

University of Groningen

Study on structure -induced heat transfer capabilities of waterborne polyurethane membranes

Li, Rui; Shan, Zhihua

Published in:

Colloids and Surfaces A-Physicochemical and Engineering Aspects

DOI:

[10.1016/j.colsurfa.2020.124879](https://doi.org/10.1016/j.colsurfa.2020.124879)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:

2020

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Li, R., & Shan, Z. (2020). Study on structure -induced heat transfer capabilities of waterborne polyurethane membranes. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 598, [124879]. <https://doi.org/10.1016/j.colsurfa.2020.124879>

Copyright

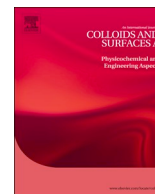
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.



Study on structure-induced heat transfer capabilities of waterborne polyurethane membranes

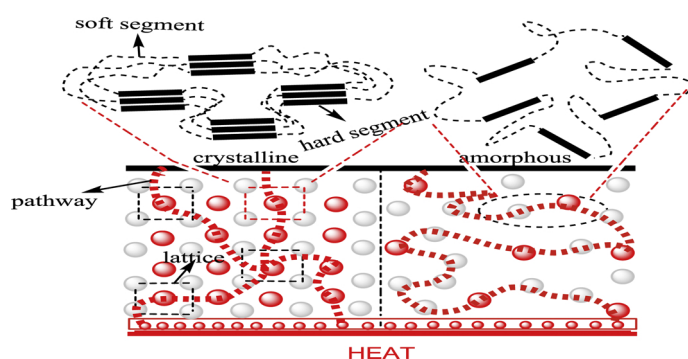
Rui Li^{a,b,*}, Zhihua Shan^{a,*}

^a The Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu, 610065, China

^b Department of Polymer Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands



GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Phonon propagation
Heat conduction
Phase behavior
Hydrogen bond
Ordered sequences
WPU membrane

ABSTRACT

Structural induced heat transfer capability of waterborne polyurethane (WPU) membrane was investigated. Hereby, WPU emulsions were synthesized with series of combinations of 2,4-Diisocyanatotoluene (TDI), poly(propylene glycol) (PPG), Poly(ethylene glycol) (PEG), dimethylolpropionic acid (DMPA) and ethylene glycol (EG) for studied membranes preparation. In this study, optimal prepolymer components, hard segment content, hydrophilic fragments and thermal annealing treatment on membrane-forming process were performed to study the structural features of WPU and corresponding heat conduction. Regarding to the results of AFM, XRD and DSC analysis, we found heat conduction was tightly related to the status of phase behaviors in studied WPU membranes. That's because phonon propagation as one primary heat carrier in polymer matrix was closely depended on the morphology of polymer chains. Good phase separation behavior could conduce to form long-range, short-range and microcrystalline ordering in WPU through intermolecular force (e.g. hydrogen bond), further pave as a conductive path for heat transmitting.

1. Introduction

Heat insulation or dissipation is an important topic in engineering fields, especially in applications such as batteries [1–4], constructions [5,6], miniaturized electrical components, but also in polymeric

materials in general since more and more polymer materials are used in thermal engineering because of their excellent comprehensive performances [7,8]. However, most polymers are generally bad thermal conductors, so the demanding of good heat conduction capability for polymeric materials is increasingly more important in specially the

* Corresponding authors at: The Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu, 610065, China.

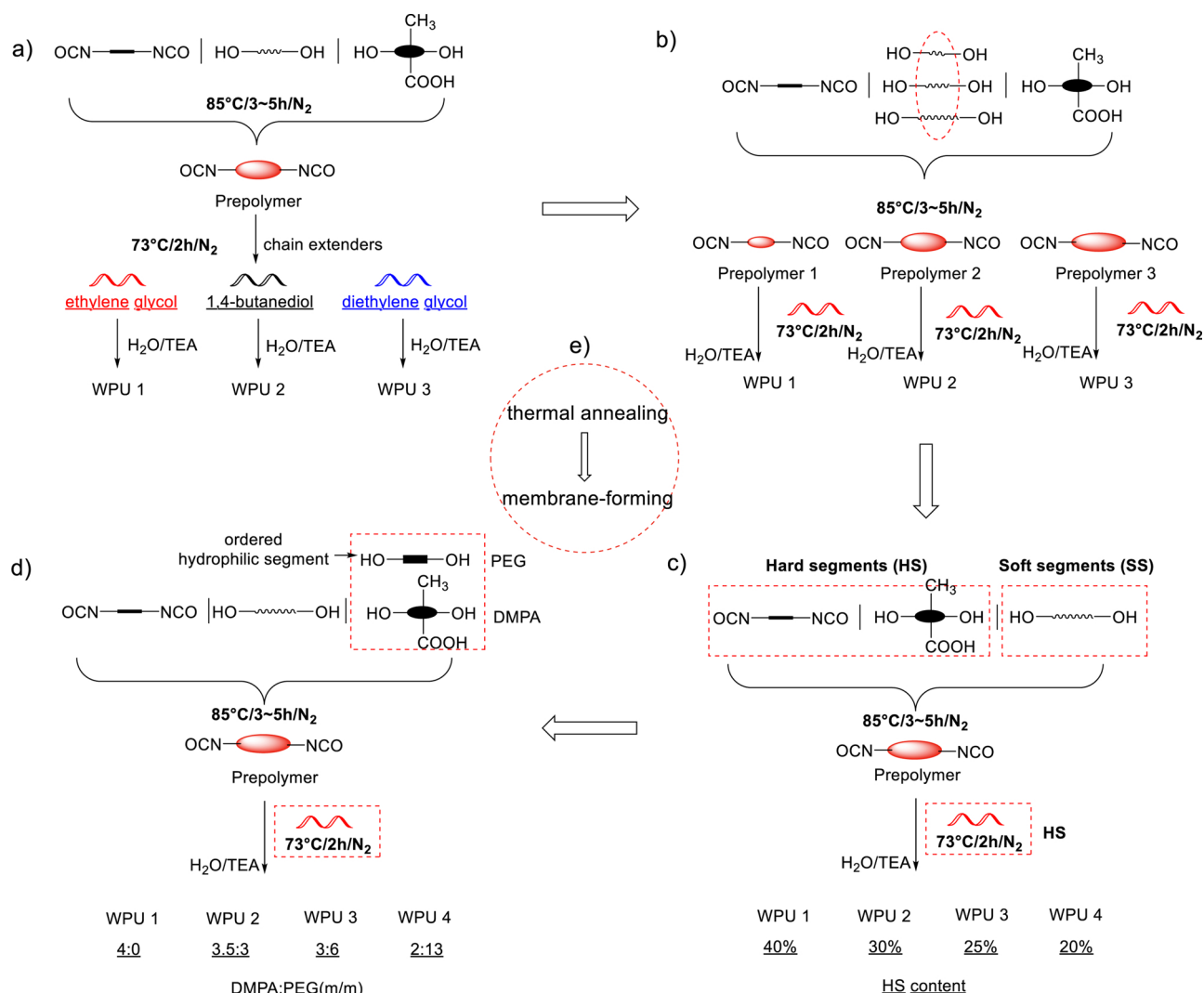
E-mail addresses: rui.li@rug.nl (R. Li), 549671254@qq.com (Z. Shan).

