Study on the factors affecting the mechanical properties and recovery force of PLA/PEEK blends

Lan Zhang, Suqian Ma, Haohua Xiu, Zhaohua Lin and Zhihui Zhang

1 The Key Laboratory of Bionic Engineering, Ministry of Education, Jilin University, Changchun 130025, People’s Republic of China
2 School of Mechanical and Aerospace Engineering, Jilin University, Changchun 130025, People’s Republic of China
E-mail: linzhaohua@jlu.edu.cn

Keywords: poly(ether ether ketone) (PEEK), Polylactic acid (PLA), mechanical properties, deformation force

Abstract
It has been found that PLA/PEEK blends have excellent mechanical properties and shape memory properties. In this article, the properties of PLA/PEEK blends were further studied. The mechanical properties of PLA/PEEK blends may be directly or indirectly affected by the molding temperature, molding method and heat treatment conditions. In this paper, PLA/PEEK blends were prepared under different processing conditions (molding temperature, molding method and heat treatment conditions) to evaluate the effects of different processing conditions on the mechanical properties of PLA/PEEK blends. In order to determine the lifting force of PLA/PEEK blends under different conditions, the effects of blends proportion and deformation temperature on the deformation force during the shape memory process were investigated. The experimental results show that the mechanical properties of PLA/PEEK blends can be improved by controlling the preparation conditions, and the deformation time and force can be effectively controlled by the proportion of the blends and recovery temperature.

1. Introduction

Shape memory polymers (SMPs) are promising smart materials due to their excellent mechanical properties, fast response and good biocompatibility [1–3]. After the temporary shape programming process, SMPs can recover its original shape under external stimulation (such as heat, light, electricity, etc) [4–8]. Among them, PLA is a typical thermal SMP [9]. PLA is a low-cost biomedical polymer with excellent performance [10–14], and because of its good shape memory behavior, it has shown potential applications in vascular stents, drug delivery, surgical sutures and tissue engineering stents [15, 16]. Polyetheretherketone (PEEK) is a high-performance, high-temperature-resistant semi-crystalline polymer, which is considered one of the best thermoplastics [17]. PEEK can be used as a metal substitute which is widely used in various kind of field [18–20]. The addition of fibers or fillers can improve the mechanical properties of PLA, but fibers and fillers will reduce the shape memory characteristics [21]. The addition of other polymers has a positive effect on the shape memory properties of PLA, but under normal circumstances it will cause a decrease in mechanical properties. In order to take into account the mechanical properties and shape memory properties of PLA, a polymer with high modulus is selected for blending with PLA. In this paper PEEK is selected for experimentation. It has been found that PLA and PEEK were blended and the PLA was modified by PEEK [22]. The prepared PLA/PEEK blends not only improved the shape memory properties, but also improved the mechanical properties of the blends.

Zhou et al [23] prepared PCL/PLA thermally responsive shape memory blends by the melt blending, which improved the shape memory performance of the blends. Don et al [24] reported a PLA/TPU/CNT blended nanocomposite and studied the influence of different carbon fiber content on mechanical, electrical, thermal properties and shape memory. Zhang et al [25] prepared a homogeneous LCNF/PLA composites by blending, which improved the compatibility of the interface and enhanced the mechanical properties of the PLA. Sharma et al [26] reported that the addition of plasticizers (lotader ax8900, polyethylene glycol and triethyl citrate)
reduced the brittleness of PLA composites, and evaluated the changes of surface morphology and mechanical properties. At present, most studies on improving the properties of PLA are focused on physical blending modification by fibers or fillers [27, 28]. There are few studies on the effect of process parameters on the properties of PLA. And the researches on shape memory properties are generally concentrated on shape fixation rate, recovery rate and deformation time, there are few quantitative studies on the deformation force during the deformation process.

In further research, we found that the molding temperature, molding method, and heat treatment conditions in the PLA/PEEK blends manufacturing process will affect the mechanical properties. And different material ratios and deformation temperatures have a significant impact on the shape recovery force of the sample during shape memory process. Therefore, the main purpose of this paper is to study the effects of processing conditions on the mechanical properties of PLA/PEEK blends and quantitatively study the influence of different material ratio and deformation temperature on the deformation force in the shape memory process. All experimental results show that the external conditions in the sample forming process mainly affect the mechanical properties rather than the shape memory characteristics. Different material ratios and deformation temperatures have a significant effect on the deformation force.

