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## ARTICLE

## Influence of treating parameters on thermomechanical properties of recycled epoxy-acid vitrimers

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Vitrimers have the characteristics of shape reforming and surface welding, and have the same excellent mechanical properties as thermosets, so vitrimers hold the promise of a broad alternative to traditional plastics. Since its initial introduction in 2011, vitrimers have produced many unique applications such as reworkable composites and liquid crystal elastomer actuators. A series of experiments have investigated the effects of reprocessing conditions (such as temperature, time, and pressure) on recycled materials. However, the effect of particle size on the mechanical properties of recycled materials has not been reported. In this paper, we conducted an experimental study on the recovery of epoxy-acid vitrimers of different particle sizes. The epoxy-acid vitrimers powders with different particle size distributions were prepared and characterized. The effects of particle size on the mechanical properties of regenerated epoxy-acid vitrimers were investigated by dynamic mechanical analysis and uniaxial tensile tests. In addition, other processing parameters such as temperature, time, and pressure are discussed, as well as their interaction with particle size. This study helped to refine the vitrimers reprocessing condition parameter toolbox, providing experimental support for the easy and reliable control of the kinetics of the bond exchange reaction.

### 1. Introduction

Vitrimers are covalently cross-linked polymer networks whose linkages undergo associative exchange reactions at an elevated temperature. Like conventional thermosets, vitrimers exhibit good dimensional stability, high mechanical properties, and excellent chemical resistance<sup>1, 2</sup>. At the same time, the network topology of vitrimers can be rearranged through associative bond exchange reactions at high temperatures, such that the crosslinking density and the network integrity are preserved. Therefore, thermoforming, reshaping, recycling, and repairing of covalently cross-linked polymers can be achieved<sup>3-9</sup>. The appearance of this kind of material provides a way to solve the shortcomings of thermosets that cannot be reshaped, reprocessed, or recycled due to their permanent molecular

architecture. In the past decade, more and more vitrimers have been developed based on different molecular mechanisms<sup>10-16</sup>, and also have been using in a myriad of areas, such as composite materials<sup>5, 17-25</sup>, 3D printing<sup>6, 13, 26</sup>, liquid-crystalline elastomer actuators<sup>27-29</sup>, soft robotics, and so on<sup>30, 31</sup>.

During reprocessing, the dynamic covalent network polymers rearrange their macromolecular chain networks by bond exchange reactions (BERs), in which the active unit replaces the unit in the existing bond to form a new bond<sup>2, 32</sup>. When these macromolecular events occur in large quantities, shape reforming and surface welding of the material can be achieved. So, during the reprocessing and recycling process, the chosen of suitable treating conditions, which can promote the dynamic reshuffling of the crosslinks in the networks, is important that can decide the thermomechanical properties of recycled materials, and thus further affect the following use of the recycled vitrimers in engineering applications. Therefore, it is necessary to study the mechanical properties of the recycled materials by studying processing conditions (such as catalyst, temperature, time, and pressure) and to save processing energies by optimizing the treating conditions.

At present, the effects of stoichiometry<sup>1, 11, 33, 34</sup>, pressure<sup>32</sup>, temperature, and time<sup>3, 32, 35</sup> on the mechanical properties of recycled materials have been thoroughly investigated. Yu et al. experimentally studied the reprocessing and recycling capabilities of an epoxy-acid vitrimers with crosslinking bonds in the powder state<sup>3</sup>. This study shows that increasing the temperature and time of treatment can improve the quality of recycled materials (such as ultimate elongation, ultimate tensile strength, glass modulus, and rubber modulus), and the

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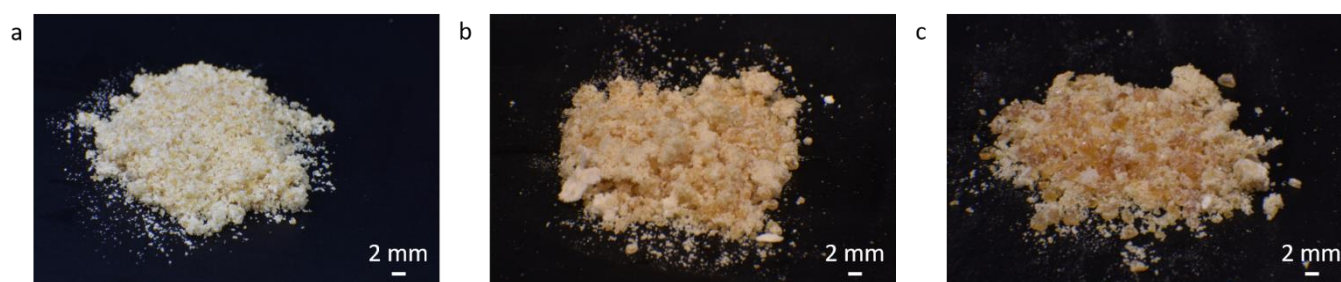


Figure 1. Powers of soft vitrimer. (a) Particle-S, (b) Particle-M, (c) Particle-L.

mechanical properties of the recycled material can reach a level close to the fresh material. To further describe the stress relaxation property of vitrimers caused by time and temperature-dependent bond-exchange reactions, Yu et al. developed a lattice model to study the surface welding of thermally induced dynamic covalent network polymers<sup>32</sup>. The dependence of the surface weld efficiency on the applied heat field is described by the model. Moreover, the study also pointed out that pressure will affect the actual contact area, and high pressure will promote the development of surface welding. In addition, Zhang et al. used composite-based strategy by simply mixing epoxy-anhydride vitrimers with epoxy-acid

vitrimers to prepare the vitrimer blends, of which the thermomechanical properties are tunable by varying the compositions and treating conditions<sup>33</sup>. Effects of processing temperature and time on the properties of recycled vitrimer blends were discussed. Besides, the particle size of vitrimers powder is also an important parameter that can affect the contacting surfaces of polymer particles in pulverous states, and thus decides the thermomechanical properties of recycled materials. Lu et al. grind a hard vitrimer with a ball mill for 8 to 32 hours<sup>36</sup>. They found that long grinding time results in finer particles and high healing efficiency. However, as one of the most important facts, there are few reports on the effect of