<https://doi.org/10.1016/j.colsurfa.2020.124879>

Received 26 February 2020; Received in revised form 7 April 2020; Accepted 16 April 2020

Available online 21 April 2020

0927-7757/ © 2020 Elsevier B.V. All rights reserved.



Scheme 1. Synthetic route of WPU emulsion.

Table 1
 Three levels and three factors of orthogonal experiments.

Number	R (—NCO/—OH)	PPG (M_n)	DMPA (%)	k (W/m K)
1	1.2	PPG-1000	4	0.193
2	1.2	PPG-2000	6	0.145
3	1.2	PPG-1500	8	0.095
4	1.3	PPG-1000	6	0.107
5	1.3	PPG-2000	8	0.142
6	1.3	PPG-1500	4	0.077
7	1.4	PPG-1000	8	0.105
8	1.4	PPG-2000	4	0.323
9	1.4	PPG-1500	6	0.056
K_1	0.144	0.135	0.160	
K_2	0.109	0.203	0.103	
K_3	0.161	0.076	0.114	
r	0.052	0.127	0.057	

applications of thermal engineering, such as many devices for long lasting applications. e.g. in narrow spaces of coil loops in electrical components, are fairly common electronics, in which dissipation of heat is crucial for prolonging the span life [9–11]. In general, thermal conductivity coefficient (TCC) [12] is commonly used to quantify heat transfer capabilities of materials. Normally, it reveals that the high TCC exhibits a strong heat dissipating capability, while the low TCC shows thermal insulation performance accordingly.

Waterborne polyurethane (WPU) materials are applying in many area where thermal properties is evolved owing to their excellent physico-chemical stability. However, the TCC of WPU is limited in engineering application, because of the poor conductor of heat in comparison to metal materials [13]. To address this issue, many methods focused on fabrication of polymer-based composites with adding high TCC of fillers were reported: introducing 3 wt% multi-walled carbon nanotubes (MWCNTs) into semicrystalline polyurethane (PU) dispersions increased TCC up to 0.47 W/m K 2 wt% graphene oxide (GO) in WPU led to 0.33 W/m K with only 38 % increases, etc. [14–16]. However, the experimental TCC only partly reflects the theoretical values, because the poor compatibility and ununiform distribution of unmodified fillers in polymer matrixes would led to interface thermal resistance. Moreover, although the modified fillers showed good compatibility and uniform distribution in polymer resin, but due to the surface modifications (e.g. chemical oxidation) could destroy the crystal structure and appear more defects, dislocations or grain boundaries accordingly, as a consequence, its intrinsic conductivities decreased significantly. So, to compensate for these defects, a high filler loading is always adopted to improve TCC, which sacrificing the mechanical properties of composites finally [17–19]. On one hand, to further overcome this disadvantage, the efficient modification methods without introducing any structural defects on fillers' lattice is still a big challenge. On the other hand, the complicated modifications procedure and expensive price of fillers make it impossible to scale-up in

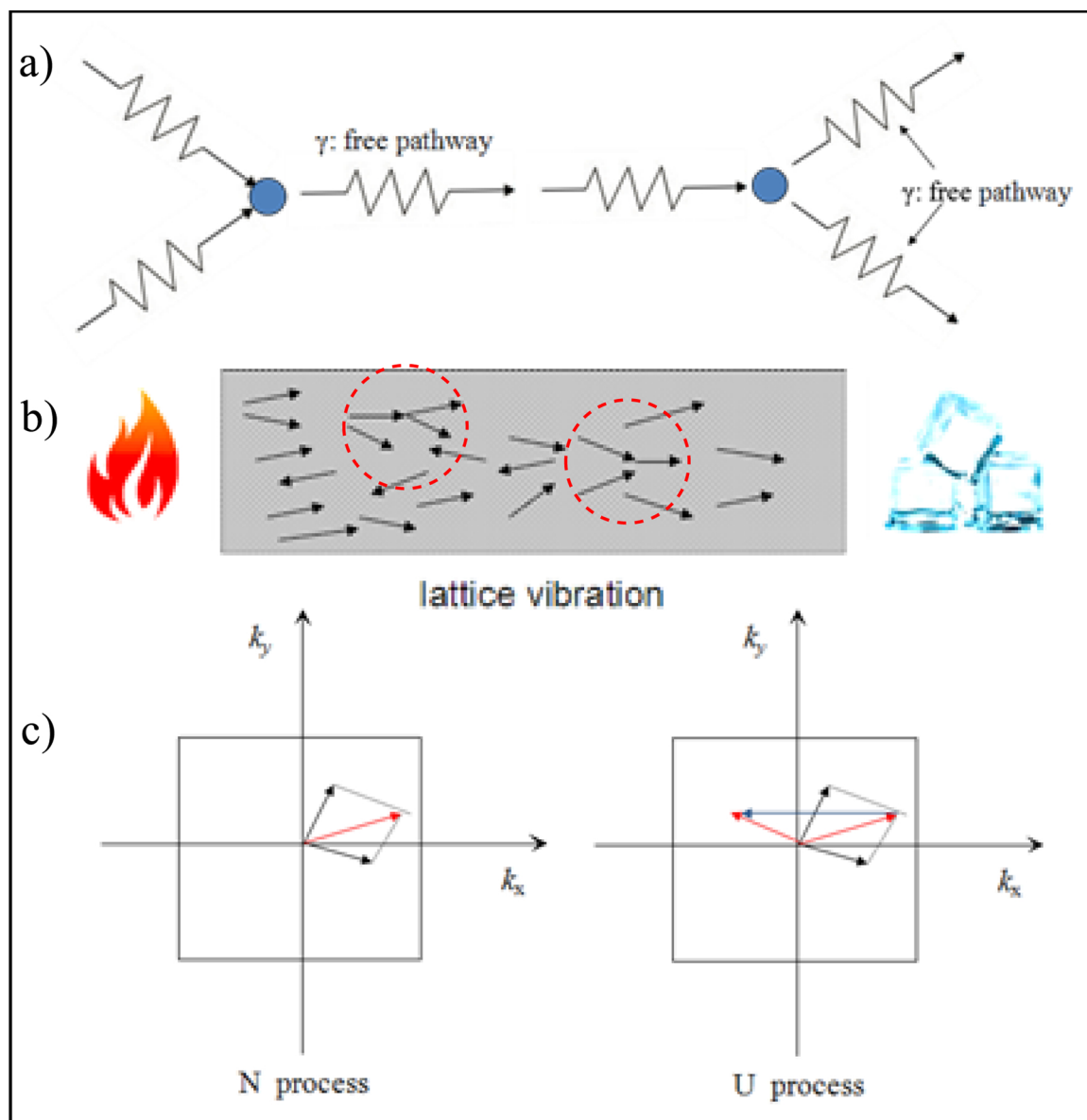


Fig. 1. a) and b) is the schematic graph of phonons collisions. c) two processes of N process and U process during phonon collisions. Here, two black vector arrows trend towards forming red arrow as final pathway in N process, while two red vector arrows in U process form blue vector arrow as final pathway which prolong heat transfer time (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

engineering. As an alternative, the research of structure-property relation of WPU on heat conduction looks more promising in industry.