2. Materials and methods

2.1. Materials
Polyactic acid (PLA) was obtained from XinCheng Engineering Company, China. Poly(ether ether ketone) (PEEK) powder was purchased from Zhongyan Polymer Material Co., Ltd, Jilin, China. Dichloromethane was produced by Aladdin Reagent Co., Ltd, Shanghai, China. All the reagents were used as received without further purification.

2.2. Parameter selection
The mechanical properties and shape memory properties of the material are affected by many factors, including composition, molding temperature, molding method and thermal processing. In previous study, we systematically studied the influence of composition on PLA/PEEK composites. In this article, the effects of three parameters—molding temperature, molding method and thermal processing—on the mechanical properties of PLA/PEEK blends were evaluated. 85% PLA/15% PEEK (15PEEK) with good mechanical and shape memory properties was selected for the experiment.

2.2.1. Molding temperature
Molding temperature refers to the ambient temperature of PLA/PEEK composites suspension during the drying and molding process. Four levels of molding temperatures were used during the experiment: 0 °C, 10 °C, 20 °C, 30 °C.

2.2.2. Molding method
PLA and PEEK were dried in a vacuum oven at 40 °C for 24 h. Firstly, PLA was dissolved in CH₂Cl₂ by magnetic stirring at room temperature for 4 h to obtain the PLA solution. Then, PEEK was added to the PLA solution and stirred for 1 h with magnetic stirring to obtain the suspension. The mass ratio of CH₂Cl₂ solvent to mixture is 5:1, so that the polymer solution has enough viscosity which ensures that the PEEK powder remains suspended in the polymer solution without sinking. The schematic diagram of the two molding methods as shown in figure 1.

Layer-by-layer molding: transfer 5 ml polymer suspension into the mold with syringe, and dry at 20 °C for 24 h.

Mould molding: transfer 1 ml polymer suspension into the mold with syringe and dry at 20 °C for 0.5 h to form a film, then repeat the process five times.

2.2.3. Thermal processing conditions
Different thermal processing conditions have direct impact on the crystallinity of the polymers. In order to study the relationship between thermal processing conditions, crystallinity, mechanical properties and shape memory properties of PLA/PEEK blends, in this paper, four thermal processing conditions were used during the experiment: quenching, air cooling, furnace cooling and annealing, and compared with the samples without any thermal processing. The specific descriptions of temperature variation in different heat treatment methods as shown in figure 2.
2.3. Characterization
The mechanical properties of the samples were detected on a uniaxial tensile testing machine (WDW-500, Weidu Electronics, China). The sizes of the strip samples were 60 mm × 10 mm × 1 mm. All tests were run at the test speed of 1 mm min⁻¹. Each set of data reported is based on characteristics obtained from five samples.

The differential scanning calorimetry (DSC) of the samples was carried out on a Q600 Simultaneous DSC of American TA Instruments. The test conditions are as follows: heating to 180 °C from 30 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere, cooling to 30 °C, then raising to 450 °C at a rate of 10 °C min⁻¹.

The fractured surfaces of samples were observed by using scanning electron microscope (SEM) (Model EVO-18, Carl Zeiss Company, Germany). Samples were fixed on the sample column surface with conductive tape and all coated with gold by ion sputter JFC-108.

3. Results and discussion

3.1. Influence of process parameters
The influence of PLA/PEEK blends on the mechanical properties formed at different temperatures as shown in figure 3(a), and the samples are prepared by mould molding. The results show that as the ambient temperature
increases, the tensile strength and breaking elongation gradually decrease. But the tensile strength of all samples are in the range 24.8–26.5 MPa, the difference in tensile strength is not significant from which it can be concluded that the ambient temperature has little effect on the tensile strength. However, we found that ambient temperature has a significant effect on breaking elongation. The breaking elongation at 0 °C was 4.882% and more than twice as the 30 °C at 2.172%. In the process of sample solvent evaporation, the part contacting the air is dried first to form a film. The high ambient temperature leads to fast solvent volatilization, and the faster the surface is dried. However, the solvent inside the sample has not yet volatilized, which causes bubbles or voids generated inside the sample and defects formed inside the sample. High ambient temperature will reduce the mechanical properties, the ambient temperature has little effect on the tensile strength but has a significant effect on the elongation at break. The SEM images of the sample fracture formed at different temperatures are respectively shown in figures 3(c)–(f). It can be seen that the sample formed at 0 °C is relatively dense and almost has no bubbles or other defects. On the contrary, there are obvious cavities inside the sample formed at 10 °C, 20 °C and 30 °C, which is caused by the rapid volatilization of internal solvent.