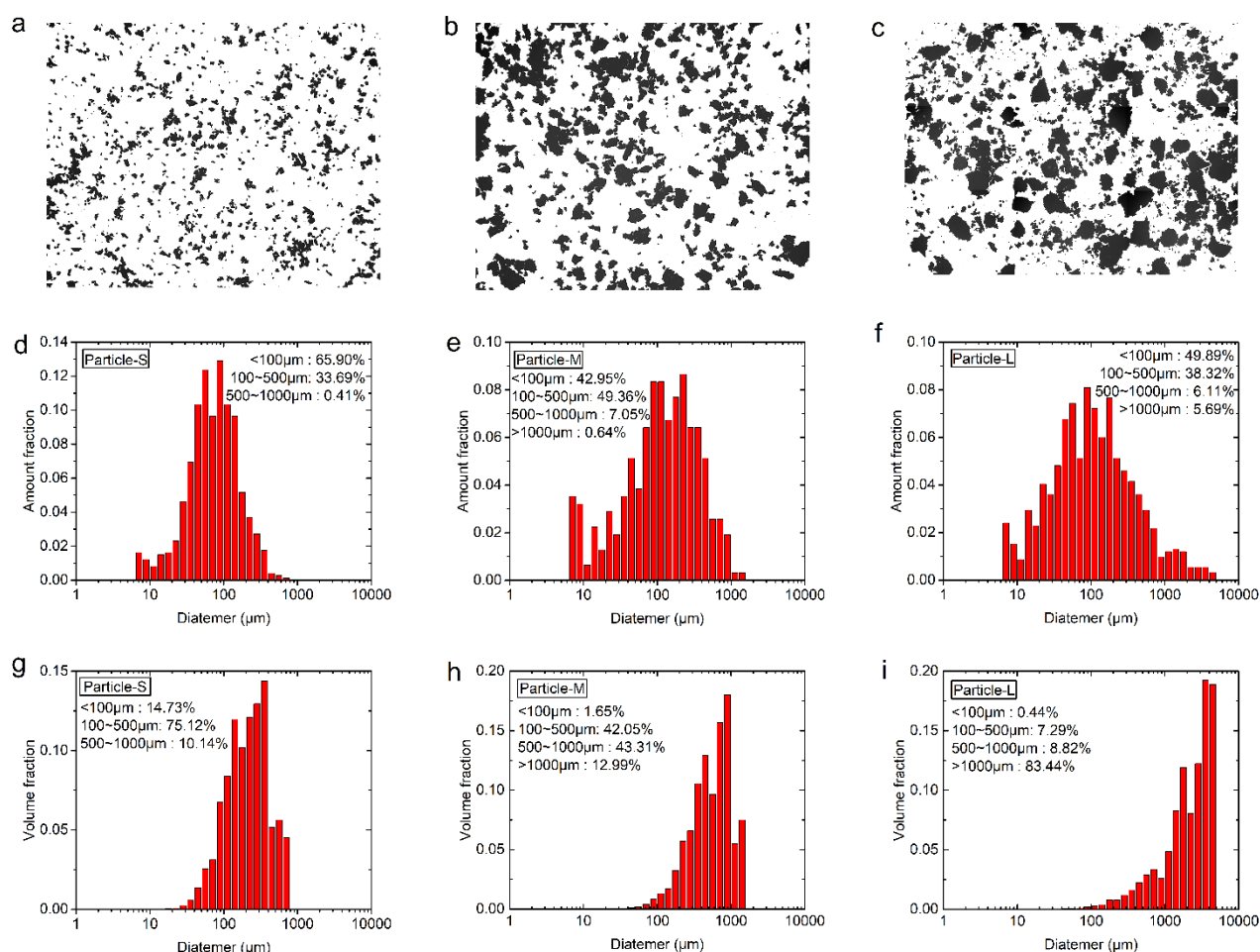


Figure 2. Polymer particles (a-c) and the corresponding distributions (d-i) from epoxy-acid vitrimers by using 0.5 mm, 1.0 mm and 2.0 mm trapezoidal perforation sieve rings, respectively.

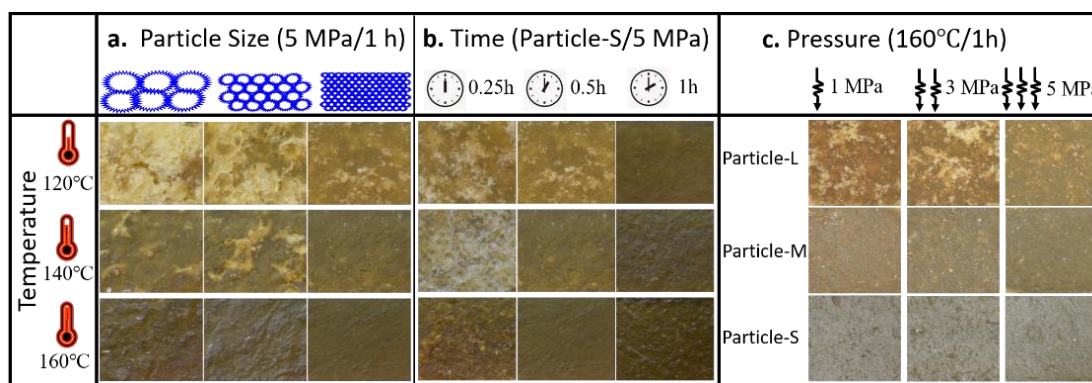


Figure 3. Photos of vitrimer samples recycled from different conditions and particle sizes. (a) Particle size and temperature effect, (b) Treating time effect, (c) Treating pressure effect. The samples in (c) and other samples are pressed from different molds, respectively.

particle size on the mechanical performance of recycled vitrimers.

In this work, we used transesterification-based epoxy-acid vitrimers to study the effect of particle sizes on the mechanical performance of recycled vitrimers. Three different vitrimer polymer particles with different size distributions were prepared and characterized. The effect of particle sizes on thermomechanical properties of recycled materials has been experimentally studied by dynamic mechanical analysis (DMA) and uniaxial tensile tests. Besides, the treating temperature, treating time, and pressing pressure have also been considered to improve the recycling quality

## 2. Materials and Characterizations

### 2.1 Material Synthesis

The epoxy-acid vitrimers were synthesized following the previously reported method<sup>1</sup>. All the chemical products are commercially available. Pripol 1040 is a mixture of C18 fatty acids derivatives, containing about 23 wt% dimers and 77 wt% trimers. Pripol 1040 and DGEBA are stoichiometrically mixed with epoxy/COOH 1:1 to provide the hydroxyl and ester groups of the transesterification reaction. Zinc acetate  $[\text{Zn}(\text{ac})_2]$  is chosen as the catalysts to control the trans-esterification kinetics.

