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Optically transparent poly(methyl methacrylate) with largely enhanced mechanical and shape memory properties via in-situ formation of polylactide stereocomplex in the matrix

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ABSTRACT

Optically transparent poly(methyl methacrylate) (PMMA)-based blends with significantly enhanced mechanical and shape memory properties have been successfully prepared via in-situ formation of micro-scale polylactide stereocomplex crystallites (sc-PLA) in the PMMA matrix in this work. To achieve this goal, a certain content of poly(L-lactide) (PLLA) was firstly melt-blended with PMMA to obtain completely miscible PMMA/PLLA blends, and then an equimolar poly(D-lactide) (PDLA) was incorporated into the blends, giving rise to the in-situ formation of sc-PLA between PLLA and PDLA. In this way, the micro-scale sc-PLA particles were successfully fabricated and homogeneously dispersed in the PMMA matrix. Consequently, these resultant PMMA/sc-PLA blends possess extremely superior optical transparency, even when the content of sc-PLA reaches up to 12 wt%. A further increase in the content of sc-PLA would lead to the formation of sc-PLA network and aggregation, resulting in the deterioration of optical transparency. Moreover, the incorporation of sc-PLA micro-particles significantly enhances the mechanical property of PMMA and the maximum (≈103 MPa) of these blends demonstrates 50% increase than that (≈70 MPa) of PMMA. More importantly, it has been found that the shape recovery performance of PMMA could be effectively improved by the incorporation of sc-PLA. The optimal shape recovery ratio (86%) and high shape fixing ratio (almost 100%) can be obtained for the PMMA/sc12 blend which exhibits excellent optical transparency. It is reasonable to believe that these optically transparent blends with largely enhanced mechanical and shape memory properties possess great application potential in advanced shape memory fields.

1. Introduction

Optically transparent functional materials have attracted increasing attention owing to their great potential applications in advanced shape memory fields, such as visible heat-shrinkable tubes and ocular tissue [1–9]. Poly(methyl methacrylate) (PMMA), as a perfect transparent polymer, is a commendable candidate for optically transparent shape memory polymers (SMPs) owing to its advantages exhibited as follows: (i) PMMA with superior optical transparency, low cost and easy processing possesses great application prospect in the field of optically transparent shape memory materials; (ii) its biocompatibility and good corrosion resistance make it suitable for biomedical applications [10–15]; (iii) PMMA with relatively high glass transition temperature (approximately 100–120 °C) could be employed as high-temperature optically transparent SMPs without the deterioration of optical and mechanical properties when compared to other conventional optically transparent SMPs [16–22]. However, its unsatisfactory mechanical properties and the fact that the amorphous PMMA chains would irreversibly slide by one another during deformation inevitably lead to poor shape memory performance of PMMA, particularly, a low shape recovery ratio [23–27]. Currently, one of the most facile methods to simultaneously enhance the shape memory performance and mechanical property of polymers is to introduce nano-fillers, such as multi-walled carbon nanotubes (MWCNTs), gaphene oxide(GO), SiO_2 and hydroxyapatite (HA) [28–35]. Although the addition of these nano-fillers could greatly enhance the mechanical and shape memory properties of polymer matrix, it would also generally lead to the reduction of optical properties due to the aggregation of nano-fillers, especially at high

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content. Hence, the key challenge is to improve the mechanical property and shape memory performance, and maintain the excellent optical property of PMMA in the meantime.

Poly(L-lactide) (PLLA) bioplastic has been regarded as the most promising biopolymer because it is biodegradable, biocompatible, producible from renewable resources, and it possesses good mechanical property and good optical property as well [36–40]. It should be attached great importance that PLLA shows good miscibility with PMMA, and there have been a lot of reports on the research about melt-blending PLLA with PMMA [41–43]. For example, C. Samuel et al. have reported that the PLLA/PMMA blends after melt-processing were transparent, and the mechanical property of PMMA could be improved by the incorporation of PLLA [41]. Interestingly, the stereoselective association between equimolar PLLA and its enantiomer, poly(D-lactide) (PDLA) during the simple melt-blending process would give rise to the formation of polylactide stereocomplex (sc-PLA), which not merely inherits the biocompatibility, biodegradability and excellent optical properties of PLLA, but also possesses higher melting temperature(T_m), improved mechanical performance and better degradation resistance than those of PLLA and PDLA homocrystallites [44–53]. It is well-documented that the sc-PLA could be served as a novel filler and physical cross-linking point to improve the mechanical and rheological properties of polymer matrix, respectively [54,55]. For example, it has been reported that the sc-PLA particles could be formed in situ through simple melt-blending and homogeneously dispersed in the poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P34HB) matrix. The mechanical property of P34HB was improved from 4.2 MPa to 6.6 MPa with 30 wt% sc-PLA and the rheological property of P34HB was greatly enhanced by the incorporation of sc-PLA micro-particles. It was very interesting that the number-average particle size of sc-PLA in the P34HB matrix could be as small as 700 nm, which was within the range of visible wavelength (390–780 nm) [55]. Therefore, the in-situ information of sc-PLA micro-particles shows a great potential for the improvement of the mechanical and shape memory properties without the sacrifice of optical properties of PMMA.