When the ambient temperature is kept at 20 °C, we found that different molding methods can affect the mechanical properties of the samples as shown in figure 3(b). The experimental result indicated that the sample formed by layer-by-layer forming has a higher tensile strength of 27.61 MPa, but a lower breaking elongation of 3.3%. This is because in the layer-by-layer forming process, each layer will generate shrinkage stress during the
drying process and will be stored in the blends. In this case, the internal stress will be released from the polymer chain by drying the blends, causing the initial curve state of the blends sample [29]. Due to the sample formed by layer-by-layer has internal stress between layers. The internal stress of the sample will resist the tensile force during the stretching process which result in breaking the sample requires more tensile force, so the tensile strength is larger. Due to the existence of internal stress, the sample will become bent which makes the sample brittle and the breaking elongation will decrease. As for the sample formed by mould has a lower tensile strength of 24.79 MPa, but a higher breaking elongation of 4.2%. This is because the samples with mould forming are more flat, and there is no internal stress, but have better ductility which leads to a better breaking elongation. In order to illustrate the influence of different molding methods at different temperatures, the tensile strength and breaking elongation of layer-by-layer molding samples at different molding temperatures are supplemented in the supporting information (available online at stacks.iop.org/MRX/8/115701/mmedia). It can be concluded that the tensile strength of layer-by-layer molding samples at different temperatures is higher, and the breaking elongation of the mould molding samples is higher. However, the above two factors have no obvious effect on the shape memory properties of the blends.

3.2. Influence of thermal processing conditions
The DSC curves of blends under different heat treatment conditions as shown in figure 4(a). The glass transition temperature \( T_g = 55 \, ^\circ\text{C} \) and the melting temperature \( T_m = 171 \, ^\circ\text{C} \) of PLA/PEEK blends. The heat treatment conditions have no obvious effect on the glass transition temperature of the blends. The tensile strength and breaking elongation curves of blends under different heat treatment conditions as shown in figure 4(b). The tensile strength of the heat-treated samples is higher than the untreated sample, but the breaking elongation is lower than the untreated sample. According to the theory of polymer physics [30], the mechanical properties of polymers are closely related to the aggregation state of macromolecular chains: the macromolecular chains in crystalline region are ordered well and have strong intermolecular forces, which leads to greater strength and rigidity. The macromolecular chains in amorphous region are easy to intertwine loosely, disperse and stretch, showing a good extensibility. Different heat treatment methods can improve the crystallinity of samples. Furnace cooling and annealing are effective methods to obtain higher crystallinity. Therefore, the furnace cooling and annealing samples have higher tensile strength but lower elongation at break. The difference between the air cooling crystallization time and furnace cooling is small, so the tensile strength and breaking elongation of air cooling sample is similar to the furnace cooling. However, compared with the above heat treatment methods, during quenching, there is not enough energy and time to crystallize, which results in mechanical properties lower than other heat treatment samples.

3.3. Influence of recovery force
The force measurement was recorded on a one-dimensional force transducer (1000 mN, NBIT, Nanjing, China). As shown in figure 5(a), the samples with temporary curved state were placed 2 mm away from the force transducer, with one end pasted on the petri dish. When hot water was poured into the petri dish, they tend to return to the permanent shape 'open' state, and then touch the force sensor, which can record the force generated by the sample. The forces during shape recovery of PLA/PEEK blends at different ratios and temperatures were measured. This evaluation was meant to be a qualitative measure of how the stiffness of the PLA/PEEK blends translates to the force during the shape recovery process. Figure 5(b) shows the recovery force
curves of PLA/PEEK blends with different ratios. As hot water was poured into the petri dish, the force gradually increases from zero and reaches the maximum, then the force is in equilibrium. This is because the shape recovery force is a slow release process, the deformation force will gradually increase and when the deformation force reaches the maximum value, the deformation force will not decrease or increase significantly, but will fluctuate slightly around a stable value. It can be seen that when the PEEK content is 0%–15%, the restoring force will increase with the increase of PEEK content. It can be found that when the PEEK content is greater than 15%, the restoring force decreases with the increase of the PEEK content, but the restoring force is second only to the 15PEEK sample. The blends show relatively larger recovery force compared with pure PLA sheets. The recovery force of 15PEEK is 11.9 times that of pure PLA. Adding PEEK could improve the stiffness of the blends due to high stiffness of PEEK [31], and the stiffening the blends translates to increased force during the shape transition, so the force of the PLA/PEEK blends is greater than the pure PLA [32]. But PLA plays a leading role in the shape memory process, when the PEEK content is large, the proportion of the PLA matrix is small which leads to the shape memory characteristics becoming worse, and the restoring force of the sample will be reduced.