The fatty acid (Pripol 1040) and the catalyst (zinc acetate dihydrate, 5 mol% to the fatty acid groups) were first mixed in a round-bottom flask at 100 °C. Then, the mixture was gradually heated to 180 °C under vacuum. The temperature was held at 180 °C for 2 hours until no gas evolution, and catalyst particles were fully solubilized. Subsequently, the melted Bisphenol A diglycidyl ether (DGEBA) was added into the prepared mixture, and the manual stir was performed at 130 °C until the solution became homogeneous and translucent. To prepare the testing dumbbell samples, the resulting mixture was then quickly poured into a customized Teflon mold and covered with a Teflon film, and baked for 6 hours at 130 °C. The fresh material has a glassy modulus of 1.575 GPa, a rubbery modulus of 3.67 MPa, a Young's modulus of about 4 MPa, and elongation and stress at break of about 180% and 9 MPa.

### 2.2 Pulverous sample preparation

Bulk samples were grinded into powders by using Variable Speed Rotor Mill PULVERISETTE 14 (Fritsch, Germany). Polymer particles with different sizes were obtained by using different sieve rings. Figure 1 shows the photos of the epoxy-acid vitrimer particles obtained by using 0.5 mm, 1.0 mm, and 2.0 mm trapezoidal perforation sieve rings, respectively. Figures 2a-c show the microscopic observations of the epoxy-acid vitrimer particles. From the microscopic morphology, it is seen that the particles are irregularly shaped in profile. The profiles of the particles were extracted and analyzed using software ImageJ. The size of each particle was described by the nominal diameter, which was used to calculate the volume of the imaginary circle that was equal to the volume of the corresponding real particle.

Figures 2d-i present the corresponding size distributions of the particles that were generated by using the three different sieve rings. Overall, larger trapezoidal perforation sieve rings result in bigger particles. Based on the analyses from Figures 2g-i, the average diameters of the particles generated from the three different sieve rings were calculated as 178  $\mu\text{m}$  (Particle-S), 304  $\mu\text{m}$  (Particle-M) and 1299  $\mu\text{m}$  (Particle-L), respectively. What stands out is that the amount of fine powder is large, but their volume fraction is very small. The statistical results show that the number of fine powders (<100  $\mu\text{m}$ ) is 66%, 43% and 50% in Particle-S, Particle-M and Particle-L, but their corresponding volume fractions are only 14.73%, 1.65% and 0.44%.

### 2.3 Preparation of recycled samples

A universal mechanical testing machine (MTS Criterion<sup>TM</sup>, Model 43.104 Dimensions) equipped with a thermal chamber was used to prepare recycled vitrimer samples. The machine was first preheated to target temperature. Then, epoxy-acid vitrimer powders were poured into a customized aluminum mold. Finally, the recycle sample was prepared by moving the mold filled with vitrimer powders into the heated chamber and applying a constant pressure onto the powders over a defined duration. Figure 3 shows healing extent of the recycled material under different processing conditions. Obviously, temperature,

time and pressure promote material healing extent. The surface morphology of the samples was affected by the surface quality of the molds.

#### 2.4 Thermomechanical characterizations

Dynamic mechanical analysis (DMA, Q800 DMA, TA Instruments) was used to characterize the dynamic thermomechanical properties of the recycled vitrimer samples in the tension film mode. Samples with a dimension of 15 mm × 5 mm × 0.5 mm were tested at a frequency of 1 Hz and an amplitude of 5 μm. The temperature was first equilibrated at -50 °C for 5 min, and then gradually increased to 70 °C at a heating rate of 2 °C/min. The glass transition temperatures ( $T_g$ ) were determined from the peak of the tan  $\delta$ <sup>37-40</sup>.

The MTS machine was used to carry out tensile tests at room temperature. The loading rate was chosen to be a small value

(5% per min for all tests) to minimize viscoelastic effects. The samples were trimmed uniformly into the size of 15 mm × 5 mm × 0.5 mm. For the recycled samples prepared under the same condition, at least three samples were tested, and the average values were reported.

### 3. Results and Discussions

#### 3.1 Effects of particle size and treating temperature

To explore the effects of particle sizes and treating temperature, the polymer powders with different size distributions (i.e. Particle-S, Particle-M and Particle-L) were thermally treated under a controlled pressure of 5 MPa for 1 hour at 120 °C, 130 °C, 140 °C, 150 °C, and 160 °C, respectively. It is found that the recycled samples with smaller particles possess higher storage modulus as well as lower  $T_g$ . This trend

