

Effect of Fluorocarbon Side Chain on the Microphase Morphology and Rheological Behavior of Thermoplastic Polyurethanes

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 Electronic Supplementary Information

Abstract Fluorinated diols (FDO) with dangling chain were introduced into polyether urethanes (PEUs) as chain extender in order to achieve internal plasticization. Based on temperature dependent Fourier transform infrared (FTIR) spectroscopy results, the fluorinated polyether urethanes (FPEUs) exhibited weaker hydrogen bonding between C=O and N—H groups with addition of FDO. The crystallinity of hard domain was destroyed determined by thermal analysis. Combined with the results of dynamic mechanical analysis (DMA) and dissipative particle dynamics (DPD) simulation, it was proved that more loosely aggregated hard domains with weakened interaction separated from soft segment were formed. Rheological analysis indicated that FDO reduced the complex viscosity and viscous flow activation energy which endowed the polymer with more flexibility. Despite the loss of hydrogen bonds, there was no significant decline in mechanical property resulting from the decrease of hard segment dissolved in soft segment phase. The presence of fluorinated carbon side chain could function as internal plasticizer and contribute to the processability of polyurethane.

Keywords Fluorocarbon side chain; Internal plasticizer; Microphase separation; Polyurethane; Segmental mobility

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INTRODUCTION

Owing to its superior general properties such as outstanding mechanical properties and biocompatibility, thermoplastic polyurethane (TPU) has been universally applied in medical devices, coatings and insulator applications.^[1–4] TPU possesses hot-melt crystalline hard domain and amorphous soft segments that tend to segregate from each other due to thermodynamic incompatibility. This provides the polyurethane with melt processing capacity, rubber like deformation recoverability as well as high elongation at break.^[5] Nevertheless, the hard segments act as physical crosslinks may also endow the polyurethane with some issues in processing.^[6] The exorbitant cohesive energy of hard segment in PEU causes serious phase separation and excessive hydrogen bonding which cannot be easily destroyed when heated. This creates an obstacle to plasticization and extrusion.^[7,8] For instance, polyurethane-urea is unable to conduct thermoplastic processing due to over high hydrogen bond energy between hard segments.^[9,10]

To improve the processing flowability of polymers, external plasticization such as adding plasticizers is universally ap-

plied. Plasticizers can develop weak interaction (mainly van der Waals forces) with polymers and shield the molecular chains from each other which could reduce the chain entanglement and improve the flexibility.^[11] The most widely used plasticizers like chlorinated paraffin, ethylene bis stearamide (EBS) and di-(2-ethylhexyl)phthalate (DEHP) all share the problems of migration and leaching which may lead to serious health and environmental concerns.^[12–14]

Different from external plasticization, internal plasticization is straightly introducing plasticizing groups into polymer by chemical methods. These groups generally originate from surfactant, vegetable oil or high flexibility segment which can be modified to copolymerize.^[15–19] Zander *et al.* synthesized a kind of sulfonate ionomers which acted as a chain extender to internally plasticize the TPU.^[20] The crystallization of hard domain was inhibited and the free volume was added. Yu *et al.* studied the influences of dangling chains with graded length of carbons and found that H-bond plays an important part in the morphology and properties of polymers.^[17] Nozaki *et al.* compared the effects of soft segment with different dangling chains on polyurethane elastomers (PUEs) and found that those have one primary and one secondary hydroxyl groups made PUEs have lower degree of microphase separation and lower dynamic storage modulus value.^[21] This kind of internal plasticization of polyurethane seems concentrating on resulting in imperfections in hard domain, decreasing the hy-

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drogen bonding and improving the segment mobility. Although the processing flowability was promoted by these ionomers and dangling chains, severe concessions were made in mechanical properties.^[22,23]

Tang *et al.* introduced short fluorocarbon side chain as chain extender into silicon-based TPUs.^[24,25] The incorporation of polydimethylsiloxane (PDMS) into TPUs resulted in severe microphase separation and make the soft segment vulnerable to chemical substance without the mask of urethane groups. However, the presence of FDO disrupted the excessive phase separation by weakening the hydrogen bonding in hard segment, contributed to the phase mixing and improved the chemical stability of silicon-containing TPUs.

As FDO could weaken the strong hydrogen bond interaction between hard segments, we are inspired to explore the possibility that whether it can be utilized as internal plasticizer in TPU to decrease the melt viscosity as well as improve the processability. In this work, we synthesized FPEUs with gradient fluorocarbon side chain content. The correlation between microphase structures, mechanical properties, and rheological behaviors of PEU were founded by both experimental and computer simulation methods.

EXPERIMENTAL

Materials

Polyoxytetramethylene (PTMO, $M_w=1000$) was supplied by PTG, Korea, and Degussa, Germany, 4,4'-methylenediphenyl diisocyanate (MDI) was purchased from Wanhua Chemical Group, Yantai, China, and 1,4-butanediol (BDO) was from Flaka Chemika, Switzerland. MDI and BDO were both dewatered by vacuum distillation before use. Fluorinated diol (FDO, $M_w=306$) was obtained from our laboratory and also purified.^[26]

Synthesis of FPEUs

With PTMO-1000 as the soft segment and MDI, BDO and FDO as the hard segment, FPEUs were prepared by a two-step bulk polymerization method which included pre-polymerization and chain extension.

Firstly, PTMO was dewatered and heated to 105 °C for 2 h. Then the system was cooled down to 60–65 °C and proper amount of FDO was added. After fully mixed, calculated amount of MDI was added and reacted for 40 min for pre-polymerization under 75 °C. After that, another chain extender BDO was added and fully mixed by stirring at a rate of 1200 r/min for 2 min. The product was poured into a Teflon tray and an air-circulating at 100 °C for 6 h was applied. The specimens were prepared by compression molding at 195 °C and cut into dog-bone shape with 20.0 mm (length), 2.0 mm (width) and 0.3–0.4 mm (thickness).

Characterization

Gel permeation chromatography (GPC)

Waters-1515, USA with two columns was used in a flow rate of 1.0 mL/min at 40 °C. The mobile phase was DMF with 0.05 mol/L LiBr. The concentration of the solution was 3 mg/mL. Polymethyl methacrylate (PMMA) standard was applied to calibrate and determine the molecular weights.

Proton nuclear magnetic resonance (¹H-NMR)

¹H-NMR spectra of samples were carried out on a Bruker AV II

HD 400 MHz at 25 °C for 64 scans. Deuterated *N,N*-dimethylformamide (DMF) was used as solvents.

