European Polymer Journal 84 (2016) 1–12

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Selectively cross-linked poly (lactide)/ethylene-glycidyl methacrylate-vinyl acetate thermoplastic elastomers with partial dual-continuous network-like structures and shape memory performances

Pengwu Xu [a], Piming Ma [a,*], Xiaoxia Cai [b], Shiqiang Song [c], Yong Zhang [c], Weifu Dong [a], Mingqing Chen [a,*]

[a] The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, Wuxi 214122, China
[b] School of Food Science and Technology, Jiangnan University, 1800 Lihu Road, Wuxi 214122, China
[c] School of Chemistry and Chemical Engineering, Shanghai JiaoTong University, Shanghai 200240, China

ARTICLE INFO

Article history:
Received 23 July 2016
Received in revised form 31 August 2016
Accepted 2 September 2016
Available online 4 September 2016

Keywords:
Poly (lactide)
Ethylene-glycidyl methacrylate-vinyl acetate
Selective cross-link
Morphology
Shape memory

ABSTRACT

Bio-based poly (lactide)/ethylene-glycidyl methacrylate-vinyl acetate (PLA/EGVA) thermoplastic vulcanizates (TPVs) with partial dual-continuous network-like structures and shape memory property were made using methylhexahydrophthalic anhydride (MHHPA) as a cross-link agent. Epoxy groups of EGVA facilitated the selective cross-link of the EGVA phase in the PLA/EGVA blends, and two different chemical structures of the TPVs are identified based on the MHHPA content. The TPVs showed a special morphology evolution of the TPV, i.e., from sea-island-type to partial dual-continuous network-like morphology. As a consequence, the PLA/EGVA-based TPVs exhibited excellent shape memory property due to the strong resilience of the selectively cross-linked EGVA phase. The selective cross-link enhanced the complex viscosity (η^*), elasticity (G') and the solid-like behavior of the PLA/EGVA-based TPVs. Meanwhile, low tensile set (30%), moderate tensile strength (12 MPa) and elongation at break (250%), and tunable hardness (60–75 Shore A) of the TPVs are achieved by tailoring the cross-link density and phase morphology.

1. Introduction

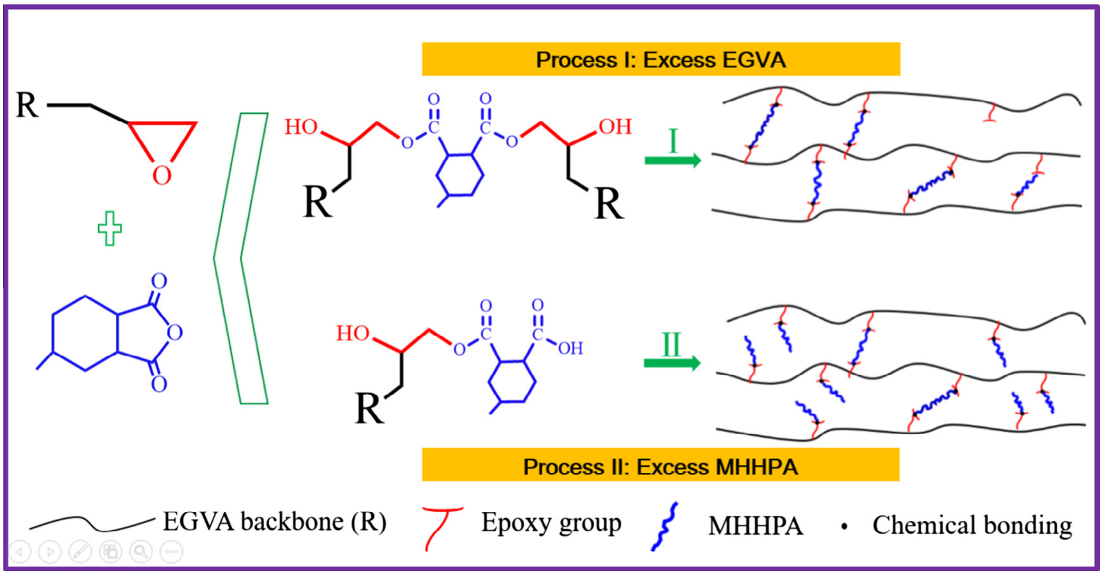
Thermoplastic vulcanizates (TPVs) is are a new generation of thermoplastic elastomers (TPE) prepared via dynamic vulcanization (DV), which consists of a dispersed cross-link-rubber phase and a continuous thermoplastic phase [1]. The DV process aims at selectively cross-link of rubber phase without extensive propagation of the cross-link into the plastic phase. Thus, it is a process of vulcanizing an elastomer during the melt mixing with a molten plastic [2].