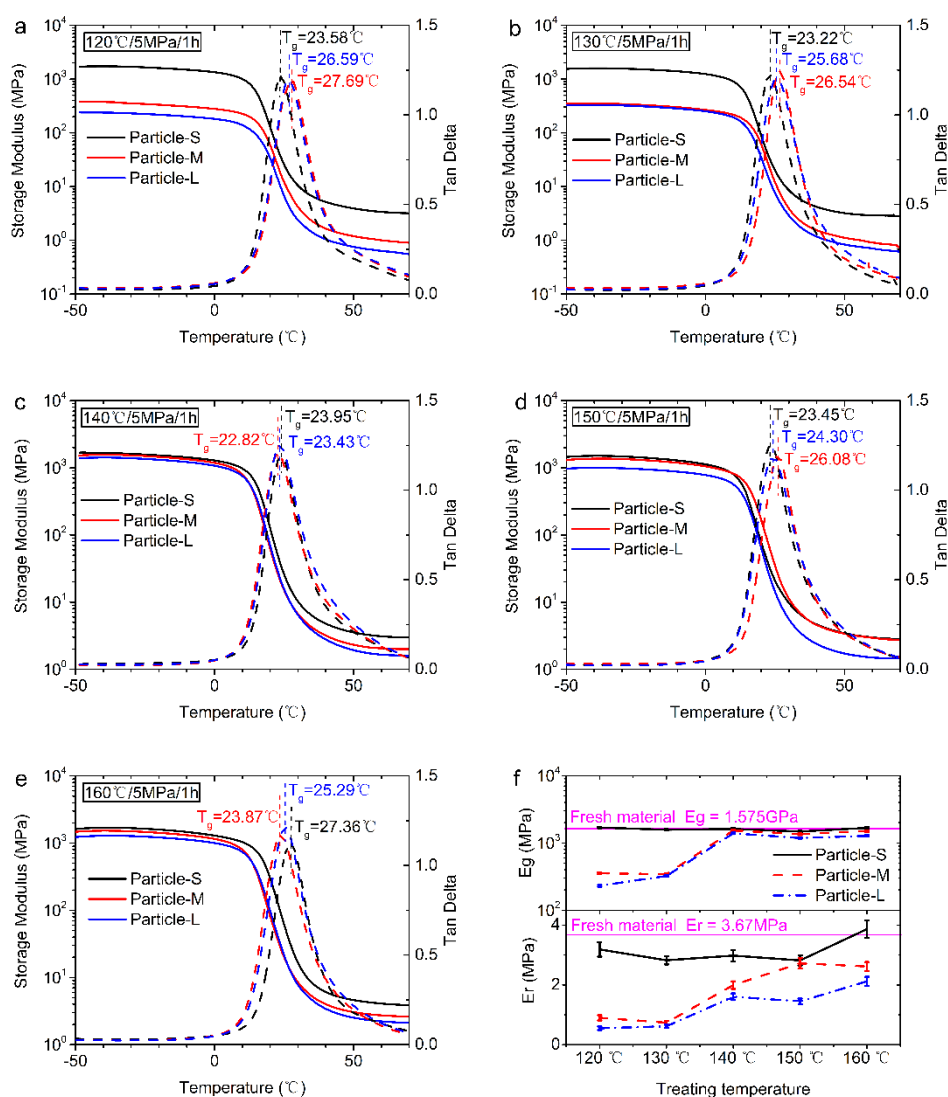


Figure 4. Effect of the particle size on thermomechanical performance of recycled epoxy-acid vitrimers. (a-e) DMA curves of recycled epoxy-acid vitrimers from polymer powders with different size distributions (i.e. Particle-S, Particle-M and Particle-L) at 120 °C, 130 °C, 140 °C, 150 °C and 160 °C, respectively. (f) The effect of particle sizes on glassy modulus ( $E_g$ ) and rubbery modulus ( $E_r$ ). All the samples were prepared under the same controlled pressure of 5 MPa for 1h.

is attributed to the fact that smaller particles facilitate the interfacial bonding between particles, which leads to more dynamic covalent bonds across particles. When the temperature is elevated, those dynamic covalent bonds become more active, and the bond exchange reaction takes less time to weld particles. Comparing Figures 4a-e, we also find that the increase in treating temperature undermines the effect of particle size. When the treating temperature is elevated to 140 °C or higher, the particle size effect is also negligible. Figure 4f summarizes the effect of particle sizes on glassy modulus ( $E_g$ ) and rubbery modulus ( $E_r$ ). For the recycled samples prepared with small particles (Particle-S), the  $E_g$  remains around 1.5-1.7 GPa under different treating temperatures. For the recycled samples prepared with medium (Particle-M) and large particles (Particle-L), the  $E_g$  maintains about 1.5 GPa when the treating temperature is 140 °C or higher, while it drops to about 350 MPa when the treating temperature is 120 °C or 130 °C. The effect of

particle size on  $E_r$  is generally consistent with the effect on  $E_g$ . These results suggest that under the same processing conditions (i.e. the same treating temperature, time, and pressing pressure), the recycled samples prepared with finer powders possess the mechanical properties that are closer to those of the fresh material (solid magenta lines in Figure 4f)<sup>1</sup>.

We performed uniaxial tensile tests at room temperature to further investigate the effect of particle size on the thermomechanical properties of the recycled samples that are prepared at different temperatures. As shown in Figures 5a-e, under the treating temperatures varying from 120 °C to 160 °C, the recycled samples prepared with smaller particles have higher stiffness and larger ultimate stress. Figure 5f summarizes the uniaxial tensile tests from Figures 5a-e: the increase in