Differential scanning calorimetry (DSC)

With TA instruments DSC250, differential scanning calorimetry (DSC) was performed. The response was detected in the temperature range from 60 °C to 210 °C under N₂ atmosphere. Samples were first cooled from ambient temperature to –60 °C and equilibrated for 5 min, then a ramp 20 °C/min heat to 210 °C was performed followed with an isothermal for 5 mins and finally cooled to –60 °C at 20 °C/min.

Dynamic mechanical analysis (DMA)

TA instrument (Q800) was used to perform dynamic thermomechanical analysis (DMA). Measurements were conducted from –110 °C to 120 °C at 1 Hz and 100 Hz with a heating rate of 3 °C/min.

Dissipative particle dynamics (DPD) simulation

The dissipative particle dynamics (DPD) simulation was performed by Accelrys Material Studio 7.0 in a cubic box with 3D periodic boundary conditions, containing 1.92×10^5 beads at $\rho=3$ to avoid the finite size effect. The box size was set as 28.46 nm $\times$ 28.46 nm $\times$ 28.46 nm. The spring constant $C=4$. The total number of steps was 1×10^5 and the time step was set as 0.05 ns. The equilibrium states were confirmed through monitoring the pressure, temperature, and morphologies. More detailed information is available in the electronic supplementary information (ESI).^[27,28]

Temperature-controlled FTIR spectroscopy analysis

Temperature-controlled FTIR spectroscopy was carried out using a Nicolet-iS50 FTIR. Samples were scanned 32 times from 650 cm^{–1} to 4000 cm^{–1} at a resolution of 4 cm^{–1}. The temperature was ranging from 40 °C to 220 °C and was controlled at a rate of 10 °C/min by Variable Temperature Cell Holders. The spectra of C=O bonds (1660–1780 cm^{–1}) and N–H bonds (3200–3500 cm^{–1}) were fitted by PeakFit 4.2 with Gaussian-Lorentzian functions. The peak area of isocyanate (2220–2300 cm^{–1}) was normalized with the absorption band of benzene (1414 cm^{–1}).

Rheological analysis

A TA instrument of Discovery HR 30 was used to measure rheological properties. 2 mm thickness samples were used and the storage modulus (G') and loss modulus (G'') were measured within a frequency ranging from 0.01 Hz to 100 Hz. The measurement was respectively conducted at 200, 210, 220 and 230 °C.

All-atom molecular dynamics simulation

An all-atom molecular dynamics (AAMD) simulation was performed by Accelrys Material Studio 7.0. The box was constructed using Amorphous Cells and each box contained 5 polymer chains. The AAMD was carried out in a 1 fs equilibration step followed by 400 ps NPT ensemble with COMPASS force field.^[29] The mean square displacement (MSD) and diffusion coefficient (D) was obtained and more specific description can be found in ESI.^[30]

Tensile measurements

Tensile measurements were conducted on Dongguan Lixian Instrument, China. All specimen were tested at a crosshead speed of 50 mm/min after placed at 23 °C for 48 h. The measurements were repeated for three times and averaged.

RESULTS AND DISCUSSION

Analysis of Chemical Structure of PEUs

The molar ratio, mass fraction in total and molar mass determined by GPC are shown in Table 1. The content of hard segment was fixed as 60 wt%. The molar ratios of FDO/(FDO+BDO) were controlled as 0%, 3%, 5%, 8% and 10%, the mass fractions in total were 0%, 1.39%, 2.21%, 3.29% and 4.35% and the samples were denoted as PEU, FPEU-3, FPEU-5, FPEU-8 and FPEU-10, respectively. As shown in Fig. 1, the FPEUs are constituted of MDI, BDO, FDO and PTMO according to the $^1\text{H-NMR}$ results. $\delta=9.79$ (Ar-NH(CO)-O-CH₂-CH-O-, g), $\delta=9.73$ (Ar-NH(CO)-O-CH-CH₂-O-, h), $\delta=9.48$ (Ar-NH(CO)-O-CH₂-CH₂-CH₂-CH₂-, b), $\delta=7.51$ (ArH, i), $\delta=7.22$ (ArH, j), $\delta=4.13$ (Ar-NH(CO)-O-CH₂-CH₂-, e), $\delta=3.83$ (Ar-CH₂-Ar, a), $\delta=3.36$ (-O-CH₂-CH₂-CH₂-CH₂-O-, d), $\delta=1.72$ (Ar-

NH(CO)-O-CH₂-CH₂-, f) and $c=1.57$ (-O-CH₂-CH₂-CH₂-CH₂-O-, c).

Analysis of DSC

Fig. 2(a) represents the DSC curves of first consecutive heating. There observed one glass transition and two endothermic peaks. As summarized in Table 2, T_g was correlated with the segmental motions of the phase that PTMO mixed with some of the hard segment. With the addition of FDO, T_g shifted gradually to lower value which illustrated that the presence of fluorocarbon side chain promoted the hard segment separate from the PTMO groups. The endotherms at around 120 and 180 °C represented the melting behaviour of hard segment of crystallites with short-range order structures and with long range order, respectively.^[31,32] Both of these two endotherms exhibited a trend of shifting to lower temperature and long

Table 1 Chemical composition and molecular weights of PEUs.

Sample	Molar ratio				Mass fraction in total (%)		Molar mass (g/mol)	
	MDI	BDO	FDO	PTMO-1000	FDO	PTMO-1000	M_n	D
PEU	2.04	1.56	0	0.44	0	40	42924	1.72
FPEU-3	2.04	1.51	0.05	0.44	1.39	40	59159	1.99
FPEU-5	2.04	1.48	0.08	0.44	2.21	40	42938	1.91
FPEU-8	2.04	1.44	0.12	0.44	3.29	39	48658	1.81
FPEU-10	2.04	1.40	0.16	0.44	4.35	39	42921	1.83