In this study, series of WPU emulsions were synthesized to select optimal prepolymer components by referring to optimization orthogonal arrays, then based on the fixed prepolymer components a further analysis of varying hard segment content and hydrophilic fragments on structural features were carried out afterwards [13,16,20–22]. Finally, thermal annealing treatment on WPU membranes was conducted as well. Here, aforementioned WPU emulsions were used for studied membranes preparation and analysis, and more characterizations of AFM, XRD and DSC were further involved to study the aspect of structure-property relation on structural features and heat conduction performances.

2. Experiment

2.1. Materials

Polypropylene glycol (PPG, $M_n = 2000$, Nanjing, China) and

polyethylene glycol (PEG, $M_n = 1000$, Chengdu, China) was pre-treated firstly to remove the residual water before use. Dimethylol propionic acid (DMPA, Perstop Chemical Co. Ltd., China) was placed in vacuum oven at 50 °C for 48 h before use. Toluene diisocyanate (TDI, BASF) was used as received. Acetone, ethylene glycol (EG), 1,4-butanediol (BDO) and diethylene glycol (DG) were purchased from Chengdu Kelong Co. Ltd. Trimethylamine (TEA) was purchased from Sigma with 4 Å molecular sieves inside before use in synthesis of WPU emulsions.

2.2. Synthesis of WPU emulsions

Here, monomers such as TDI and PPG were obtained from industry for our research. The whole process (scheme 1) was divided to five steps continuously: a) selection of chain extenders, b) optimization of prepolymer, c) optimization of hard segment content, d) construction of hydrophilic chains and e) thermal annealing on membrane-forming. Briefly, step a): mixture of 5.7 g TDI (32.75 mmol), 17.1 g PPG (8.55 mmol) and 0.92 g DMPA (6.81 mmol) was placed in three-neck flask to stir homogeneously and then heated at 85 °C for 3 h with

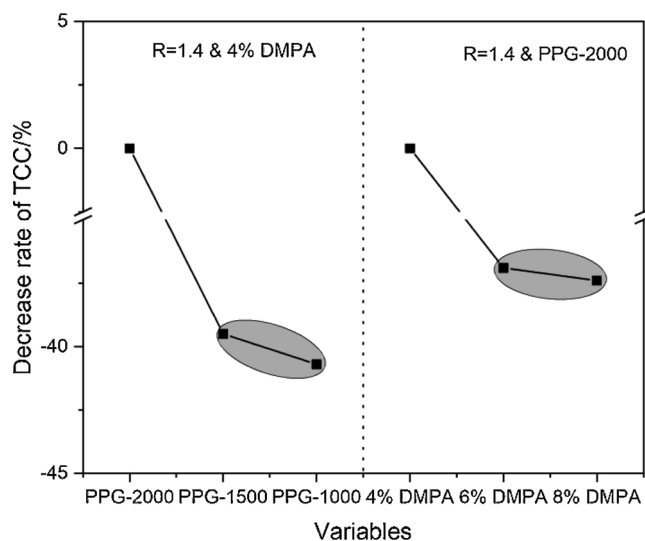


Fig. 2. Changes of TCC of WPU membranes with varying molecular weight of PPG and DMPA dosage.

connection of water condenser and nitrogen bag, afterwards prepolymer was obtained and divided to three portions for further reaction with three chain extenders (150 μ L EG, 240 μ L BDO and 255 μ L DG) at 73 $^{\circ}$ C for another 2 h. Then, the mixture in flask was cooled down to room temperature and neutralization step using TEA was conducted for 10 min, afterwards DI water was added in flask with 30 min vigorous stirring and finally WPU emulsions with 30 % solid content were obtained.

Next, step b): optimization orthogonal arrays (Table 1) were adopted to study the impact order of monomers on heat conduction and further get the optimized prepolymer formula. Here, the specific weight of reactants in this series was not given because of too much data to list. Stoichiometric amount of TDI, PPG and DMPA was heated in flask at 85 $^{\circ}$ C for 3 h, with connection of water condenser and nitrogen bag. Then, reaction temperature was decreased to 73 $^{\circ}$ C and stoichiometric amount of EG was added in mixtures to keep another 2 h. Afterwards, neutralization step and phase-inversion emulsification were carried out as step a) did.

Further, step c): this part is further analyzing the impact of hard segment content on heat conduction. Here, the specific weight of reactants can be seen in supporting file (Table S2). Obviously, the procedure to synthesize corresponding WPU emulsion with different hard segment content can also be referred to step b).

Next, step d): this part is studying the impact of hydrophilic fragments (DMPA/PEG) on heat conduction, since hydrophilic fragment is important for synthesis of WPU emulsion. The specific weight of reactants can also be seen in supporting file (Table S3) as well. Here, it is noticed that PEG is not acted as soft segment, while it works as hydrophilic chain extender to partly replace DMPA. The protocol to synthesize this series experiment was given below. Stoichiometric amount of TDI, PPG and DMPA was heated in flask at 85 $^{\circ}$ C for 3 h, with connection of water condenser and nitrogen bag. Then, stoichiometric amount of PEG was added for another 2 h reaction, followed with reduce the reaction temperature to 73 $^{\circ}$ C and stoichiometric amount of EG was added in mixtures to keep another 2 h. Afterwards, neutralization step and phase-inversion emulsification were carried out as step a) did.

Finally, step e): thermal annealing treatment on membrane-forming process. WPU emulsion was casted in petri-dish at room temperature for 4 days, then placed in oven with different annealing temperature of 150 $^{\circ}$ C, 120 $^{\circ}$ C, 100 $^{\circ}$ C, 80 $^{\circ}$ C and 60 $^{\circ}$ C to keep 5 h, after that the temperature gradually decreased to room temperature and membranes were collected for analysis.

2.3. Methodology to prepare membrane

Aforementioned WPU emulsions were poured in PTFE petri-dish and dried at room temperature for 4 days. Next, WPU membranes were placed in vacuum oven overnight at 80 $^{\circ}$ C to fully remove residue water, and then collected for analytic characterizations.

2.4. Characterization

Differential scanning calorimetry (DSC) was carried out with a DSC 200PC (NETZSCH, Germany) at a heating rate of 5 $^{\circ}$ C/min from -100 $^{\circ}$ C to 100 $^{\circ}$ C under nitrogen, and heat history was erased firstly. Morphologies of the WPU membranes were observed using tapping-mode atomic force microscope (AFM SPM-9600, SHIMADZU, Japan). TCC of the WPU membranes was measured at least five times by using thermal conductivity coefficient instrument (DRP-II), and the average was reported. X-ray diffraction (XRD) was carried out in X'Pert Pro MPD DY129 X-ray diffractometer (Netherlands) equipped with CuK_{α} radiation ($\lambda = 1.54178 \text{ \AA}$) as the X-ray source, among membranes were tested with a scanning rate of 4 $^{\circ}$ /min from 5 $^{\circ}$ to 50 $^{\circ}$.

