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Bio-based poly(lactide)/ethylene-*co*-vinyl acetate thermoplastic vulcanizates by dynamic crosslinking: structure vs. property

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Abstract: Bio-based thermoplastic vulcanizates (TPV) from poly(lactide) (PLA) and ethylene-*co*-vinyl acetate rubber (EVA) was fabricated by using dicumyl peroxide (DCP) as a curing agent, which is the first time to show the application of PLA in elastic materials. A two-stage competing reaction mechanism as a function of peroxide content is revealed via gel analysis. The crosslink of EVA is dominate at low DCP content (< 1 wt%) which leveled off when the DCP content exceeded 1 wt%. The gel fraction of the EVA and PLA phases can be tuned by the DCP content and fabrication techniques. A desirable phase inversion of the PLA/EVA blends due to the selective dynamic curing was monitored by both atomic force microscope (AFM) and dynamic mechanical analysis (DMA). Consequently, PLA/EVA thermoplastic vulcanizates with high strength, high elongation at break, low tensile set and intermediate hardness were obtained. Moreover, the mechanical properties can be tuned by DCP content and plasticization. The correlation between the structures and the properties is investigated.

Keywords: Poly(lactide); ethylene-*co*-vinyl acetate; thermoplastic vulcanizates; phase morphology; mechanical properties.

1. Introduction

The wide use of traditional rubber and plastic has been received considerable attention recent years due to their unsustainability and environmental pollution. The use of bio-based and biodegradable polymers provides a possible solution to the above issues.[1,2] The well-known bio-based and degradable plastics are poly(hydroxyalkonates) (PHA), poly(lactide) (PLA) and thermoplastic starch (TPS) etc.[3-5]

PLA with high strength, transparency and relatively low cost is derived from bio-resources. It is regarded as one of the most promising bio-based polymers.[4] However, PLA is too brittle at room temperature (elongation at break < 10%, impact toughness < 3 kJ/m^2) for applications where plastic deformation at high stress levels is required.[6] As a result, many approaches such as plasticization, blending and copolymerization have been attempted to improve its toughness and flexibility.[7-9] Plasticizers e.g. oligomeric lactic acid, citrate esters and poly(ethylene glycol) could improve the flexibility and ductility of PLA, but lead to leaching in environments and phase separation with storage time.[10] Another effective approach is blending PLA with rubbery polymers such as ethylene-*co*-vinyl acetate copolymer (EVA),[6] natural rubber (NR),[11] ethylene-*co*-octane copolymer (POE)[12] and poly(ether-*b*-amide) (PEBA).[13-15] The introduction of PEBA can enhance the flexibility and toughness of PLA, however the enhancement was limited due to the immiscibility and the weak interfacial adhesion.[14,15]

Compared with plastics, less bio-based elastomer or rubber, except the well-known natural rubber, was commercially available due to the chain stiffness and relatively high glass transition temperature (T_g) of the bio-based polymers. Thermoplastic elastomer (TPE) is a new class of copolymers or polymer blend that exhibits rubber-like behavior but can be melt-processed like thermoplastics. The well-known TPE are styrene-b-(ethylene-*co*-butylene)-b-styrene (SEBS) copolymer and poly(propylene)/poly(ethylene-propylene-diene) (PP/EPDM) blends.[16-19] The combination of these properties is resulted from a two-phase structure: a soft phase gives the rubbery properties in the solid state, whereas a hard phase provides crosslinks and retains melt processability. Thermoplastic vulcanizates (TPV) are a highly engineered class of TPE, comprising a cross-linked elastomeric dispersed phase and a melt processable plastic matrix. TPV is usually fabricated via dynamic vulcanization where mixing and cross-linking are carried out simultaneously.