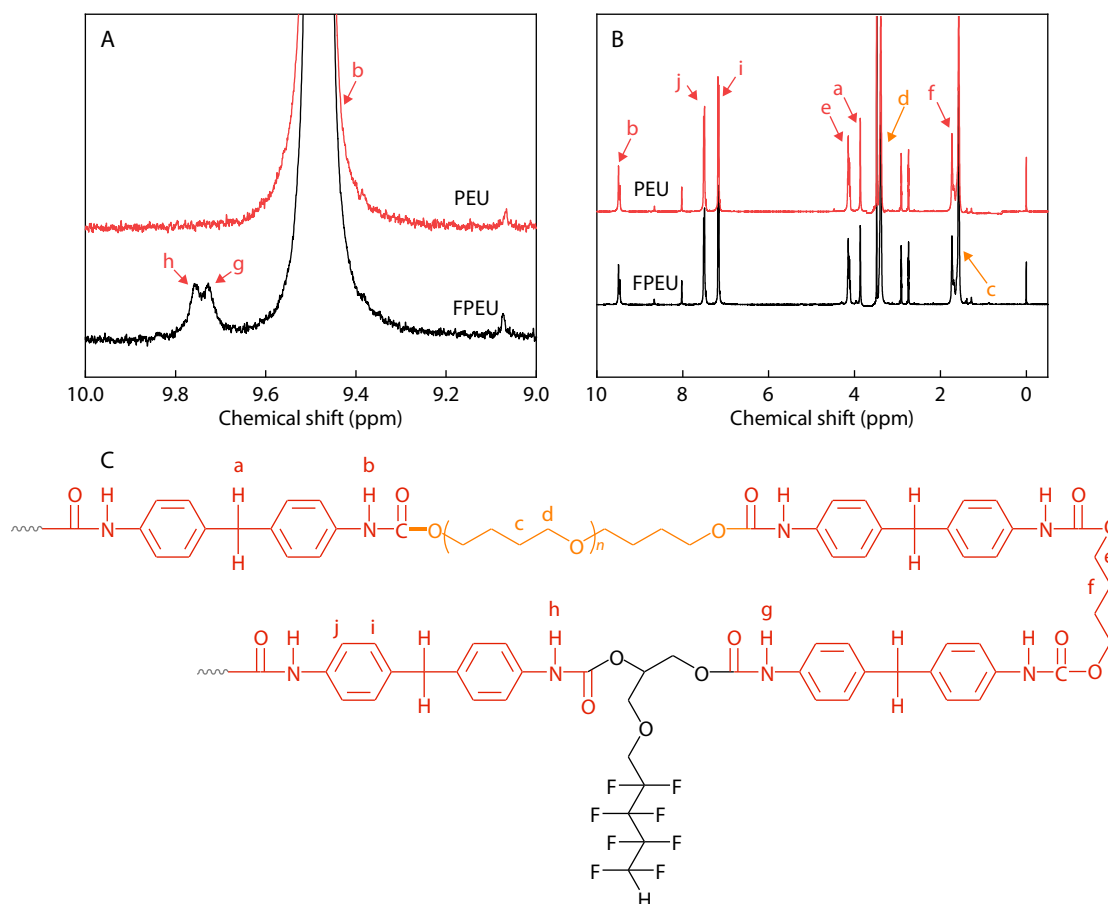


Fig. 1 (A) Part of spectrogram in the range from 10.0 ppm to 9.0 ppm; (B) $^1\text{H-NMR}$ spectra of PEUs from 10 ppm to -0.5 ppm; (C) Schematic structure of FPEUs.

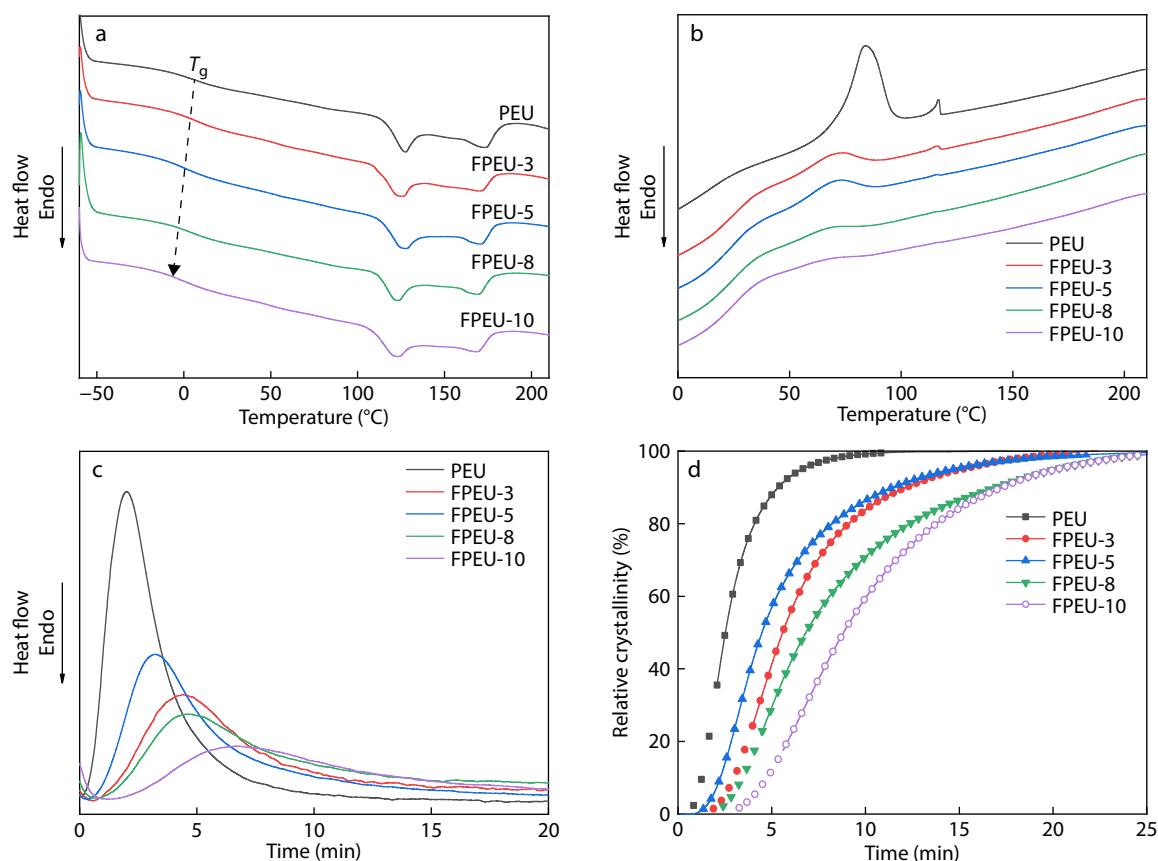


Fig. 2 (a) DSC thermograms of rise in temperature; (b) DSC thermograms of drop in temperature; (c) Isothermal crystallization curves and (d) relative crystallinity of samples.