2.5. Heat conduction mechanism

As reported, phonon, electron and photon are three types of heat carriers in solid materials [23]. However, only phonon that plays an important role on heat conduction in polymer materials. As molecules in a high temperature region move to a low temperature region, the average kinetic energy is transferred to other molecules through collisions, and this kind of energy transmission is macroscopically called heat conduction k [24]. Accordingly, the k can be given in Eq. (1) [25]:

$$k = \frac{1}{3} C_v \gamma \bar{v} \quad (1)$$

Where C_v is heat capacity in per unit volume, γ is mean free pathway, \bar{v} is average rate of heat flowing.

Due to the existence of phonons collisions, it keeps a heat energy equilibrium from a high to a low temperature region. As a result, heat energy is transferred through the pathway that formed after collisions in different defects and crystal boundaries [12,26], which is shown in Fig. 1a. In addition to this, the Normal Process (N process) and Umklapp Process (U process, Flip Process) are the two main processes during phonon collisions [27]. Generally, the N process contributes to the phonon momentum distribution and gradually leads to a heat equilibrium, while U process acts as barrier to prolong heat transfer time, to some extent, and can even be as thermal resistance during phonon propagation.

3. Results and discussion

3.1. Optimization orthogonal arrays

It is known that chain extender is important to increase the molecular weight of WPU materials, and further shows significant effects on physico-chemical properties as well [28]. Here, three alcohol chain extenders (EG, BDO, EG) were used for WPU emulsions preparation via the reaction with same prepolymer resin. As a result, EG was specified as chain extender for latter experiments, because of the higher TCC value than other two WPU membranes (Table S1). Next, a study of prepolymer formula on structure features and heat conduction performance was investigated. EG was chain extender to synthesize final WPU emulsion for membrane preparation. Here, a useful method, orthogonal experiments, used to optimize the synthetic crafts was shown in Table 1.

Orthogonal experimental design is an efficient way to qualitatively analyze the correlations between the relevant variables with different levels through statistic analysis, which make it fast to get the optimized

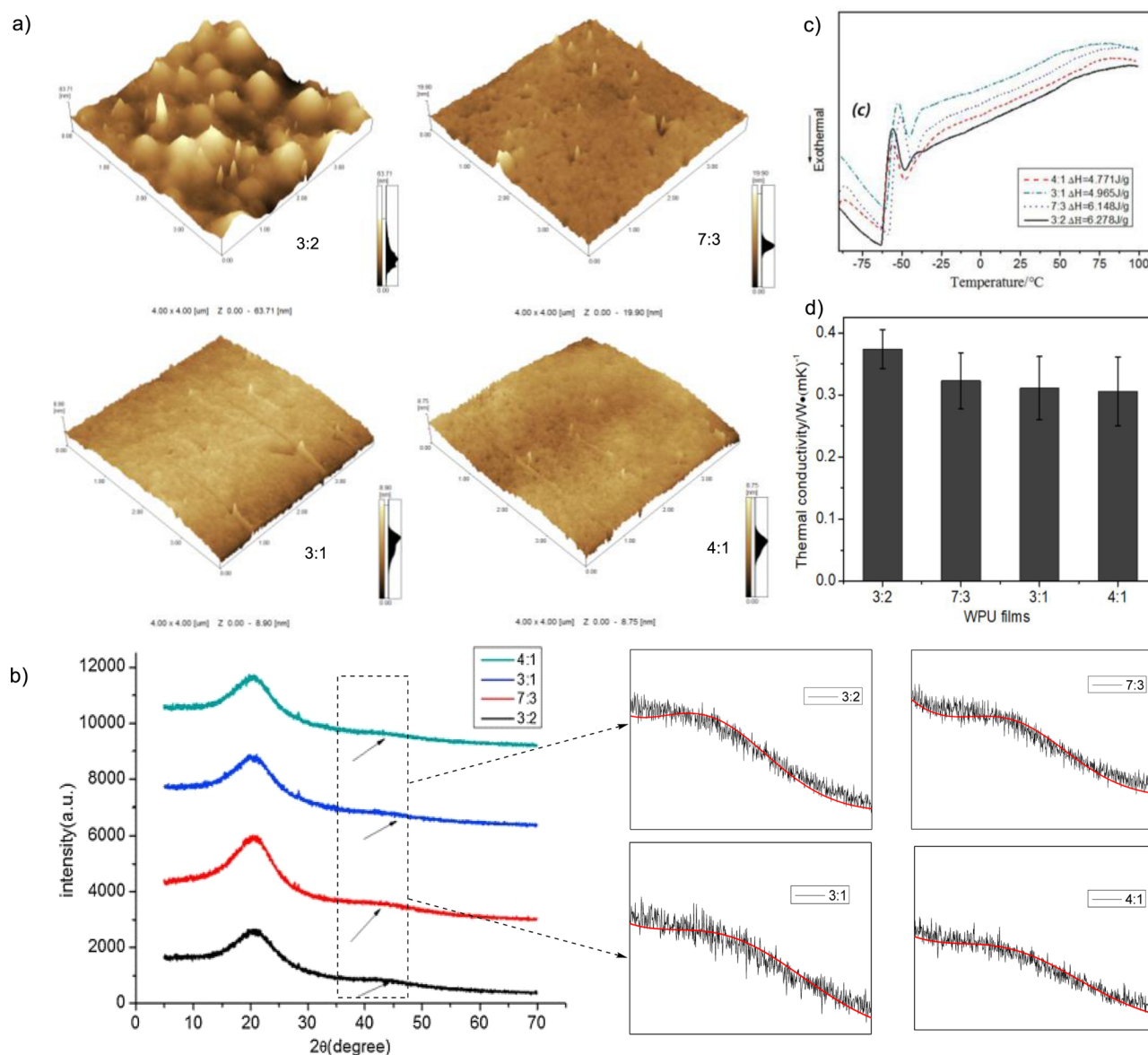


Fig. 3. AFM observation, DSC, XRD and TCC measurement of WPU membranes. a) 3D morphology of WPU membranes with ratio of soft segment to hard segment of 3:2, 7:3, 3:1 and 4:1 respectively, among the membrane with 40 % of hard segment content showed a significant distribution of hard segment and soft segment. And phase separation degree decreased with the decreasing of hard segment content; b) XRD analysis showed two diffraction peaks at 2θ of 20° and 45° respectively in XRD spectra, and the amplification of 2θ of 45° and corresponding calculation of crystal size of lattice showed a higher value in WPU membrane (0.146 \AA) with 40 % of hard segment content, while the crystalline sizes of 30 %, 25 % and 20 % of hard segment content are 0.074 \AA , 0.065 \AA and 0.064 \AA respectively; c) DSC analysis showed a higher enthalpy in WPU membrane with 40 % of hard segment content during the whole heating process, and enthalpy was decreased with decreasing of hard segment content; d) TCC measurement of WPU membranes²¹. Copyright 2019. Adapted with permission from Elsevier Science Ltd.