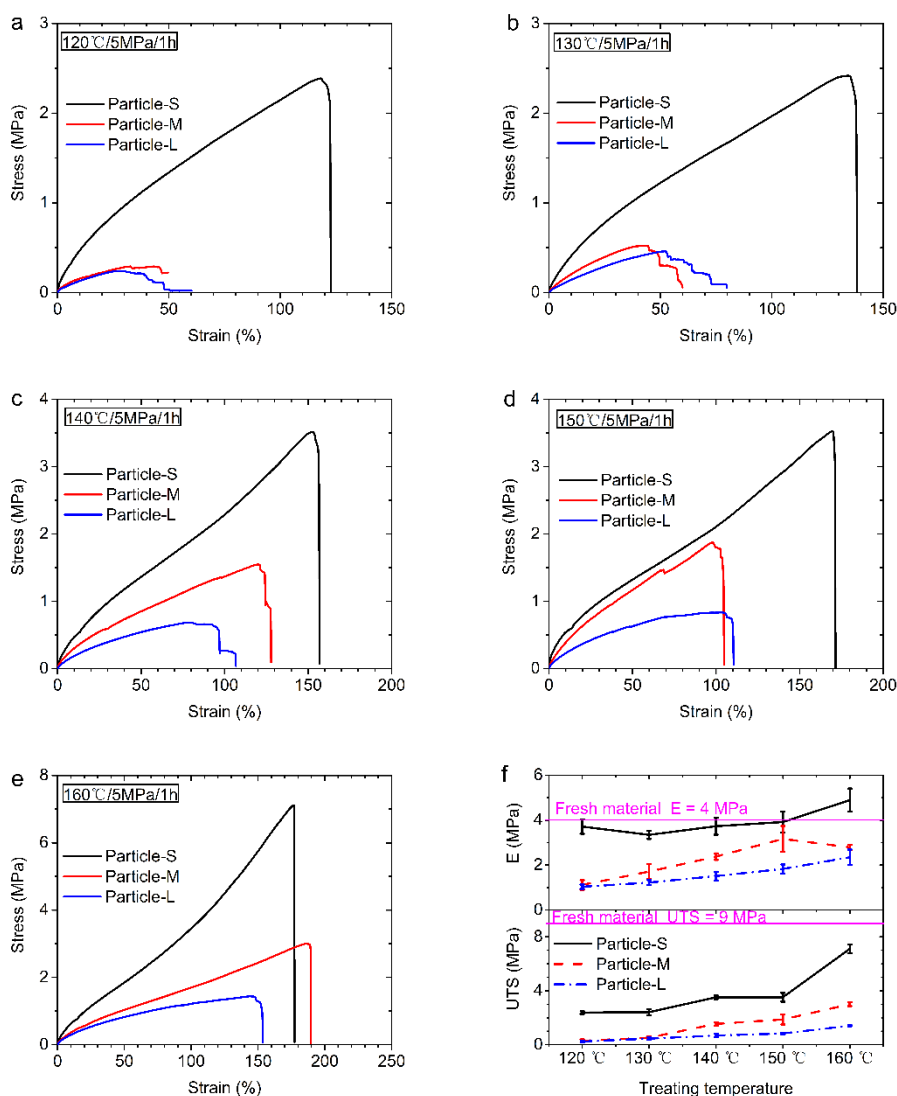


Figure 5. Effect of the particle size on mechanical performance of recycled epoxy-acid vitrimers. (a-e) Uniaxial tensile test results of recycled epoxy-acid vitrimers from polymer powders with different size distributions (i.e. Particle-S, Particle-M and Particle-L) at 120 °C, 130 °C, 140 °C, 150 °C and 160 °C, respectively. (f) The effect of particle sizes on Young's modulus (E) and strength (UTS). All the samples were prepared under the same controlled pressure of 5 MPa for 1h.

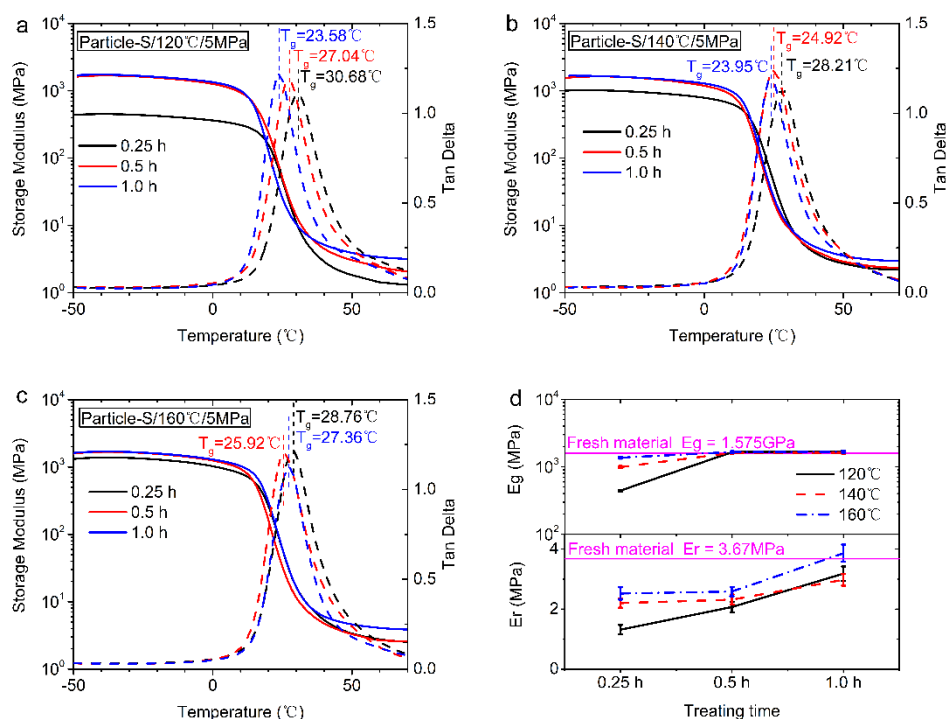


Figure 6. Effect of treating time on thermomechanical performance of recycled epoxy-acid vitrimers. (a-c) DMA curves of recycled epoxy-acid vitrimers treated at 120  $^{\circ}\text{C}$ , 140  $^{\circ}\text{C}$  and 160  $^{\circ}\text{C}$  from polymer powders at Particle-S. (d) The effect of treating time on glassy modulus ( $E_g$ ) and rubbery modulus ( $E_r$ ). All the samples were prepared under the same controlled pressure of 5 MPa.

treating temperature results in the increase in both stiffness and ultimate stress. For the recycled samples prepared with small particle (Particle-S) at 160  $^{\circ}\text{C}$ , the stiffness is greater than the fresh material (4 MPa)<sup>1</sup>, and 80% ultimate tensile stress (9 MPa)<sup>1</sup> are recovered.

Comparing Figure 4f and 5f, we conclude the following two common trends: 1) For Particle-M and Particle-L, the modulus increase resulting from the increase in treating temperature is remarkable. However, for Particle-S, the temperature effect of the rubbery