Table 2 Thermal properties of PEUs from DSC.

Sample	T_g (°C)	T_{m1} (°C)	ΔH_1 (J/g)	T_{m2} (°C)	ΔH_2 (J/g)
PEU	7.4	127.0	4.5	174.0	4.2
FPEU-3	6.5	123.0	5.3	171.2	2.4
FPEU-5	3.4	125.3	5.4	171.5	2.9
FPEU-8	3.2	121.7	4.7	170.1	2.7
FPEU-10	-2.7	120.9	5.2	169.5	2.2

range order structures experienced a decrease in melting enthalpy, which indicated that the close packing of hard segment was reduced by fluorocarbon side chain. According to the result of non-isothermal crystallization (Fig. 2b), a crystalline peak appeared at 120 °C with the absence of FDO and gradually shifts to lower temperature accompanied with widening of peak shape. The isothermal crystallization kinetics (Figs. 2c and 2d) also exhibited that the crystallization rate decreased with the increase of FDO content. The results proved that the fluorocarbon side chain could function as plasticizer to inhibit the crystallinity of hard segment domain.

Dynamic Mechanical Analysis (DMA) and DPD Simulation

The curves of storage modulus and $\tan\delta$ obtained by DMA with different FDO contents are demonstrated in Figs. 3(a)–3(c). Sample PEU, FPEU-5 and FPEU-10 were selected to analysis for their similar molecular weight. As shown in Fig. 3(a), a sharp decline of storage modulus was observed at around 20 °C and the storage modulus declined obviously with the addition of

FDO which showed the significant plasticization. There were several glass transitions as summarized in Table 3. T_{g1} and T_{g2} were tested at 1 Hz and represented PTMO segments and hard domains respectively. T_{g1} decreased with the addition of FDO which indicated the hard segment gradually separated from the soft segment. Since the hysteresis loss of the segment mobility increases at higher frequency, the detection sensitivity will also be improved.^[33] T_{g2} showed not much difference when tested at 1 Hz. But it was split into two different transitions (T_{g2a} and T_{g2b}) when the frequency was raised to 100 Hz, as illustrated in Fig. 3(c). T_{g2a} was related to loosely packed hard domain originated from those dissolved in soft segment or containing FDO and T_{g2b} represented pure hard domain. The split of T_{g2} was not observed at 1 Hz because the little content of hard domain with fluorinated side chain and can only be detected at higher frequency. T_{g2a} grew higher with the addition of FDO which indicated more hard segments segregated from the soft segments and formed into loosely packed phase in FPEUs. Due to the low cohesive energy density of fluorinated side chain,

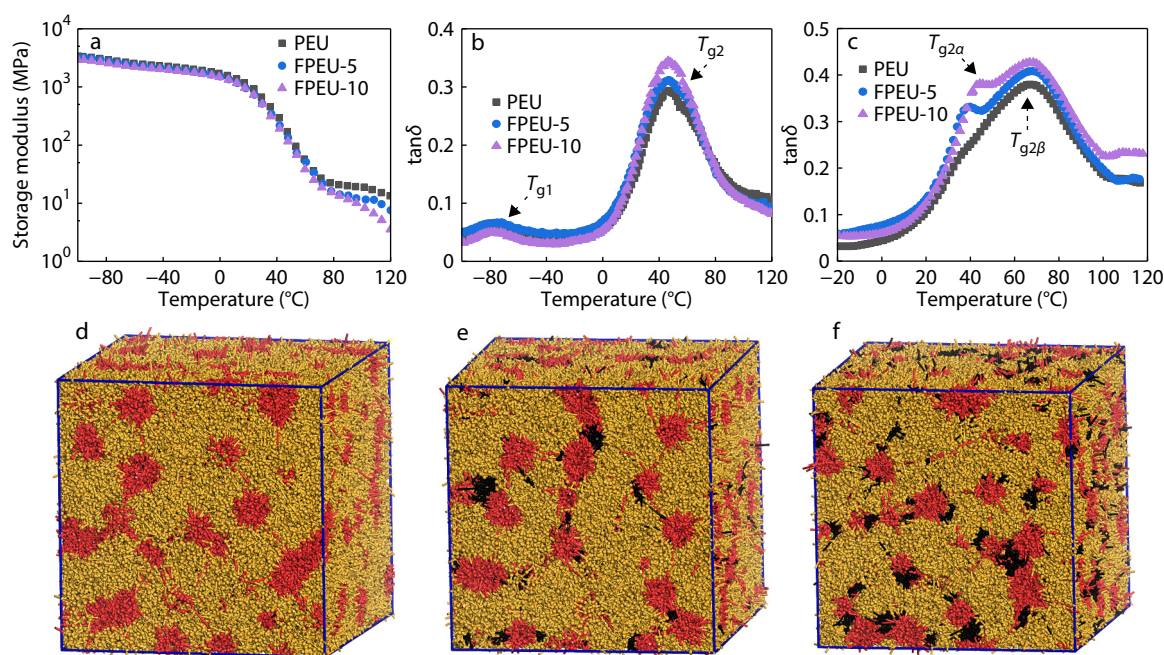


Fig. 3 DMA results of PEUs. (a) Storage modulus-temperature curves at 1 Hz from $-100\text{ }^{\circ}\text{C}$ to $120\text{ }^{\circ}\text{C}$; (b) Loss factor-temperature curves at 1 Hz from $-100\text{ }^{\circ}\text{C}$ to $120\text{ }^{\circ}\text{C}$; (c) Loss factor-temperature curves at 100 Hz from $-20\text{ }^{\circ}\text{C}$ to $120\text{ }^{\circ}\text{C}$; DPD simulated microphase morphologies of (d) PEU, (e) PEU-5 and (f) PEU-10.

Table 3 Thermal properties of PEUs from DMA.

Sample	T_{g1} ($^{\circ}\text{C}$) (1 Hz)	T_{g2} ($^{\circ}\text{C}$) (1 Hz)	$T_{g2\alpha}$ ($^{\circ}\text{C}$) (100 Hz)	$T_{g2\beta}$ ($^{\circ}\text{C}$) (100 Hz)
PEU	-77.2	47.9	37.8	66.2
FPEU-5	-77.4	47.6	40.1	68.6
FPEU-10	-79.1	46.4	46.5	68.4

those hard segments with FDO chain extender become more difficult to dissolve in soft segments and form hydrogen bonding inside. Therefore, they showed a tendency to aggregate by itself to create an independent hard domain with weakened interaction.