The most successful TPV is the propylene/ethylene-propylene-diene (PP/EPDM) compounds which have been used in the auto industry [3,4]. EPDM is a synthetic rubber with a small portion of —C=C— bonds that facilitate the selective cross-link of the rubber phase. So far, the preparation of TPV is mainly limited to unsaturated rubbers such as EPDM, natural rubber (NR)

---

[*] Corresponding authors.
E-mail addresses: p.ma@jiangnan.edu.cn (P. Ma), mq-chen@jiangnan.edu.cn (M. Chen).

http://dx.doi.org/10.1016/j.eurpolymj.2016.09.004
0014-3057/© 2016 Elsevier Ltd. All rights reserved.



Scheme 1. The schematic illustration of the chemical reactions between the EGVA and MHHPA as a function of MHHPA content. Only the dominant reactions are illustrated while some reactions with low possibility are neglected.

and styrene-butadiene rubber (SBR) while the plastic is limited to polyolefin, which however is not preferably designed in terms of sustainability and environmental protection [5–9].

Poly (lactide), PLA, is a promising biopolymer because of its biobased and biodegradable features, superior physical-mechanical properties, easy process ability and relatively low cost [10]. Thus, it is potential to serve as the thermoplastic phase of a new type of TPV. Chen et al. prepared PLA/NR blends where the NR dosage was below 40 wt% and the cross-linked NR phase showed a continuous network-like dispersion [11]. Liu et al. reported a biobased and super-tough TPV consisting of 80 wt% of PLA, 20 wt% of unsaturated aliphatic polyester elastomer (UPE) and initiator [12]. However, the properties of the PLA/NR and PLA/UPE compounds are more like rubber-toughened plastics rather than elastomers.

Ethylene-co-vinyl acetate copolymer varies from thermoplastic to rubber and then to thermoplastic again with increasing the vinyl acetate (VAc) content from 0 to 100 wt%. It can be made from either petroleum-based or biobased raw materials since biobased ethylene (e.g., Braskem, Brazil) and vinyl acetate (e.g., Wacker, Germany) are already available on the market. The well-known rubber grade EVA, Levapren EVM®, are saturated copolymers showing activity with peroxide [13]. In our previous study [14,15], PLA/EVA-based TPV with superior mechanical properties were fabricated using peroxide as a cross-link agent. Whereas the continuous PLA phase could not get rid of cross-linking in the presence of peroxide, consequently the flow ability, i.e., thermoprocessability, of the resulting TPV is affected to a certain extent. Therefore, it would be interesting to make PLA/EVA-based TPV without cross-link of the PLA phase.

The structural of the ethylene-glycidyl methacrylate-vinyl acetate copolymers (EGVA) is similar to the EVA, but the only difference is that glycidyl methacrylate units (epoxy groups) was grafted to the structural unit in the EGVA as shown in Scheme 1. Only the epoxy groups in EGVA would provide the cross-link points and the matrix would not be affected. Therefore the EGVA would be valuable to fabricate the TPV.

In this work, the EGVA and PLA are used to prepare partially biobased TPVs by using methylhexahydrophthalic anhydride (MHHPA) as a cross-link agent. A small amount of glycidyl methacrylate units (epoxy groups) as cross-link points leave the PLA free of reaction. It is hopeful to create specific niche applications of the PLA/EGVA-based TPVs in intelligent medical devices due to their shape memory features. The chemical structure, rheology, (dynamic) mechanical properties and shape memory features of the TPV are discussed in detail, and the structure-property relationship is investigated.

2. Experimental section

2.1. Materials

Poly (lactide) (PLA, Ingeo 2003D) with a melt flow index (MFI) of 3.25 g/10 min (190 °C, 2.16 kg) was purchased from Nature Works LLC, USA. Rubber grade EGVA (Levapren®600 NPG) with a vinyl acetate (VAc) content of 60 wt% and a glycidyl methacrylate content of 1.9 wt% was kindly supplied by Lanxess Chemical Co., Ltd., Qingdao, China. Chloroform and methylhexahydrophthalic anhydride (MHHPA) were supplied by Zhejiang Alpharm Chemical Technology Co., Ltd., China. All chemicals were used as received.