parameters with high confidence interval through statistic principle. Here, $K_{1(R)} = (k_1 + k_2 + k_3)/3$, $K_{1(PPG)} = (k_1 + k_4 + k_7)/3$, $K_{1(DMPA)} = (k_1 + k_5 + k_9)/3$, $K_{2(R)} = (k_4 + k_5 + k_6)/3$, $K_{2(PPG)} = (k_2 + k_5 + k_8)/3$, $K_{2(DMPA)} = (k_2 + k_4 + k_9)/3$, $K_{3(R)} = (k_7 + k_8 + k_9)/3$, $K_{3(PPG)} = (k_3 + k_6 + k_9)/3$ and $K_{3(DMPA)} = (k_3 + k_5 + k_7)/3$. Range value r is difference between the maximal and minimal value of K_n ($n = 1, 2, 3$). Clearly, the order of influences on TCC is PPG > DMPA > R by referring to r value in Table 1, and number 8 (Table 1) with the combination of 'R = 1.4, PPG-2000 and 4% DMPA' showed higher TCC than other combinations. So, further analysis based on the fixed R value with varying molecular weight of PPG and DMPA dosage was conducted (see Fig. 2). The results showed that the TCC decreases a lot as the molecular weight of PPG decrease from 2000 g/mol to 1000 g/mol, in comparison to the DMPA dosage increases from 4% to 8%. It means that the molecular weight of PPG played an important role on heat conduction

while in comparison to DMPA dosage, which was consistent with the result of Table 1. Summarily, short PPG chains with low molecular weight were less inclined to give phase separation than long chains, and as a result, phase separation could contribute to forming ordered sequences (long-range, short-range and microcrystalline ordering) and correspondingly accelerates the phonon propagation in polymer matrix [13]. Besides, the amount of DMPA also had impact on microphase separation behavior. The higher amount of DMPA the less possibility of ordered sequences forming in hard segment domains, which is owing to the interferences from methyl group of DMPA on hydrogen bonding behavior in hard segment domains.

3.2. Hard segment content and TCC of WPU

Aforementioned study found that the existence of ordered sequences

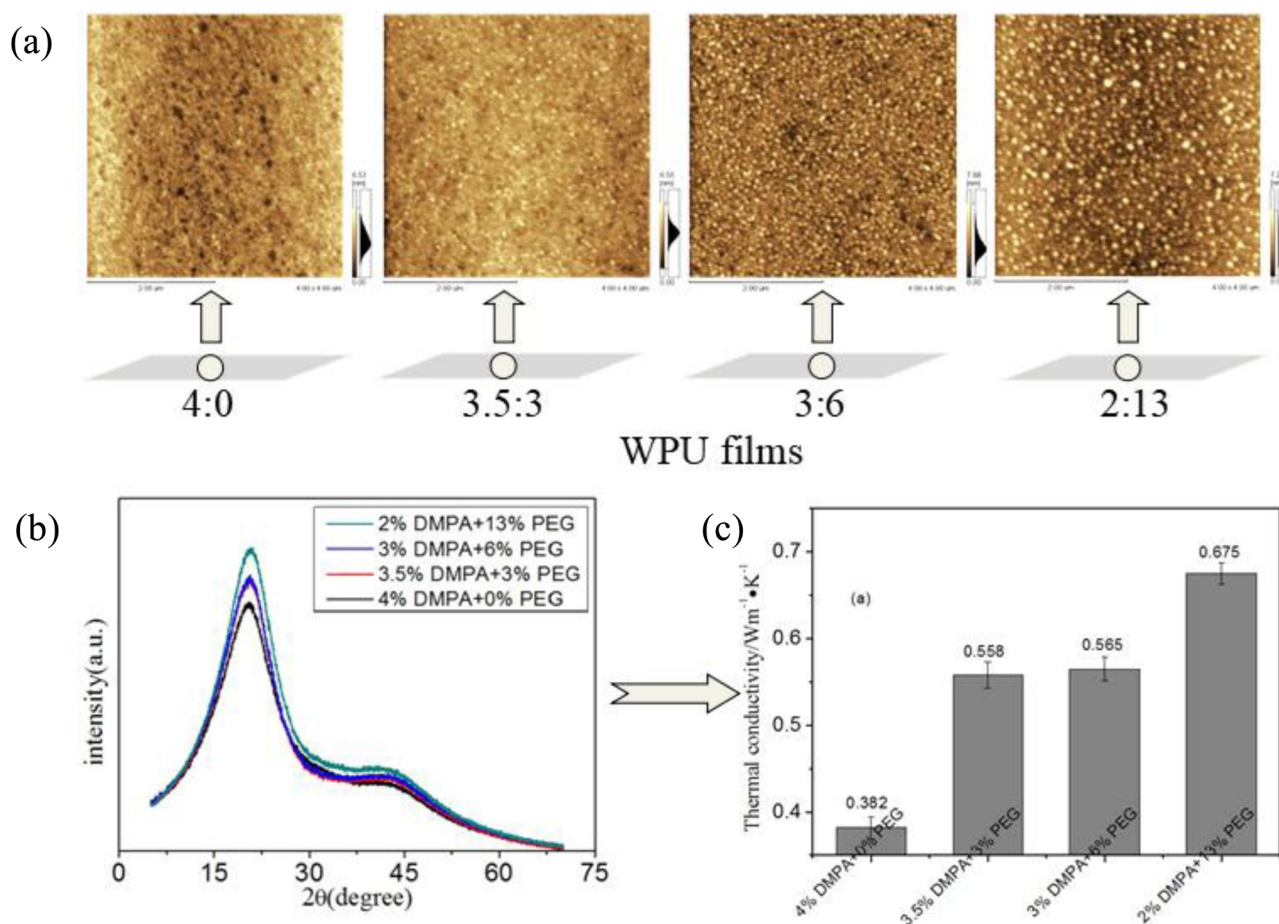


Fig. 4. Height diagram, XRD and TCC measurement of WPU membranes. (a) Phase separation situation was observed by using AFM. Clearly, the phase separation degree was increased with the increasing of PEG content, especially the WPU membrane with a combination of 13 % PEG and 2 % DMPA presented a significant distribution of bright area and gray area in height diagram; (b) XRD analysis was used to compare the crystallinity of WPU membranes. The WPU membrane with a combination of 13 % PEG and 2 % DMPA showed a higher crystallinity than other combinations of membranes. (c) TCC measurement of WPU membranes by using steady-state method. Obviously, the TCC was increased with the increasing of PEG proportion in studied WPU membranes²⁰. Copyright 2018. Adapted with permission from Elsevier Science Ltd.

(short-range, long-range and microcrystalline ordering) is critical to enhance the TCC of WPU materials, and that is directly depending on the interaction forces between hard segment and soft segment. It is well known that phase separation appears in WPU due to the thermodynamic incompatibilities of hard segment and soft segment [29,30]. Meaningfully, AFM observation can be intuitively shown the situations of two phases, because hard segment has strong cohesion which appears as a bright area in the AFM image, while soft segment appears as a gray area in AFM image. Therefore, it is interesting to study how the ratio of hard segment to soft segment affect on polymer micro-morphology and TCC. Based on the fixed parameters of $R = 1.4$, PPG-2000 and 4% DMPA, the experiments with different hard segment contents (40 %, 30 %, 25 % and 20 %) were carried out. These WPU membranes (see recipe in Table S2) were characterized to investigate the structural features and TCC performances.