Since DPD simulation can be of great convenience to illustrate the mesostructure of the materials, we utilized it to investigate whether this mixed hard segment phase was formed. The process of coarse graining of DPD is shown in Fig. S1 (in ESI) and calculated bead-bead repulsion parameters (a_{ij}) are summarized in Table S2 (in ESI). As exhibited in Figs. 3(d)–3(f), the FDO side chain did present obvious aggregation and formed a new domain (black beads) beside the hard segment (red beads) which proved the conclusion of thermal analysis. The area of fluorinated hard domain increased gradually with the increasing addition of FDO and this newly formed domain tended to collect the separated hard segment from soft segment (yellow beads).

Temperature Dependent FTIR Experiment

Degree of microphase separation of polyurethane is closely tied up with hydrogen bonding between hard and soft segment.^[34–36] Generally speaking, the separation increases with the reinforcement of the hydrogen bonding. For PEU, N—H in urethane group functions as the donor and C=O along with ether bond (—O—) play as receptors of hydrogen bonding. The formation of H-bond will make the stretching

vibration of N—H and the positions of absorption band of carbonyl and ether bond shift to lower wavenumber in FTIR.

In this study, temperature dependent FTIR spectroscopy was applied to monitor the variation of hydrogen bonding in polyurethane with the temperature. According to the different locations of FTIR bands, which can be divided into strongly hydrogen-bonded C=O and at 1701 cm^{-1} and non-hydrogen bonded carbonyls at 1730 cm^{-1} . The fraction of these two different carbonyl groups (P_i) can be quantitatively described by the corresponding peaks' area (S_i), which can be illustrate as:^[37]

$$P_i = \frac{S_i}{S_{1701\text{cm}^{-1}} + S_{1730\text{cm}^{-1}}} \quad (1)$$

However, the peak area of N—H varies with the changing temperature so it is hard to quantitatively described like carbonyl groups.^[38] The N—H bond spectra will shift to higher wavenumber (from 3320 cm^{-1} to 3360 cm^{-1}) when H-bond is formed. The spectra of carbonyls ($1660\text{--}1780\text{ cm}^{-1}$) and N—H group ($3200\text{--}3500\text{ cm}^{-1}$) were fitted by PeakFit 4.2 with Gaussian-Lorentzian functions. As is shown on the Figs. 4(a)–4(c), with the increase of the temperature, the absorbance intensity of carbonyls at 1701 cm^{-1} gradually declined and the growth of bands at 1730 cm^{-1} was observed, which indicated the occurrence of the transformation from strongly hydrogen-bonded carbonyls to free carbonyls. In Figs. 4(d)–4(f), these two types of carbonyls experienced a drastic

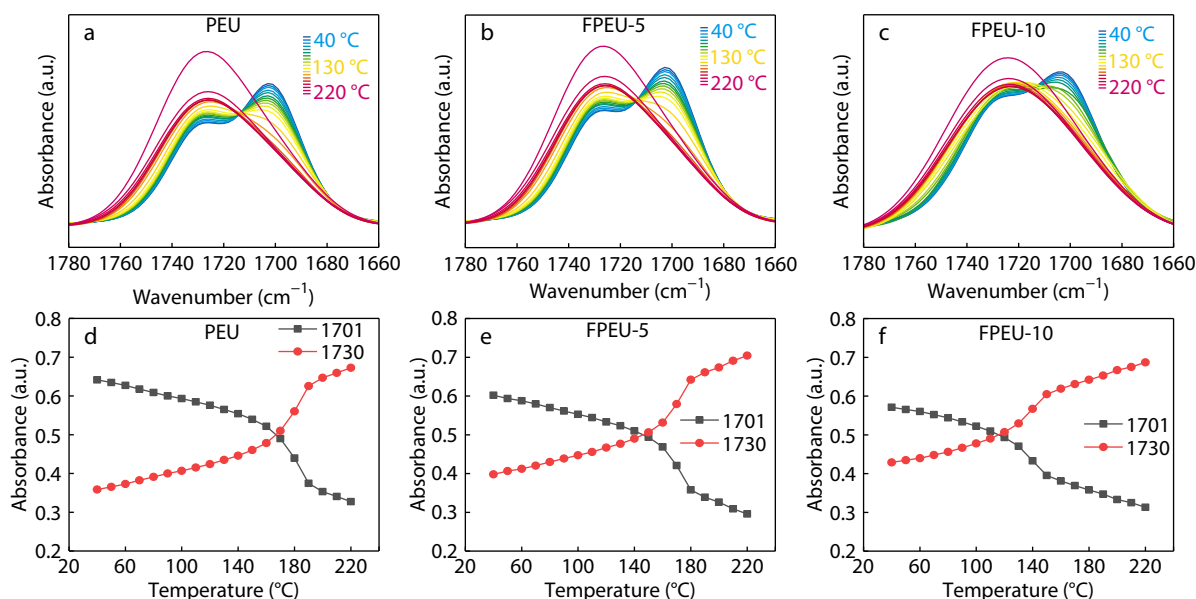


Fig. 4 Fitted FTIR spectra from 1660 cm^{-1} to 1780 cm^{-1} as a function of temperature for different samples: (a) PEU, (b) FPEU-5 and (c) FPEU-10. The fractions of non-bonded (●), and strongly hydrogen-bonded (■) urethane carbonyl groups for different samples in the temperature range from $40\text{ }^{\circ}\text{C}$ to $220\text{ }^{\circ}\text{C}$: (d) PEU (e) FPEU-5 and (f) FPEU-10.