The recovery time of 15PEEK at different temperatures as shown in figure 5(c) and the photographs of shape recovery processes under different recovery temperature as shown in figures 6(b)–(f). It can be found that the deformation time gradually decreases with the increase of temperature. This is because when the shape recovery process is carried out at or above the glass transition temperature, the sharp change of polymer chain mobility caused by glass transition promotes the shape recovery of sample [33]. The higher recovery temperature lead the heated sample has higher chain fluidity, resulting in shorter recovery time. The recovery force curves of 15peek at different temperatures as shown in figure 5(d). When the temperature is 60 °C, the force increases gradually and reaches the maximum. When the deformation temperature is between 70 °C and 100 °C, the force increases rapidly and then decreases. Among them, the recovery force begins to decrease before reaching the maximum except at 70 °C. This is because when a certain temperature is reached, most of the soft segment crystals melt and the molecular chain becomes softer, and stress relaxation begins in the sample, so the deformation force begins to decrease [34].
4. Conclusions

In this paper, the properties of PLA/PEEK blends were studied. The mechanical properties of PLA/PEEK blends under different processing conditions and the deformation force under different blend proportion and deformation temperature of PLA/PEEK blends have been systematically studied. The key findings of this study can be summarized as follows:

(1) The addition of appropriate proportion of PEEK has a positive effect on the deformation force of PLA.

(2) High recovery temperature will reduce the deformation force of PLA/PEEK blends and the deformation time.

(3) The high ambient temperature during molding makes the solvent volatilize fast, which will cause the internal defects of PLA/PEEK blends and reduce its mechanical properties.

(4) Heat treatment can increase the crystallinity of PLA/PEEK blends, resulting increase in the tensile strength, but reduction in the breaking elongation.

Acknowledgments

This work was supported by the Project of National Key Research and Development Program of China (2018YFB1105100, 2018YFC2001300), the National Natural Science Foundation of China (5167050531, 51822504, 91848204, 91948302, 52021003), Key Scientific and Technological Project of Jilin Province.
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Lan Zhang https://orcid.org/0000-0002-6256-5264
Zhaohua Lin https://orcid.org/0000-0002-4416-6067