Fig. 3a showed that the WPU membrane with 40 % of hard segment content presented a significant distribution of hard segment and soft segment in 3D morphology respectively, along with hard segment content decreases the mixing degree of two phases was increased conversely. Simultaneously, the TCC (Fig. 3d) of WPU membranes were measured as well, which showed a similar trend as phase separation behavior. That is, heat conductive capacity was decreased as hard segment content decreased. This is because phase separation could contribute to forming ordered sequences in two phases, due to the self-aggregation of hard segment chains and soft segment chains through

hydrogen bonding behavior. In order to confirm this, more details of DSC and XRD measurements were performed. The DSC spectra showed, as expected, a higher crystal melting enthalpy and a lower glass transition temperature (T_g) for the WPU membrane with a hard segment content of 40 %, while the enthalpy decreases and T_g increases as hard segment content decreases. Also, the measurement of XRD on WPU membrane with 40 % of hard segment content showed a higher diffraction peak at 2θ of 45° than the other WPU membranes. Moreover, the crystal size of lattice (0.146 \AA) calculated by Scherrer equation (supporting file) is also higher than other samples, indicating a relative high density of ordered sequences in WPU membrane with 40 % of hard segment content. In summary, the high content of hard segment fragments in WPU could contribute to increasing the hydrogen bonding degree in hard segment domains, because of the existence of more polar urea and urethane groups. Further, this behavior hinders two phases mixing and provides more driving forces to form orderly stacked structures [31], as a result, reducing the phonon scattering and improving the TCC accordingly [13]. However, the more higher hard segment content (e.g. 50 %) in WPU emulsion we prepared didn't show us a nice comprehensive properties, as the membrane is very fragile and can't be able to use in practical application.

3.3. Hydrophilic fragments: PEG and DMPA

DMPA is commonly used to prepare WPU in industry, and the

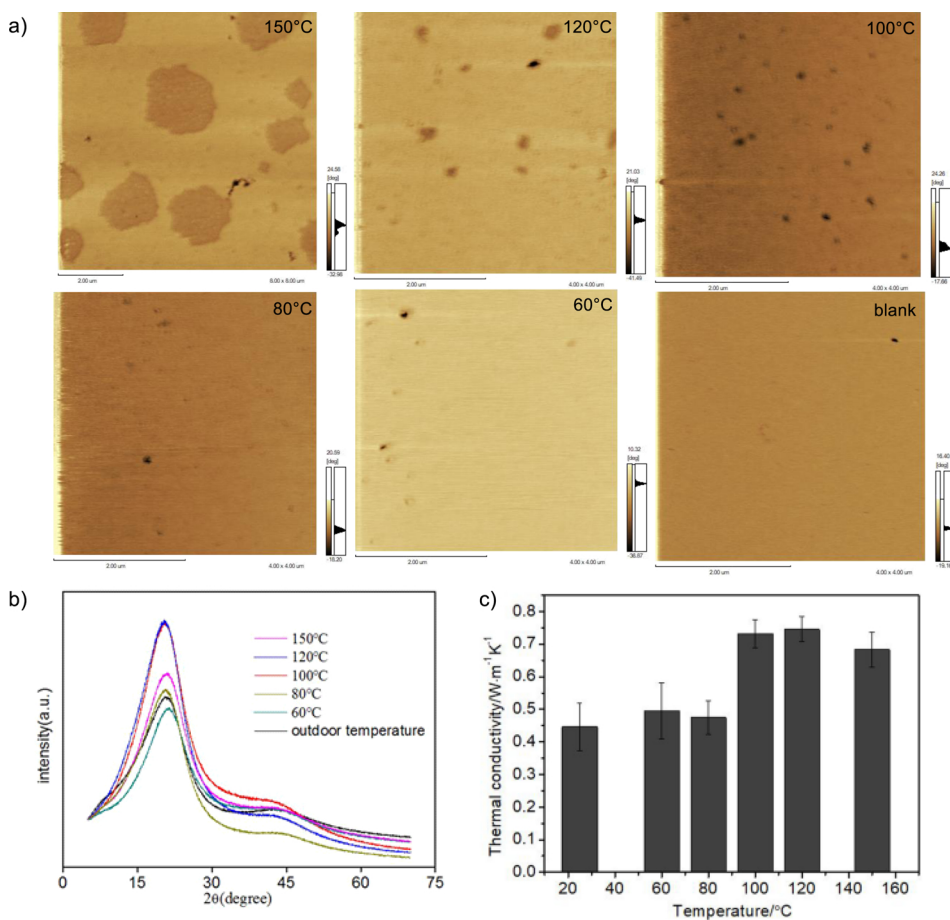


Fig. 5. Phase diagram, XRD analysis and TCC measurements of WPU membranes with different thermal annealing temperature treatment. a) AFM-phase diagram showed the situation of two phases in studied WPU membrane. As annealing temperature above 100 °C the hard segment fragments were aggregated as gray area in phase diagram, and phase separation behavior was present due to the rearrangement of polymer chains; b) XRD analysis was used to characterize the crystallization behavior of membranes. Clearly, as annealing temperature above 100 °C the WPU membrane showed higher diffraction intensity than other membranes; c) TCC was measured by using steady-state method. As expected, TCC was increased as annealing temperature above 100 °C.

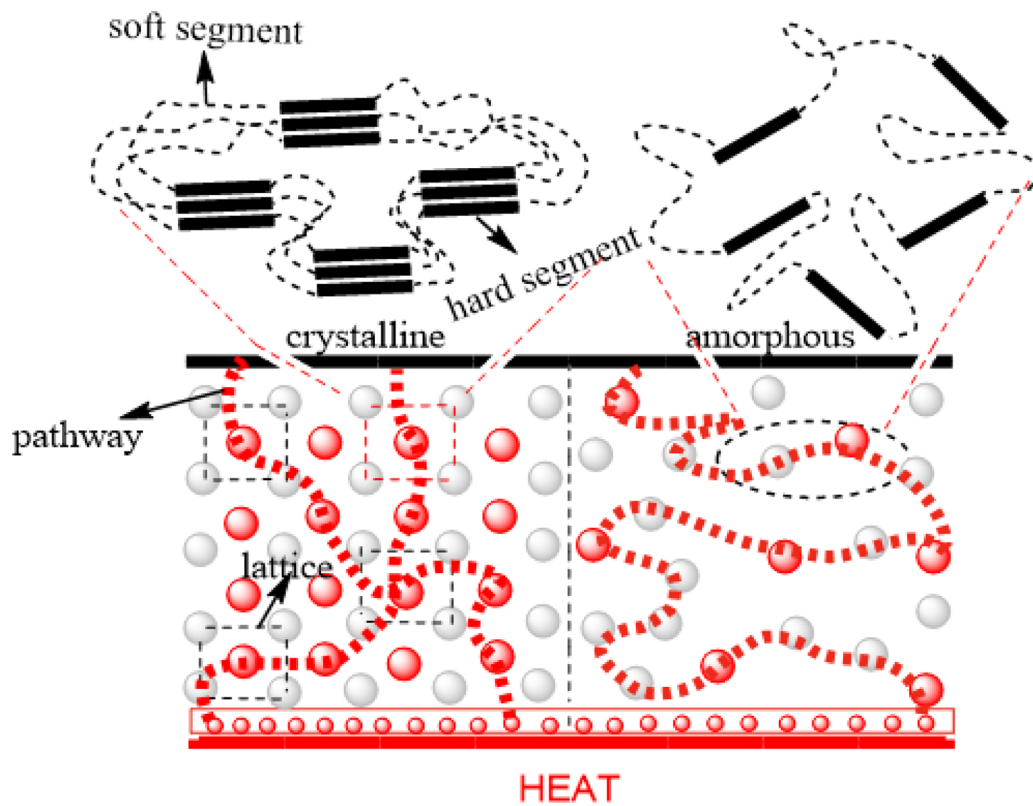


Fig. 6. Heat flowing in amorphous and crystalline polymer.