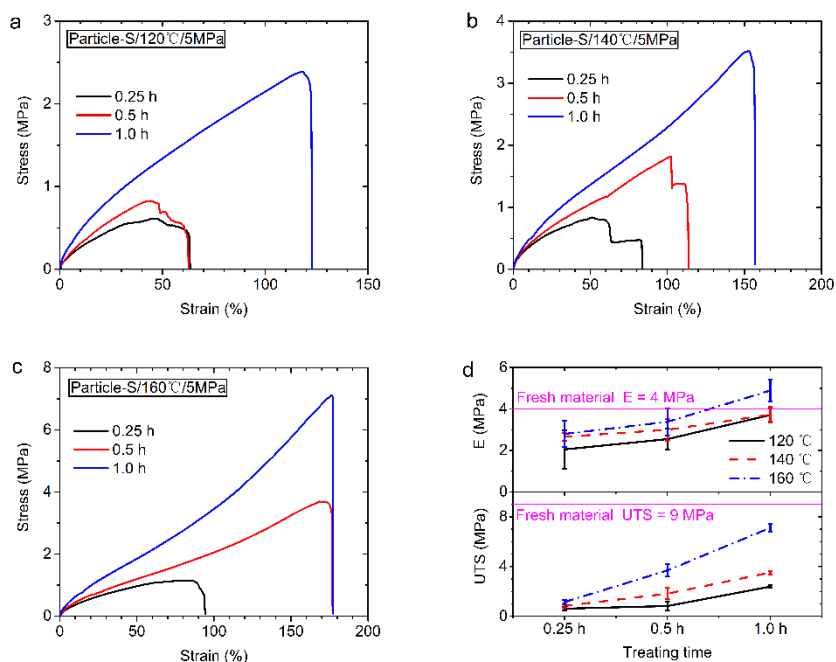


Figure 7. Effect of treating time on mechanical performance of recycled epoxy-acid vitrimers. (a-c) Uniaxial tensile test results of recycled epoxy-acid vitrimers treated at 120  $^{\circ}\text{C}$ , 140  $^{\circ}\text{C}$  and 160  $^{\circ}\text{C}$  from polymer powders at Particle-S. (d) The effect of treating time on Young's modulus ( $E$ ) and strength (UTS). All the samples were prepared under the same controlled pressure of 5 MPa.

modulus of the recycled samples is negligible. 2) When the particle size gets smaller, the modulus of the recycled sample increases, and the modulus of the samples recycled with Particle-S could almost recover to the one of a fresh sample. The reasons leading to the two trends are: 1) the smaller particle size leads to more interfacial bonds which facilitate the welding between particles and therefore result in high modulus of recycled samples. 2) The bond exchange reaction is time-temperature dependent. When the treating temperature increases, the reaction proceeds faster and more particles bond together. 3) When the particles become as small as Particle-S, under the treatment conditions of 5 MPa pressure and 1 hour treating time, the treating temperature of 120 °C is higher enough to realize the full recovery.

### 3.2 Effect of treating time

To explore the effect of treating time on the thermomechanical performance of recycled samples, we used the small particles (Particle-S) to prepare the recycled samples, and thermally treated them at 120 °C, 140 °C, and 160 °C under a pressing pressure of 5 MPa for 0.25, 0.5 and 1 hour, respectively. Figures 6a-c present the DMA results for the recycled samples prepared with different treating time. As shown in Figure 6a, when the treating temperature is 120 °C, the effect of treating time is significant: longer treating time results in higher storage modulus but lower  $T_g$ . This trend is attributed to the fact that longer treating time leads to more covalent dynamic bonds across particles and forms stronger bonds between particles. The effect of treating time weakens and even becomes invisible when the treating temperature is increased to 140 °C (Figure 6b) and 160 °C (Figure 6c). This is because the increase in

treating temperature leads to a higher mobility of the dynamic covalent bonds and reduces the time to reach the saturated number of the covalent dynamic bonds between the particle interfaces. Figure 6d summarizes the effect of treating time on the  $E_g$  and  $E_r$  of recycled epoxy-acid vitrimer samples. In conclusion, in order to make the thermomechanical performance of recycled sample close to that of the fresh material, the treating time needs to increase from 0.25 hour to 1 hour if the treating temperature decrease from 160 °C to 120 °C.

To further study the influence of treating time on the mechanical performance of recycled epoxy-acid vitrimer samples, uniaxial tension tests were carried out at room temperature, and the results are shown in Figure 7. As seen in Figure 7a-c, when the treating time increases from 0.25 hour to 1 hour, both stiffness and ultimate tensile strength (UTS) are improved. As summarized in Figure 7d, 1 hour heating can recover most of the stiffness even the treating temperature is 120 °C. However, 1 hour heating at 160 °C can only recover ~80% ultimate tensile strength of the fresh material.

### 3.3 Effect of pressing pressure

The previous work<sup>3, 22</sup> shows that the increase in pressing pressure significantly improves the welding efficiency of epoxy-acid vitrimers. Here, we investigate the coupled effects of pressing pressure and particle size on the efficiency of recovering the thermomechanical performances by recycling the vitrimer samples with different particle sizes at 160 °C, for 1 hour and under pressing loads of 1 MPa, 3 MPa, and 5 MPa, respectively. As seen in Figure 8a, when the particles are small

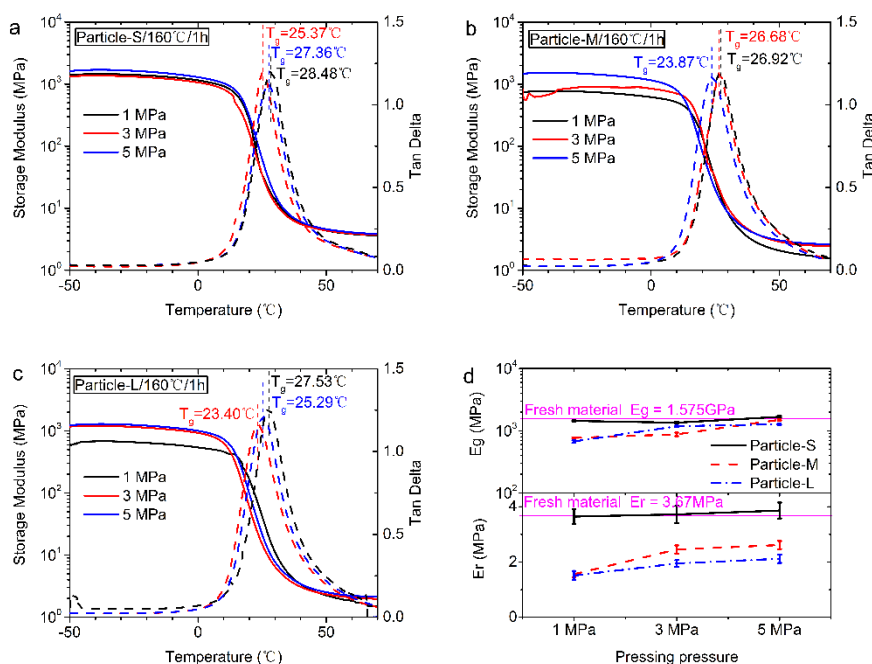


Figure 8. Effect of pressing pressure on thermomechanical performance of recycled epoxy-acid vitrimers. (a-c) DMA curves of recycled epoxy-acid vitrimers treated under the pressure of 1 MPa, 3 MPa and 5 MPa from polymer powders with different size distributions at Particle-S, Particle-M and Particle-L, respectively. (d) The effect of pressing pressure on glassy modulus ( $E_g$ ) and rubbery modulus ( $E_r$ ). All the samples were prepared in the same temperature of 160 °C for 1h.