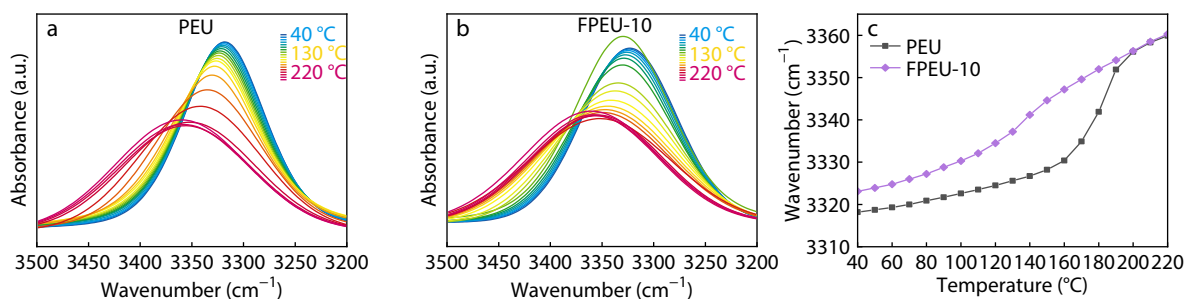


Fig. 5 FTIR spectra of N—H bonds from 3200 cm^{-1} to 3500 cm^{-1} as a function of temperature for different samples: (a) PEU and (b) FPEU-10; (c) The wavenumber shifts of N—H bonds in the temperature range from $40\text{ }^{\circ}\text{C}$ to $220\text{ }^{\circ}\text{C}$.

change in ratio for each sample calculated from the fitting curve of FTIR. For PEU, the change occurred at about $165\text{ }^{\circ}\text{C}$ and decreased to around $140\text{ }^{\circ}\text{C}$ in FPEU-5. When FDO content further increased as FPEU-10, the change happened at around $110\text{ }^{\circ}\text{C}$. In Fig. 5, the shifts of N—H groups exhibited a similar trend: the transformation from hydrogen bonded N—H to free N—H gradually dropped at lower temperature with the increasing ratio of the FDO. This indicated that the fluorocarbon side chain weakened the hydrogen bond between C=O and N—H groups and contributed to the dissociation of urethane linkages in hard segments when heated.

Figs. S2(a)–S2(c) (in ESI) exhibit the absorbance intensity of isocyanate at around 2260 cm^{-1} of different temperatures in each sample. Isocyanate is the thermal decomposition product of carbamate and the relative amount reflects the thermal stability of hard segment. The intensity of the spectra of isocyanate grew with the increasing temperature and shifted to the high wavenumber region which indicated that the probability of decomposition was improved. In Fig. S2(d) (in ESI), for FPEU-5, a decline of the relative amount of isocyanate at higher temperature appeared compared with PEU,

nevertheless the release of isocyanate grew heavier when the FDO content was further increased as FPEU-10. It was assumed that this thermal decomposition could be inhibited due to the steric effect of side chain at lower ratio. When the addition of FDO was increased to a greater extent, the intramolecular hydrogen bonding among crystalline region was further destroyed and the thermal stability of polyurethane sustained more losses. The isocyanate, as a decomposition product, was consequently released.

Rheological Analysis and Mechanical Properties

The flow behavior and the flow activation energies (E_a) of polymer melts were investigated as well. Other than chemical structures, molecular weight also have profound influence on rheological properties of TPU.^[39] By using logarithm of viscosity as vertical and $1000/T$ as abscissa, the E_a can be calculated from the slope of linear fitting curve.^[40] In this work, it was calculated according to the zero shear viscosities at temperatures of each sample fitted with Carreau-Yasuda model which was universally applied in describing rheological behaviour of non-Newtonian viscous fluid.^[41–43]

As shown in Figs. 6(a) and 6(b), both E_a and complex viscosity appear downtrends following the increase of FDO con-

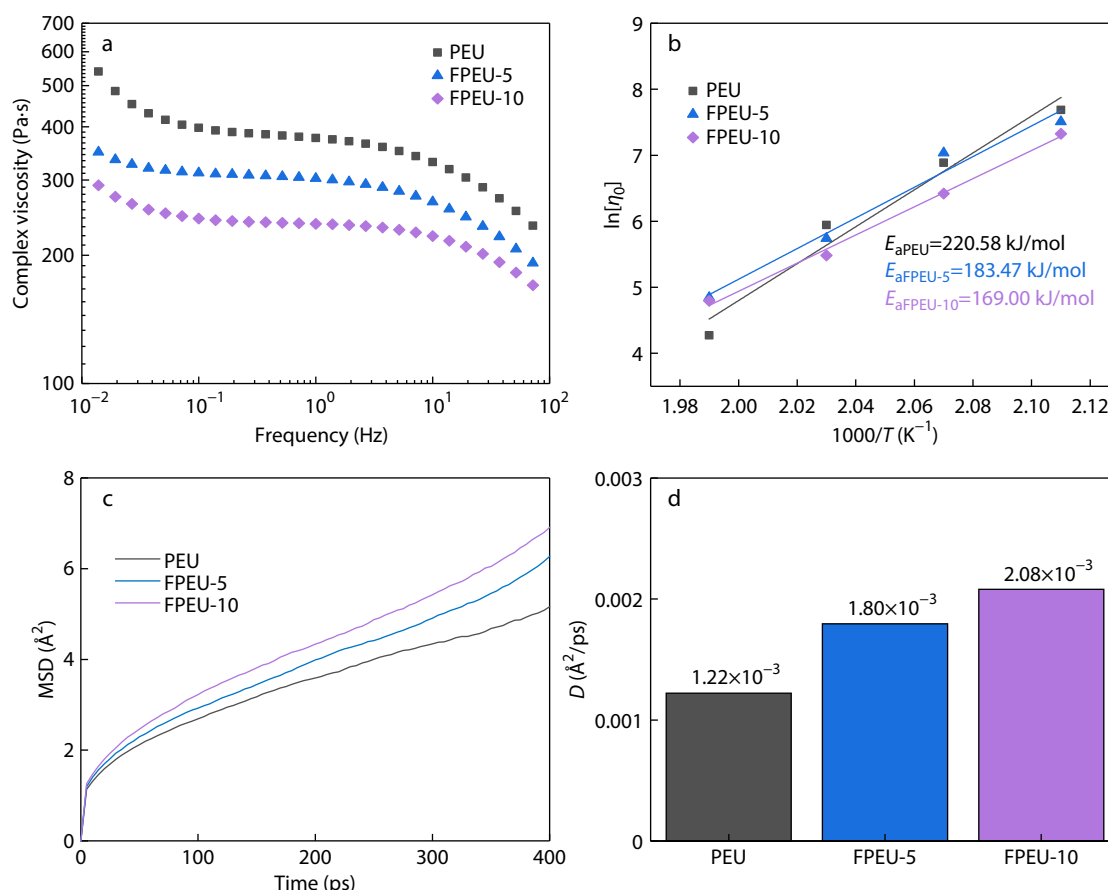


Fig. 6 (a) Complex viscosity as a function of frequency at 220 °C; (b) The Arrhenius plot of the zero shear viscosities fitted with Carreau-Yasuda model and calculated flow activation energies; (c) MSDs of PU chains as a time function; (d) Diffusion coefficients of PU chains.

Table 4 Summary of mechanical properties of PEUs.