higher amount of DMPA the more stable of WPU emulsion will be. However, a high amount of DMPA in WPU would decrease the heat conductive capacity as the interferences of methyl group on forming ordered sequences in hard segment domain. Therefore, to control the minimal amount of DMPA dosage in synthesized WPU, one ordered hydrophilic fragment, PEG, was investigated as an alternative strategy to reduce DMPA amount in synthesis. So, the experiments with a fixed hard segment content of 40 % and the varying mass ratios of DMPA to PEG of 4:0, 3.5:3, 3:6 and 2:13 were prepared. Here, the emulsion wasn't stable by only using PEG as hydrophilic chain extender without DMPA. Next, aforementioned WPU emulsions were casted to WPU membranes for characterizations.

Fig. 4a depicts the AFM-height diagram of WPU membranes with varying combinations of DMPA and PEG. It is shown that the distribution of hard segment and soft segment depends on the PEG content. The density and size of bright domains increased significantly with the increasing of PEG content, indicating an increased phase separation degree as the PEG content increased. Certainly, it is also related to the decreases of DMPA dosage and further reduces the interferences on forming ordered sequences in hard segment domains. All in all, it is a comprehensive result with combine DMPA and PEG to increase phase separation and further form more ordered structures in WPU. In addition to this, XRD analysis was performed as well. The diffraction peak intensity of WPU membrane with 13 % PEG and 2 % DMPA at 2θ of 20° and 45° was all higher than the other combinations, indicating a higher crystallization degree than others as due to the existence of more ordered structures in membrane. Naturally, as expected, the TCC of corresponding WPU membrane with combined 13 % PEG and 2 % DMPA is increased a lot as compared to the WPU membrane with only DMPA. As a summary, the comprehensive performances of combined DMPA and PEG in WPU present an alternative strategy to enhance TCC by increasing phase separation and further forming more ordered structures. As expected, more orderly stacked structures are formed in hard segment and soft segment domains respectively, which accelerates the phonon propagation in WPU and further enhances heat transfer performances correspondingly.

3.4. Thermal annealing on membrane-forming process

Thermal annealing treatment has a significant effect on phase separation, as heat-induced movements of polymer chains will be occurred and further alter polymer morphologies accordingly [32–34]. Therefore, It is interesting to study the effect of thermal annealing on structural features and TCC of studied WPU membrane. Also, only through physical adjustments to control polymer morphology and further achieve expected aim makes it more simple. The membrane-forming at room temperature (RT) without thermal treatment was used as a control, and thermal annealing temperature of 60°C , 80°C , 100°C , 120°C and 150°C was conducted for 5 h respectively. Next, samples were gradually cooled down to RT and then collected for analysis.

It was noticed that thermal annealing indeed has produced impacts on WPU membrane's morphologies, as heat driving force on occurring rearrangement of polymer chains was conducted. Especially, as annealing temperature above 100°C the movements of polymer chains were accelerated to rearrange and present an equilibrium status with lowest free energy, that is, hard segment fragments and soft segment fragments were self-aggregated with minimal interactions, and as a result, phase separation and ordered sequences were present naturally [35–37]. Thus, phonon propagation was facilitated in solid membrane and TCC was improved accordingly (Fig. 5c). Also, to further prove this behavior AFM observation (Fig. 5a) on phase separation and XRD analysis (Fig. 5b) on crystallization were all pointed to this as well. However, a relative high annealing temperature (e.g. 150°C) showed the decreases of crystalline degree and TCC in WPU membrane as compared to annealing temperature of 100°C and 120°C , and it might be caused by the too fast movements of polymer chains made it hard to

form crystal nucleation, and the growth is limited as a consequence. Certainly, the low annealing temperature generated annealing energy was probably too low to cause a rearrangement of polymer chains, and thus TCC only showed slight changes.

As a summary, heat conductive capacity is directly enhanced by increasing phase separation behavior in WPU, as due to long-range short-range and microcrystalline ordering were formed and further acted as free pathway to accelerate phonon propagation in polymer. Hence, the possible schematic graph is shown in Fig. 6.

4. Conclusion

Series of experiments were performed to study the structural features and corresponding heat conduction performance of waterborne polyurethane (WPU). In this study, the results showed that the interactions between hard segment and soft segment were played an important role on heat conduction. That is to say, as phase separation took place in two phases the ordered sequences (long-range, short-range and microcrystalline ordering) were formed due to intermolecular force (e.g. hydrogen bond) induced rearrangement of polymer chains, and further acted as free pathway for phonon propagation. And as a result, heat conduction was improved accordingly. On the contrary, more interaction forces caused two phases mixing well and that could hinder phonon propagation and decrease heat conductivity capacity as disordered sequences in two phase may produce thermal resistance. All in all, it is an alternative strategy to enhance heat conduction performance of WPU materials through structure-property aspects, and not needed to fabricate complicated composites, which may also provide a possibility for polymer to expand their application in thermal engineering.

CRediT authorship contribution statement

Rui Li: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **Zhihua Shan:** Supervision.

Declaration of Competing Interest

The authors declare no conflict of interest.

Acknowledgements

This work was supported by Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (201410110) and Chinese Scholarship Council (201706240045), and thanks Professor J. A. Ton Loontjens for some contributions on this manuscript.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.colsurfa.2020.124879>.

References

- [1] X. Duan, G.F. Naterer, Heat transfer in phase change materials for thermal management of electric vehicle battery modules, *Int. J. Heat Mass Tran.* 53 (2010) 5176–5182.
- [2] N. Javani, I. Dincer, G. Naterer, B. Yilbas, Heat transfer and thermal management with PCMs in a Li-ion battery cell for electric vehicles, *Int. J. Heat Mass Tran.* 72 (2014) 690–703.
- [3] Z. Rao, S. Wang, M. Wu, Z. Lin, F. Li, Experimental investigation on thermal management of electric vehicle battery with heat pipe, *Energ. Convers. Manage.* 65 (2013) 92–97.
- [4] A. De Vita, A. Maheshwari, M. Destro, M. Santarelli, M. Carello, Transient thermal analysis of a lithium-ion battery pack comparing different cooling solutions for automotive applications, *Appl. Energ.* 206 (2017) 101–112.
- [5] K.O. Lee, M.A. Medina, E. Raith, X. Sun, Assessing the integration of a thin phase change material (PCM) layer in a residential building wall for heat transfer reduction and management, *Appl. Energ.* 137 (2015) 699–706.