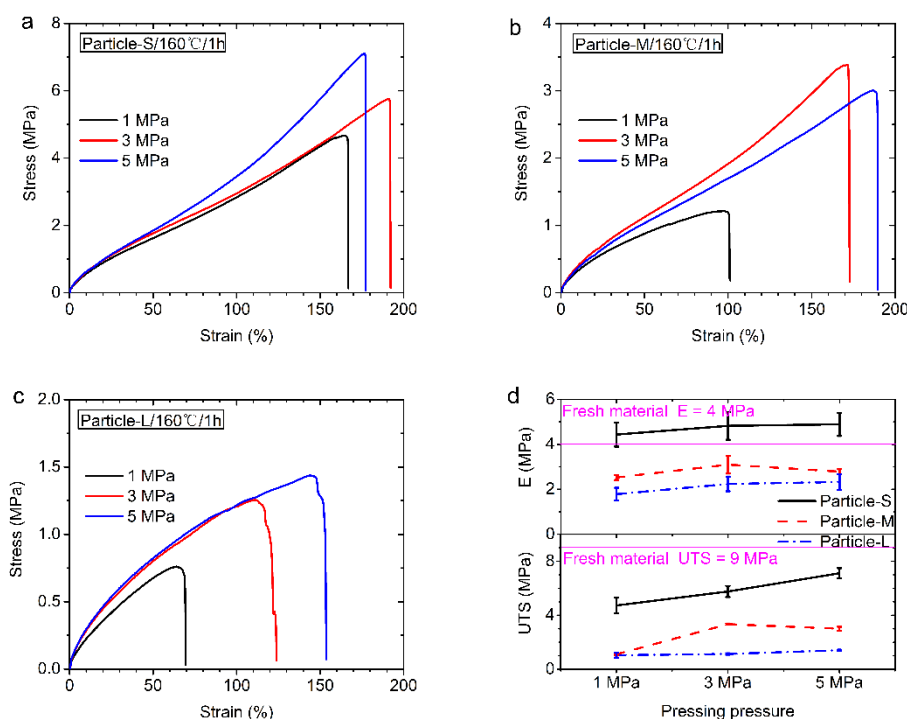


Figure 9. Effect of pressing pressure on mechanical performance of recycled epoxy-acid vitrimers. (a-c) Uniaxial tensile test results of recycled epoxy-acid vitrimers treated under the pressure of 1 MPa, 3 MPa and 5 MPa from polymer powders with different size distributions at Particle-S, Particle-M and Particle-L, respectively. (d) The effect of pressing pressure on Young's modulus ( $E$ ) and strength (UTS). All the samples were prepared in the same temperature of 160 °C for 1h.

(Particle-S with the average diameter of 178  $\mu\text{m}$ ), the thermomechanical performance of the recycled samples does not change by increasing the pressing pressure from 1 MPa to 5 MPa. In comparison, Figure 8b and c roughly show the trend that higher pressing load results in higher storage modulus and lower  $T_g$ . The tendencies of glassy and rubbery modulus with different pressing pressures and particle sizes are summarized in Figure 8d. It shows that the rubbery modulus of the Particle-S recycled vitrimers is much higher than that of the Particle-M and Particle-L recycled vitrimers. For the recycled samples prepared with Particle-M and Particle-L, both glassy and rubbery moduli increase slightly with the increase in the pressing pressure.

The influence of pressing pressure on the mechanical performance of recycled epoxy-acid vitrimers was further studied by the uniaxial tensile test. As shown in Figure 9a-c, improved elongation strength and ultimate tensile strength could be obtained with decreasing polymer particle sizes or the increasing of the pressure. Figure 9d summarizes the tendencies of Young's modulus and ultimate tensile strength with polymer particles sizes and pressing pressures. As the rubbery modulus (Figure 8d), the ultimate tensile strength of recycled samples from small polymer particles shows higher values compared to that of middle polymer particles and large polymer particles. The Particle-S recycled vitrimers achieved similar mechanical properties to the fresh material at a pressure of 1 MPa. The ultimate elongation and ultimate tensile strength of Particle-M recycled vitrimers gave a good improvement at a pressure of 3 MPa or more relative to a treatment pressure of 1 MPa. The

formation quality and mechanical properties of large particles are very poor, especially with very low ultimate tensile strength.

#### 4. Conclusions

This study provides a data reference to optimize the mechanical reprocessing of epoxy-acid vitrimers to meet practical engineering applications. Among the different properties that were investigated, the recovery of both rubbery modulus and ultimate tensile strength (UTS) is essential to assess the efficiency of the parameters selected for the recycling process. The set of experimental results shows that an acceptable recovery of both properties requires the lowest particle size coupled to the highest values of temperature, time and pressure. Moving away from these conditions produced a significant decrease in the recovery of the UTS (the effect of pressure was less relevant). The effect of particle size on the molding quality is remarkable. In addition, the particle size changes other conditions (temperature, time, and pressure) required to achieve the same mechanical properties. The interfacial welding of vitrimers follows the Arrhenius-type time and temperature superimpositions (TTSP), to increase the efficiency of reprocessing, it is possible to regenerate large particles with higher treating temperatures or longer treating times. Surprisingly, increased pressing pressure improved the mechanical properties of Particle-S and Particle-M recycled materials, especially Particle-S recycled materials, but only improved the ultimate elongation of Particle-L recycled materials. The rubbery modulus, Young's modulus and ultimate tensile strength of the Particle-L recycled material did not

increase significantly with the increase of pressure. This phenomenon is attributed to the small volume fraction of fine powder in Particle-L (Figure 2), which is insufficient to fill the gaps between large particles.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references

