14 Pongkitwitoon, S.; Hernandez, R.; Weksler, J.; Padsalgikar, A.; Choi, T. Temperature dependent microphase mixing of model polyurethanes with different intersegment compatibilities. *Polymer* **2009**, *50*, 6305–6311.
 - 15 Wu, H.; Dai, T.; Ao, W.; Shao, S.; Li, Z.; Luo, F.; Li, J.; Zhao, D.; Lan, W.; Zhang, H.; et al. The role of segmental mixing on the mechanical properties and oxidative stability of polydimethylsiloxane-based polyetherurethane. *Polymer* **2022**, *261*, 125401.
 - 16 Li, Y.; Yuan, L.; Ming, H.; Li, X.; Tang, L.; Zhang, J.; Wang, R.; Wang, G.; Jiang, Y.; Li, Z.; Luo, F.; Li, J. H.; Tan, H.; Fu, Q. Enhanced hydrolytic resistance of fluorinated silicon-containing polyether urethanes. *Biomacromolecules* **2020**, *21*, 1460–1470.
 - 17 Le Gac, P. Y.; Choqueuse, D.; Melot, D. Description and modeling of polyurethane hydrolysis used as thermal insulation in oil offshore conditions. *Polym. Test.* **2013**, *32*, 1588–1593.
 - 18 Gerlock, J. L.; Braslaw, J.; Mahoney, L. R.; Ferris, F. C. Reaction of polyurethane foam with dry steam: kinetics and mechanism of reactions. *J. Polym. Sci., Part A: Polym. Chem.* **1980**, *18*, 541–557.
 - 19 Murata, S.; Nakajima, T.; Tsuzaki, N.; Yasuda, M.; Kato, T. Synthesis and hydrolysis resistance of polyurethane derived from 2,4-diethyl-1,5-pentanediol. *Polym. Degrad. Stabil.* **1998**, *61*, 527–534.
 - 20 Li, Z.; Yang, J.; Ye, H.; Ding, M. M.; Luo, F.; Li, J. S.; Li, J. H.; Tan, H.; Fu, Q. Simultaneous improvement of oxidative and hydrolytic resistance of polycarbonate urethanes based on polydimethylsiloxane/poly(hexamethylene carbonate) mixed macrodiols. *Biomacromolecules* **2018**, *19*, 2137–2145.
 - 21 Van Bogart, J. W. C.; Bluemke, D. A.; Cooper, S. L. Annealing-induced morphological changes in segmented elastomers. *Polymer* **1981**, *22*, 1428–1438.
 - 22 Dempsey, D. K.; Carranza, C.; Chawla, C. P.; Gray, P.; Eoh, J. H.; Cereceres, S.; Cosgriff-Hernandez, E. M. Comparative analysis of in vitro oxidative degradation of poly(carbonate urethanes) for biostability screening. *J. Biomed. Mater. Res. Part A* **2014**, *102*, 3649–3665.
 - 23 Speckhard, T. A.; Cooper, S. L. Ultimate tensile properties of segmented polyurethane elastomers: factors leading to reduced properties for polyurethanes based on nonpolar soft segments. *Rubber Chem. Technol.* **1986**, *59*, 405–431.
 - 24 Runt, S. P. J. Temperature dependent microphase mixing of model polyurethanes with different intersegment compatibilities. *Polymer* **2009**, *7*, 6305–6311.
 - 25 Wang, A.; Shao, S. R.; Wu, H. C.; Tian, C. X.; Luo, F.; Li, J. H.; Li, Z.; Tan, H. Effect of fluorocarbon side chain on the microphase morphology and rheological behavior of thermoplastic polyurethanes. *Chinese J. Polym. Sci.* **2022**, 10.1007/s10118-022-2865-3.
 - 26 Teo, L. S.; Chen, C. Y.; Kuo, J. F. Fourier transform infrared spectroscopy study on effects of temperature on hydrogen bonding in amine-containing polyurethanes and poly(urethane-urea)s. *Macromolecules* **1997**, *30*, 1793–1799.