Sample	Young's modulus (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)
PEU	58.6±2.0	60.9±6.9	211.9±19.0
FPEU-5	53.8±3.2	56.8±10.7	186.4±14.4
FPEU-10	53.3±4.9	54.4±5.1	176.9±12.2

tent. Since E_a reflects the polymer's sensitivity to temperature and molecular segmental mobility, this kind of downtrends indicated that the fluorocarbon side chain promoted the mobility of hard segment and endowed the polymer with more flexibility while heated. This was attributed to the low cohesive energy density of fluorine and the decrease of polymer chain friction caused by short side chain of FDO.

An all-atom molecular dynamics (AAMD) simulation was applied to investigate the mobility of samples. The model molecule structures are shown at Table S1 (in ESI). MSD determines the displacement of molecules followed with time and the diffusion coefficient (D) was calculated from the slope. They both reflected the molecular segmental mobility. According to the result of AAMD (Figs. 6c and 6d), both MSD and diffusion coefficient increased with the growth of FDO content. It indicated that the PEU with fluorinated carbon side chain possesses higher chain mobility which validated the result of rheological analysis.

Mechanical properties of PEUs are all summarized in Table

4. Although the hydrogen bond inside the hard domain was declined by FDO, the aggregation of fluorinated hard domain inhibited the dissolution of hard segment in soft segment. The increased microphase separation compensated for the loss of mechanical properties caused by weakened intermolecular interactions. Therefore, the addition of FDO had little impact on mechanical properties.

CONCLUSIONS

By introducing fluorinated diols into hard segment of polyether urethanes, the crystallinity of hard domain was reduced and the hydrogen bonding was weakened. This aggregation of fluorinated hard domain may inhibit the dissolution of hard segment in soft segment and more loosely packed hard segment domain with FDO was formed. The increased microphase separation compensated for the loss of mechanical properties caused by weakened intermolecular interactions. The presence of fluorinated carbon side chain could improve molecular segmental mobility and flexibility in FPEUs. With

proper addition of FDO as FPEU-5 (2.21 wt%), both inhibition of isocyanate release and internal plasticization can be achieved with little impact on mechanical properties.

NOTES

The authors declare no competing financial interest.

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/s10118-022-2865-3>.

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REFERENCES

- Wiggins, M. J.; MacEwan, M.; Anderson, J. M.; Hiltner, A. Effect of soft-segment chemistry on polyurethane biostability during in vitro fatigue loading. *J. Biomed. Mater. Res. Part A* **2004**, *68*, 668–683.
- Wu, H. C.; Feng, Y.; Song, X. Y.; Song, C. Y.; Chen, J. L.; Wang, Y. C.; He, X. L.; Liang, R. C.; Li, J. H.; Tan, H. Implantable polyurethane scaffolds loading with peg-paclitaxel conjugates for the treatment of glioblastoma multiforme. *Chinese J. Polym. Sci.* **2022**, *40*, 491–503.
- Song, N. J.; Zhou, L. J.; Liu, W. K. Effect of Trastuzumab on the micellization properties, endocytic pathways and antitumor activities of polyurethane-based drug delivery system. *Chinese J. Polym. Sci.* **2017**, *35*, 909–923.
- Matějka, L.; Špírková, M.; Dybal, J.; Kredatusová, J.; Hodan, J.; Žhigunov, A.; Šlouf, M. Structure evolution during order-disorder transitions in aliphatic polycarbonate based polyurethanes. Self-healing polymer. *Chem. Eng. J.* **2019**, *357*, 611–624.
- Yanagihara, Y.; Osaka, N.; Murayama, S.; Saito, H. Thermal annealing behavior and structure development of crystalline hard segment domain in a melt-quenched thermoplastic polyurethane. *Polymer* **2013**, *54*, 2183–2189.
- Castagna, A. M.; Fragiadakis, D.; Lee, H.; Choi, T.; Runt, J. The role of hard segment content on the molecular dynamics of poly(tetramethylene oxide)-based polyurethane copolymers. *Macromolecules* **2011**, *44*, 7831–7836.
- Pelúfo, D. I.; Neto, S. C.; Gobbo, R. C. B.; dos Santos, A. J.; Terezo, A. J.; de Siqueira, A. B. Kinetic study of the thermal decomposition of castor oil based polyurethane. *J. Polym. Res.* **2020**, *27*, 143.
- Rotival, C.; Renacco, E.; Arfi, C.; Pauli, A. M.; Pastor, J. Gases emitted during thermal decomposition of a polypropylene film and a polyurethane adhesive. *J. Therm. Anal.* **1994**, *41*, 1519–1527.
- Lyon, R. E.; Wang, D. X.; Farris, R. J.; Macknight, W. J. Polyurethane-urea elastomers as working substances in rubber heat engines. *J. Appl. Polym. Sci.* **1984**, *29*, 2857–2872.
- Qin, X. M.; Xiong, J. W.; Yang, X. H.; Wang, X. L.; Zheng, Z. Preparation, morphology, and properties of polyurethane-urea elastomers derived from sulphone-containing aromatic diamine. *J. Appl. Polym. Sci.* **2007**, *104*, 3554–3561.
- Coleman, E. A. 21 - Plastics Additives. In *Applied Plastics Engineering Handbook (Second Edition)*, Kutz, M. Ed.; William Andrew Publishing, **2017**; pp 489–500.
- Cooper, S. L.; Tobolsky, A. V. Anomalous depression of rubbery modulus through crosslinking. *J. Appl. Polym. Sci.* **2010**, *11*, 1361–1369.
- Rezaei-Vahidian, H.; Farajpour, T.; Abdollahi, M. Using an inhibitor to prevent plasticizer migration from polyurethane matrix to EPDM based substrate. *Chinese J. Polym. Sci.* **2019**, *37*, 681–686.
- Al Salloum, H.; Saunier, J.; Tfayli, A.; Yagoubi, N. Studying DEHP migration in plasticized PVC used for blood bags by coupling Raman confocal microscopy to UV spectroscopy. *Mater. Sci. Eng. C* **2016**, *61*, 56–62.
- Petrovic, Z. Polyurethanes from vegetable oils. *Polym. Rev.* **2008**, *48*, 109–155.
- Shi, M.; Yang, J.; Wang, X. Preparation castor oil-modified high bio-based waterborne polyurethane and its application. *J. Polym. Res.* **2021**, *28*, 1–12.
- Yu, W.; Du, M.; Zhang, D.; Lin, Y.; Zheng, Q. Influence of dangling chains on molecular dynamics of polyurethanes. *Macromolecules* **2013**, *46*, 7341–7351.
- Wang, C. L.; Chao, D. Y. Study of oxygen-permeable polyurethane ionomer. II. *J. Appl. Polym. Sci.* **2000**, *78*, 1932–1938.
- Clint, J. H. Surfactants: applications in plastics. In *Plastics Additives: An A-Z reference*, Pritchard, G. Ed.; Springer Netherlands, **1998**; pp. 604–612.
- Zander, Z. K.; Wang, F.; Becker, M. L.; Weiss, R. A. Ionomers for tunable softening of thermoplastic polyurethane. *Macromolecules* **2016**, *49*, 926–934.
- Nozaki, S.; Hirai, T.; Higaki, Y.; Yoshinaga, K.; Kojio, K.; Takahara, A. Effect of chain architecture of polyol with secondary hydroxyl group on aggregation structure and mechanical properties of polyurethane elastomer. *Polymer* **2017**, *116*, 423–428.
- Chen, L.; Ma, W.; Yu, X.; Yang, C. Syntheses and antimicrobial activity of novel polyurethane ionomers. *Chinese J. Polym. Sci.* **1996**, *14*, 209–210.
- Mondal, S.; Hu, J. L. Structural characterization and mass transfer properties of nonporous-segmented polyurethane membrane: influence of the hydrophilic segment content and soft segment melting temperature. *Polym. Eng. Sci.* **2010**, *48*, 233–239.
- Tang, L.; Long, X.; He, X.; Ding, M.; Zhao, D.; Luo, F.; Li, J.; Li, Z.; Tan, H.; Zhang, H. Improved in vivo stability of silicon-containing polyurethane by fluorocarbon side chain modulation of the surface structure. *J. Mater. Chem. B* **2021**, *9*, 3210–3223.
- Tang, L.; Shao, S.; Wang, A.; Tian, C.; Luo, F.; Li, J.; Li, Z.; Tan, H.; Zhang, H. Influence of fluorocarbon side chain on microphase separation and chemical stability of silicon-containing polycarbonate urethane. *Polymer* **2022**, *242*, 124538.
- 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.
- Bunte, S. W.; Sun, H. Molecular modeling of energetic materials: the parameterization and validation of nitrate esters in the COMPASS force field. *J. Phys. Chem. B* **2000**, *104*, 2477–2489.
- Groot, R. D.; Warren, P. B. Dissipative particle dynamics: bridging the gap between atomistic and mesoscopic simulation. *J. Chem. Phys.* **1998**, *107*, 4423–4435.
- Sun, H. COMPASS: an ab initio force-field optimized for condensed-phase applications overview with details on alkane