1. D. Montarnal, M. Capelot, F. Tournilhac and L. Leibler, *Science*, 2011, **334**, 965-968.
2. W. Denissen, J. M. Winne and F. E. Du Prez, *Chem Sci*, 2016, **7**, 30-38.
3. K. Yu, P. Taynton, W. Zhang, M. L. Dunn and H. J. Qi, *RSC Adv.*, 2014, **4**, 10108-10117.
4. Q. Shi, K. Yu, M. L. Dunn, T. Wang and H. J. Qi, *Macromolecules*, 2016, **49**, 5527-5537.
5. X. Kuang, Y. Zhou, Q. Shi, T. Wang and H. J. Qi, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 9189-9197.
6. B. Zhang, K. Kowsari, A. Serjouei, M. L. Dunn and Q. Ge, *Nat Commun*, 2018, **9**, 1831.
7. R. L. Snyder, D. J. Fortman, G. X. De Hoe, M. A. Hillmyer and W. R. Dichtel, *Macromolecules*, 2018, **51**, 389-397.
8. K. Yu, H. Yang, B. H. Dao, Q. Shi and C. M. Yakacki, *Journal of the Mechanics and Physics of Solids*, 2017, **109**, 78-94.
9. K. Yu, Q. Shi, M. L. Dunn, T. Wang and H. J. Qi, *Advanced Functional Materials*, 2016, **26**, 6098-6106.
10. D. J. Fortman, J. P. Brutman, C. J. Cramer, M. A. Hillmyer and W. R. Dichtel, *J Am Chem Soc*, 2015, **137**, 14019-14022.
11. L. Zhou, G. Zhang, Y. Feng, H. Zhang, J. Li and X. Shi, *Journal of Materials Science*, 2018, **53**, 7030-7047.
12. E. B. Stukalin, L. H. Cai, N. A. Kumar, L. Leibler and M. Rubinstein, *Macromolecules*, 2013, **46**.
13. Q. Shi, K. Yu, X. Kuang, X. Mu, C. K. Dunn, M. L. Dunn, T. Wang and H. Jerry Qi, *Materials Horizons*, 2017, **4**, 598-607.
14. T. Liu, C. Hao, L. Wang, Y. Li, W. Liu, J. Xin and J. Zhang, *Macromolecules*, 2017, **50**, 8588-8597.
15. F. I. Altuna, C. E. Hoppe and R. J. J. Williams, *RSC Advances*, 2016, **6**, 88647-88655.
16. L. Rovigatti, G. Nava, T. Bellini and F. Sciortino, *Macromolecules*, 2018, **51**, 1232-1241.
17. A. Legrand and C. Soulié-Ziakovic, *Macromolecules*, 2016, **49**, 5893-5902.
18. W. Denissen, I. De Baere, W. Van Paepegem, L. Leibler, J. Winne and F. E. Du Prez, *Macromolecules*, 2018, **51**, 2054-2064.
19. Z. Yang, Q. Wang and T. Wang, *ACS Appl Mater Interfaces*, 2016, **8**, 21691-21699.
20. Y. Liu, Z. Tang, Y. Chen, C. Zhang and B. Guo, *ACS Appl Mater Interfaces*, 2018, **10**, 2992-3001.
21. M. H. Akonda, C. A. Lawrence and B. M. Weager, *Composites Part A: Applied Science and Manufacturing*, 2012, **43**, 79-86.
22. X. Yang, Y. Guo, X. Luo, N. Zheng, T. Ma, J. Tan, C. Li, Q. Zhang and J. Gu, *Composites Science and Technology*, 2018, **164**, 59-64.
23. Y. Yang, Z. Pei, X. Zhang, L. Tao, Y. Wei and Y. Ji, *Chem. Sci.*, 2014, **5**, 3486-3492.
24. A. Ruiz de Luzuriaga, R. Martin, N. Markaide, A. Rekondo, G. Cabañero, J. Rodríguez and I. Odriozola, *Materials Horizons*, 2016, **3**, 241-247.
25. E. Chabert, J. Vial, J. P. Cauchois, M. Mihaluta and F. Tournilhac, *Soft Matter*, 2016, **12**, 4838-4845.
26. X. He, Z. Lei, W. Zhang and K. Yu, *3D Printing and Additive Manufacturing*, 2019, **6**, 31-39.
27. D. W. Hanzon, N. A. Traugutt, M. K. McBride, C. N. Bowman, C. M. Yakacki and K. Yu, *Soft Matter*, 2018, **14**, 951-960.
28. Q. Chen, Y. Li, Y. Yang, Y. Xu, X. Qian, Y. Wei and Y. Ji, *Chem Sci*, 2019, **10**, 3025-3030.
29. Z. Pei, Y. Yang, Q. Chen, E. M. Terentjev, Y. Wei and Y. Ji, *Nat Mater*, 2014, **13**, 36-41.
30. B. Jin, H. Song, R. Jiang, J. Song, Q. Zhao and T. Xie, *Science advances*, 2018, **4**, eaao3865.
31. Y. Li, O. Rios, J. K. Keum, J. Chen and M. R. Kessler, *ACS Appl Mater Interfaces*, 2016, **8**, 15750-15757.
32. K. Yu, Q. Shi, H. Li, J. Jabour, H. Yang, M. L. Dunn, T. Wang and H. J. Qi, *Journal of the Mechanics and Physics of Solids*, 2016, **94**, 1-17.
33. B. Zhang, C. Yuan, W. Zhang, Martin L. Dunn, H. J. Qi, Z. Liu, K. Yu and Q. Ge, *RSC Advances*, 2019, **9**, 5431-5437.
34. W. Liu, D. F. Schmidt and E. Reynaud, *Industrial & Engineering Chemistry Research*, 2017, **56**, 2667-2672.
35. F. I. Altuna, C. E. Hoppe and R. J. J. Williams, *Polymers (Basel)*, 2018, **10**.
36. L. Lu, J. Pan and G. Li, *J. Mater. Chem. A*, 2017, **5**, 21505-21513.
37. D. L. Safranski and K. Gall, *Polymer*, 2008, **49**, 4446-4455.
38. H. J. Qi, T. D. Nguyen, F. Castro, C. M. Yakacki and R. Shandas, *Journal of the Mechanics and Physics of Solids*, 2008, **56**, 1730-1751.
39. C. M. Yakacki, R. Shandas, C. Lanning, B. Rech, A. Eckstein and K. Gall, *Biomaterials*, 2007, **28**, 2255-2263.
40. K. Yu, Q. Ge and H. J. Qi, *Nat Commun*, 2014, **5**, 3066.

## Table of Contents

The effects of particle size, temperature, time, and pressure on the mechanical properties of regenerated epoxy-acid vitrimers were investigated, which helped to refine the vitrimers reprocessing condition parameter toolbox.