References

[1] Xia Y-L, He Y, Zhang F-H, Liu Y-J and Leng J-S 2021 A review of shape memory polymers and composites: mechanisms, materials, and applications Adv. Mater. 33 2000713
[2] Zhang W, Zhang F-H, Lan X, Leng J-S, Wu A S, Bryson T M, Cotton C, Gu B, Sun B and Chou T-W 2018 Shape memory behavior and recovery force of 4D printed textile functional composites Compos. Sci. Technol. 160 224–30
[3] Hager M D, Bode S, Weber C And Schubert U S 2015 Shape memory polymers: past, present and future developments Prog. Polym. Sci. 49 9–33
[4] Li J-J and Xie T 2011 Significant impact of thermo-mechanical conditions on polymer triple-shape memory effect Macromolecules 44 75–80
[5] Gunes I S, Jimenez G A and Jana S C 2009 Carbonaceous fillers for shape memory actuation of polyurethane composites by resistive heating Carbon 47 981–97
[6] Lu H-B, Liu Y-J, Gou J-H, Leng J-S and Du S-Y 2010 Electroactive shape-memory polymer nanocomposites incorporating carbon nanofiber paper Int. J. Smart Nano Mat. 1–2–12
[7] Chen S-J, Hu J-L and Zhuo H-T 2011 Study on the moisture absorption of pyridine containing polyaniline for moisture-responsive shape memory effects J. Mater. Sci. 46 6581–8
[8] Wei K, Zhu G-M, Tang Y-S, Tian G-M and Xie J-Q 2012 Thermodmechanical studies of shape-memory hydro-epoxy resin Smart Mater. Struct. 21 055022
[9] Barmout M and Behravesh A H 2017 Shape memory behaviors in cylindrical shell PLA/TPU-cellulose nanofiber bio-nanocomposites: analytical and experimental assessment Compos. Part A-Appl. S. 101 160–172
[10] Jia W-W, Gong R-H and Hogg P J 2014 Poly(lactic acid) fibre reinforced biodegradable composites Compos. Part B-Eng. 62 104–12
[11] Castro-Aguirre E, Iniguez-Franco F, Samsudin H, Fang X and Auras R 2016 Polyetheretherketone (PEEK) shape memory composites with controllable sequential deformation behavior: a theoretical & experimental assessment Tribol. Int. 80 136–47
[12] Chen G-Q and Patel M K 2012 Plastics derived from biological sources: present and future: a technical and environmental review Chem. Rev. 112 2082–99
[13] Saini P, Arora M and Kumar M N V R 2016 Poly(lactic acid) blends in biomedical applications Adv. Drug Deliv. Rev. 107 47–59
[14] Zalaznik M, Kalin M and Novak S 2016 Influence of the processing temperature on the tribological and mechanical properties of polylactic acid–ether–ketone (PEEK) polymer Compos. Part A-Appl. S. 69 94–2–7
[15] Fujita N, Osawa N and Mitsuhashi K 2012 Polyetheretherketone (PEEK) for medical applications J. Mater. Sci-Mater. Med. 23 118
[16] Kurzt S M and Devine J N 2007 PEEK biomaterials in trauma, orthopedic, and spinal implants Biomaterials 28 4845–69
[17] Vaezi M and Yang S-F 2013 Extrusion-based additive manufacturing of PEEK for biomedical applications Virtual Phys. Prototy. 10 123–35
[18] Zhang L, Lin Z-H, Zhou Q, Ma S-Q, Liang Y-H and Zhang Z-H 2020 PEEK modified PLA shape memory blends: towards enhanced mechanical and deformation properties Front. Mater. Sci. 14 177–87
[19] Murariu M and Dubois P 2016 PLA composites: from production to properties Adv. Drug Deliv. Rev. 107 17–46
[20] Zhou H-M, Xue Y, Mu G-Q, Gao Y-M, Liang S, Li G-Z, Wang Q, Lin X-X and Qian F 2021 The preparation and characterization of biodegradable PCL/PLA shape memory blends J. Macromol. Sci. A. 58 669–76
[21] Dong K, Panahi-Sarmad M, Cui Z, Huang X and Xiao X 2021 Electro-induced shape memory effect of 4d printed auxetic composite using PLA/TPU/CNT filament embedded synergistically with continuous carbon fiber: a theoretical & experimental analysis Compos. B 220 108994
[22] Zhang Q, Ma R, Ma L, Zhang L-L, Fan Y-M and Wang Z-G 2021 Contribution of lignin in esterified lignocellulose nanofibers (LCNFs) prepared by deep eutectic solvent treatment to the interface compatibility of LCNF/PLA composites Ind. Crop. Prod. 166 113460
[23] Sharma S, Majumdar A and Butola B S 2021 Tailoring the biodegradability of polylactic acid (PLA) based films and ramie–PLA green composites by using selective additives Int. J. Biol. Macromol. 181 1092–105
[24] Marius M and Philippe D 2016 PLA composites: from production to properties Adv. Drug Deliv. Rev. 107 17–46
[25] Bajpai P K, Singh I and Madaan J 2012 Comparative studies of mechanical and morphological properties of polylactic acid and polypropylene based natural fiber composites J. Rein. Plast. Comp. 31 1712–24
[26] Ma S-Q, Jiang Z-Y, Wang M, Zhang L, Liang Y-H, Zhang Z-H, Ren L and Ren L-Q 2021 4D printing of PLA/PCL shape memory composites with controllable sequential deformation bio-des Manuf. 4 867–78
[27] Mark J E 2007 Physical Properties of Polymers Handbook (New York: Springer)
[31] Liu Y-M and Sinha S-K 2013 Mechanical and tribological properties of peek particle-filled uhmwpe composites: the role of counterface morphology change in dry sliding wear J. Reinf. Plas. Comp. 32 1614–23
[32] Liu W, Wu N and Pochiraju K 2018 Shape recovery characteristics of SCI/C/PLA composite filaments and 3D printed parts Compos. Part A- Appl. S. 108 1–11
[33] Wu W-Z, Ye W-L, Wu Z-C, Geng P, Wang Y-L and Zhao J 2017 Influence of layer thickness, raster angle, deformation temperature and recovery temperature on the shape-memory effect of 3d-printed polylactic acid samples Materials 10 970
[34] Chen H-J, Zhang F-H, Sun Y, Sun B-Z, Gu B-H, Leng J-S and Zhang W 2021 Electrothermal shape memory behavior and recovery force of four-dimensional printed continuous carbon fiber/polyactic acid composite Smart Mater. Struct. 30 025040