- and benzene compounds. *J. Phys. Chem. B* **1998**, *102*, 7338–7364.
- 30 Chen, X.; Zhu, J.; Luo, Y.; Chen, J.; Ma, X.; Bukhvalov, D.; Liu, H.; Zhang, M.; Luo, Z. Molecular dynamics simulation insight into the temperature dependence and healing mechanism of an intrinsic self-healing polyurethane elastomer. *Phys. Chem. Chem. Phys.* **2020**, *22*, 17620–17631.
 - 31 Seymour, R. W.; Allegranza, A. E.; Cooper, S. L. Segmental orientation studies of block polymers. I. Hydrogen-bonded polyurethanes. *Macromolecules* **1973**, *6*, 896–902.
 - 32 Bogart, J.; Bluemke, D. A.; Cooper, S. L. Annealing-induced morphological changes in segmented elastomers. *Polymer* **1981**, *22*, 1428–1438.
 - 33 Xiang, D.; He, J.; Cui, T.; Liu, L.; Shi, Q. S.; Ma, L. C.; Liang, Y. Multiphase structure and electromechanical behaviors of aliphatic polyurethane elastomers. *Macromolecules* **2018**, *51*, 6369–6379.
 - 34 Pongkitwitoon, S.; Hernández, R.; Weksler, J.; Padsalgikar, A.; Choi, T.; Runt, J. Temperature dependent microphase mixing of model polyurethanes with different intersegment compatibilities. *Polymer* **2009**, *50*, 6305–6311.
 - 35 Chen, H.; Li, Y.; Liu, Y.; Gong, T.; Wang, L.; Zhou, S. Highly pH-sensitive polyurethane exhibiting shape memory and drug release. *Polym. Chem.* **2014**, *5*, 5168–5174.
 - 36 Yang, X.; Wang, L.; Wang, W.; Chen, H.; Yang, G.; Zhou, S. Triple shape memory effect of star-shaped polyurethane. *ACS Appl. Mater. Interfaces* **2014**, *6*, 6545–6554.
 - 37 Kong, Z.; Tian, Q.; Zhang, R.; Yin, J.; Shi, L.; Ying, W. B.; Hu, H.; Yao, C.; Wang, K.; Zhu, J. Reexamination of the microphase separation in MDI and PTMG based polyurethane: fast and continuous association/dissociation processes of hydrogen bonding. *Polymer* **2019**, *185*, 121943.
 - 38 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(urethaneurea)s. *Macromolecules* **1997**, *30*, 1793–1799.
 - 39 Lu, Q.-W.; Hernandez-Hernandez, M. E.; Macosko, C. W. Explaining the abnormally high flow activation energy of thermoplastic polyurethanes. *Polymer* **2003**, *44*, 3309–3318.
 - 40 Hablot, E.; Zheng, D.; Bouquey, M.; Avérous, L. Polyurethanes based on castor oil: kinetics, chemical, mechanical and thermal properties. *Macromol. Mater. Eng.* **2008**, *293*, 922–929.
 - 41 Abbasi, F. M.; Hayat, T.; Ahmad, B. Numerical analysis for peristaltic transport of Carreau-Yasuda fluid with variable thermal conductivity and convective conditions. *J. Cent. South Univ.* **2015**, *22*, 4467–4475.
 - 42 Hayat, T.; Abbasi, F. M.; Ahmad, B.; Alsaedi, A. Peristaltic transport of Carreau-Yasuda fluid in a curved channel with slip effects. *PLoS One* **2014**, *9*, e95070.
 - 43 Abd elmaboud, Y.; Mekheimer, K. S. Non-linear peristaltic transport of a second-order fluid through a porous medium. *Appl. Math. Modell.* **2011**, *35*, 2695–2710.