- [6] X. Chen, Y. Su, D. Reay, S. Riffat, Recent research developments in polymer heat exchangers—A review, *Renew. Sust. Energ. Rev.* 60 (2016) 1367–1386.
- [7] Q. Li, L. Chen, M.R. Gadinski, S. Zhang, G. Zhang, H.U. Li, E. Iagodkine, A. Haque, L.Q. Chen, T.N. Jackson, Flexible high-temperature dielectric materials from polymer nanocomposites, *Nature* 523 (2015) 576–579.
- [8] K.S. Yang, T.Y. Yang, C.W. Tu, C.T. Yeh, M.T. Lee, A novel flat polymer heat pipe with thermal via for cooling electronic devices, *Energ. Convers. Manage.* 100 (2015) 37–44.
- [9] N. James, K. Pielichowski, Polymer nanocomposites for aerospace applications: properties, *Adv. Eng. Mater.* 11 (2003) 769–778.
- [10] R. Prasher, J.Y. Chang, I. Sauciu, S. Narsimhan, D. Chau, G. Chrysler, A. Myers, S. Prstic, C. Hu, Nano and Micro Technology-Based Next-Generation Package-Level Cooling Solutions, *Intel. Technol. J.* 9 (2005) 285–296.
- [11] J.F. Feller, P. Chauvelon, I. Linossier, P. Glouanec, Characterization of electrical and thermal properties of extruded tapes of thermoplastic conductive polymer composites (CPC), *Polym. Test.* 22 (2003) 831–837.
- [12] N. Burger, A. Laachachi, M. Ferriol, M. Lutz, V. Toniazio, D. Ruch, Review of thermal conductivity in composites: mechanisms, parameters and theory, *Prog. Polym. Sci.* 61 (2016) 1–28.
- [13] R. Li, Z. Shan, Research on structural features and thermal conductivity of waterborne polyurethane, *Prog. Org. Coat.* 104 (2017) 271–279.
- [14] D. Cai, M. Song, Latex technology as a simple route to improve the thermal conductivity of a carbon nanotube/polymer composite, *Carbon* 15 (2008) 2107–2112.
- [15] C. Bernard, D.G. Goodwin Jr, X. Gu, M. Celina, M. Nyden, D. Jacobs, L. Sung, T. Nguyen, Graphene oxide/waterborne polyurethane nanocoatings: effects of graphene oxide content on performance properties, *J. Coat. Technol. Res.* 17 (2020) 255–269.
- [16] R. Li, Z.H. Shan, Research for waterborne polyurethane/composites with heat transfer performance: a review, *Polym. Bull.* 75 (2018) 4823–4836.
- [17] H. Zhou, S. Zhang, M. Yang, The effect of heat-transfer passages on the effective thermal conductivity of high filler loading composite materials, *Compos. Sci. Technol.* 67 (2007) 1035–1040.
- [18] G.W. Lee, M. Park, J. Kim, J.I. Lee, H.G. Yoon, Enhanced thermal conductivity of polymer composites filled with hybrid filler, *Compos. Part A-Appl. s* 37 (2006) 727–734.
- [19] J.F. Zou, Z.Z. Yu, Y.X. Pan, X.P. Fang, Y.C. Ou, Conductive mechanism of polymer/graphite conducting composites with low percolation threshold, *J. Polym. Sci.: Polym. Phys. Ed.* 40 (2002) 954–963.
- [20] R. Li, Z.H. Shan, Enhancement of thermal conductivity of PEG-PPG-based waterborne polyurethane coating by incorporating ordered polyethylene glycol fragment, *Polym. Test.* 69 (2018) 125–132.
- [21] R. Li, J.A.T. Loontjens, Z.H. Shan, The varying mass ratios of soft and hard segments in waterborne polyurethane films: performances of thermal conductivity and adhesive properties, *Eur. Polym. J.* 112 (2019) 423–432.
- [22] R. Li, Z.H. Shan, Asynchronous synthesis method of waterborne polyurethane with the differences of structural features and thermal conductivity, *J. Polym. Res.* 25 (2018) 197–208.
- [23] J.C. Klöckner, R. Siebler, J.C. Cuevas, F. Pauly, Thermal conductance and thermoelectric figure of merit of C 60-based single-molecule junctions: electrons, phonons, and photons, *Phys. Rev. B* 95 (2017) 245404–245415.
- [24] J.H. Lee, S.H. Lee, C. Choi, S. Jang, S. Choi, A review of thermal conductivity data, mechanisms and models for nanofluids, *Int. J. Micro-Nano Scale Trans.* 4 (2011) 269–321.
- [25] C. Toher, J.J. Plata, O. Levy, M. de Jong, M. Asta, M.B. Nardelli, S. Curtarolo, High-throughput computational screening of thermal conductivity, Debye temperature, and Grüneisen parameter using a quasiharmonic Debye model, *Phys. Rev. B* 90 (2014) 174107–174121.
- [26] G. Fugallo, A. Cepellotti, L. Paulatto, M. Lazzeri, N. Marzari, F. Mauri, Thermal conductivity of graphene and graphite: collective excitations and mean free paths, *Nano Lett.* 14 (2014) 6109–6114.
- [27] H.E. Jackson, C.T. Walker, Thermal conductivity, second sound, and phonon-phonon interactions in NaF, *Phys. Rev. B* 3 (1971) 1428–1439.
- [28] A. Strachan, B.L. Holian, Energy exchange between mesoparticles and their internal degrees of freedom, *Phys. Rev. Lett.* 94 (2005) 014301–014305.
- [29] B.K. Kim, J.C. Lee, Waterborne polyurethanes and their properties, *J. Polym. Sci.: Polym. Chem. Ed.* 34 (1996) 1095–1104.
- [30] M. Fuensanta, J.A. Jofre-Reche, F. Rodríguez-Llansola, V. Costa, J.I. Iglesias, J.M. Martín-Martínez, Structural characterization of polyurethane ureas and waterborne polyurethane urea dispersions made with mixtures of polyester polyol and polycarbonate diol, *Prog. Org. Coat.* 112 (2017) 141–152.
- [31] S.Y. Lee, J.S. Lee, B.K. Kim, Preparation and properties of water-borne polyurethanes, *Polym. Int.* 42 (1997) 67–76.
- [32] B. Kim, Aqueous polyurethane dispersions, *Colloid Polym. Sci.* 274 (1996) 599–611.
- [33] J. Garrett, J. Lin, J. Runt, Influence of preparation conditions on microdomain formation in poly (urethane urea) block copolymers, *Macromolecules* 35 (2002) 161–168.
- [34] V.P. Saraf, W.G. Glasser, G.L. Wilkes, J.E. McGrath, Engineering plastics from lignin. VI. Structure–property relationships of PEG-containing polyurethane networks, *J. Appl. Polym. Sci.* 30 (1985) 2207–2224.
- [35] R.W. Seymour, S.L. Cooper, Thermal analysis of polyurethane block polymers, *Macromolecules* 6 (1973) 48–53.
- [36] Y. Li, T. Gao, J. Liu, K. Linliu, C.R. Desper, B. Chu, Multiphase structure of a segmented polyurethane: effects of temperature and annealing, *Macromolecules* 25 (1992) 7365–7372.
- [37] D.J. Martin, G.F. Meijs, P.A. Gunatillake, S.J. McCarthy, G.M. Renwick, The effect of average soft segment length on morphology and properties of a series of polyurethane elastomers. II. SAXS-DSC annealing study, *J. Appl. Polym. Sci.* 64 (1997) 803–817.