In this work, the in-situ information and homogeneous dispersion of the micro-scale sc-PLA particles in the PMMA matrix have been successfully obtained through simple melt-blending. As a result, the mechanical property and shape memory performance of PMMA have been greatly enhanced, and its excellent optical transparency has been maintained simultaneously. It has been proven that, when the content of sc-PLA was less or equal to 12 wt%, sc-PLA particles with an average size (720–760 nm) were homogenously dispersed in PMMA matrix and had little influence on the optical property of PMMA. However, the optical properties of the resultant blends were deteriorated greatly by a further increase in the content of sc-PLA due to the formation of a network and aggregation of sc-PLA particles. Moreover, the prepared blends possessed much greater mechanical properties when compared with pure PMMA. Most interestingly, the effect of incorporation of sc-PLA on the shape memory performance of PMMA was investigated. The results demonstrated that the shape recovery ratio was improved from 48% to 86% when 12 wt% sc-PLA were incorporated into PMMA matrix and the outstanding shape fixing performance and excellent optical transparency were maintained. Hence, it is believed that PMMA with greatly enhanced mechanical and shape memory properties possesses great application prospect in the advanced shape memory fields.

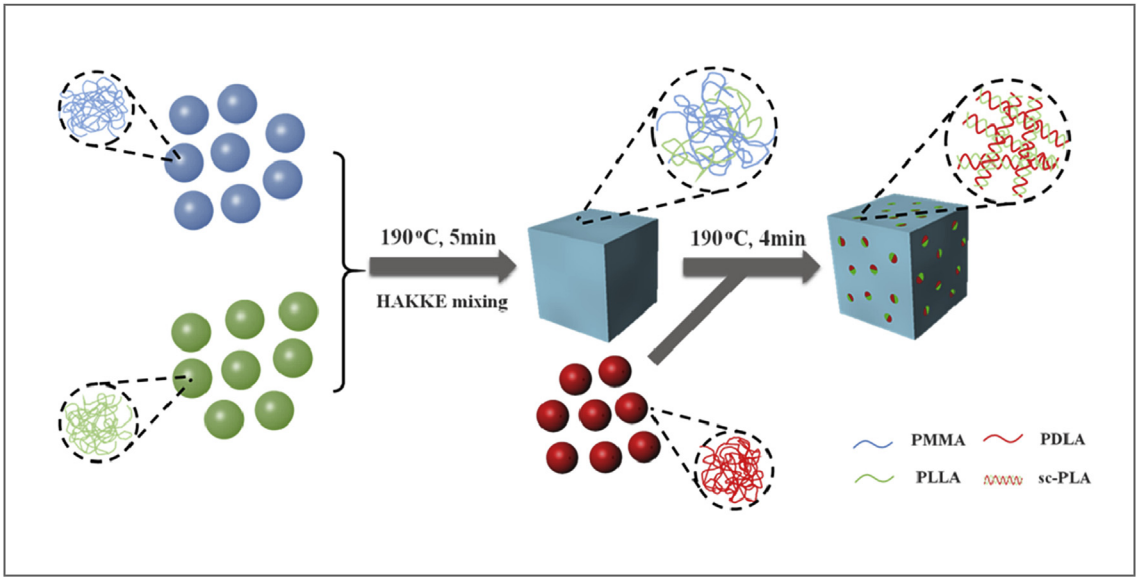
2. Materials and methods

2.1. Materials

A commercial PMMA pellets (CM205, density = 1.19 g/cm^3) was supplied by Taiwan Qimei Company. Poly(L-lactide) (PLLA, 4032D, density = 1.25 g/cm^3, M_w = 2.07 × 10^5 g mol^{-1}, polydispersity index = 1.74) with a D-isomer content of 1.2–1.6% was friendly provided by NatureWorks Co. Ltd., USA. Poly(D-lactide) (PDLA) with was purchased from Zhejiang Hisun Biomaterial Co., Ltd, China. Its D-isomer content and Mw were about 99.5% and 1.2 × 10^5 g mol^{-1}, respectively.

2.2. Preparation of PMMA/sc-PLA blends

Firstly, all polymers were dried in a vacuum oven at 60 °C for 48 h to remove any moisture. Then, in order to obtain homogeneous ternary blends, the melt compounding of the PMMA, PLLA, and PDLA were carried out by a Haake internal mixer (Thermo Fisher Scientific, USA) at 190 °C and 60 rpm. Specifically, PLLA and PMMA were first melt compounded for 5 min. Then, PDLA was



Scheme 1. Schematic representation of in-situ sc-PLA in the PMMA melting during melt blending.