Besides typical elastomeric behavior, TPV also possess advantages in comparison with traditional rubber vulcanizates such as reusable after disposal, short processing time and energy saving.[20,21] So far, the most commercialized TPV is PP/EPDM compounds which has been widely used in auto industry.[22,23] Recently, EVA-based TPV were reported as well in literature, e.g. PP/EVA, poly(ethylene)/EVA and polyamide/EVA thermoplastic vulcanizates.[24-26]

EVA is a commodity copolymer which can be either thermoplastic or rubber depending on the vinyl acetate (VAc) content. It shows typical rubbery behavior when the VAc content is between 40 and 90 wt% (LEVAPREN® EVM, Lanxess) with excellent flexibility, transparency, weather resistance, oil resistance and good affinity with filler and pigment. It can be cured by peroxide.[27] EVA currently is mainly derived from petroleum, however it can also be made from bio-resources since both bio-based ethylene (e.g. Braskem, Brazil) and vinyl acetate (e.g. Wacker, Germany) are already commercialized based on the new developed bioethanol technology. In our previous study, compatible PLA/EVA blends with high strength and super (low temperature) toughness were obtained by physical compounding.[6] Therefore, PLA and EVA rubber might be an ideal combination for bio-based TPV. To the authors' knowledge, the bio-based TPV is hardly reported.

The prime objective of this paper is to provide a simple route to prepare bio-based thermoplastic vulcanizate by dynamic vulcanization of PLA/EVA blends in the presence of dicumyl peroxide. To reveal the relationship between structure and properties, crosslink of each phase, phase morphology, phase inversion, rheological behavior and (dynamic) mechanical properties were systematically investigated. The present work not only provides a fundamental investigation on the PLA/EVA-based TPV, but may also broaden the application range of both PLA and EVA rubber.

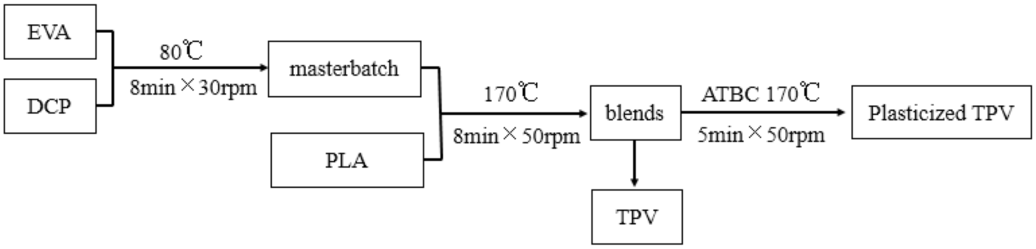
2. Experimental section

2.1 Materials

Poly(lactide) (PLA, Ingeo 2003D) was purchased from Nature Works LLC, U.S.A, with a melt flow index (MFI) of 3.25 g/10min (190 °C, 2.16 kg). The content of L-lactide in the PLA is approximately 96%. Rubber grade EVA (Levapren® EVM500) with a Mooney Viscosity of 27±4 MU (ML (1+4) 100℃) was supplied by Lanxess Chemical Co., Ltd., Qingdao, China. The average vinyl acetate (VAc) content in the EVA is 50 wt% Chloroform (AR) and Dicumyl peroxide (DCP, purity ⩾ 99.5 %) were supplied by Sinopharm Group Chemical Reagent Co., Ltd., China. Acetyl tributyl citrate (ATBC, purity ⩾ 99.5 %) was purchased from Guangzhou Chemical Industry Co. Ltd., China. All chemicals were used as received.

2.2. Sample Preparation

Prior to blending, PLA and EVA were dried overnight in a vacuum oven at 80°C and 60°C, respectively. In order to crosslink EVA phase rather than PLA phase, DCP was premixed with EVA at 80 °C in a internal mixer (RM-200, HABO Electrical Appliance Manufacturing Company, China) for 8 min at a rotor speed of 30 rpm to form a homogeneous EVA/DCP rubber compound. The rubber compound was then blended with molten PLA at 170°C by using the same device for 8 min at a rotor speed of 50 rpm, where dynamic crosslink occurred. Since DCP content is so crucial to the structure and properties of the TPV that different amounts of DCP (0 - 3 wt% based on EVA) were investigated while the weight ratio of PLA/EVA was fixed at 40/60 (wt/wt). Plasticized TPV was obtained by feeding ATBC at the end of above process and continue mixing for 5 minutes. All the samples were finally compression molded into sheets (1 mm in thickness) at 170 °C for 3 min. The compression-molded samples were used for characterizations. The above preparation routes are summarized in Scheme 1.



Scheme 1. Preparation routes of PLA/EVA-based TPV.

2.3 Characterizations

Crosslink structure analysis: The crosslink structures of the TPV were studied by swelling equilibrium experiments. Specimens ($2\times1\times0.5$ mm^3) of each sample were accurately weighted (M_0) and then immersed in chloroform for 72 hours to reach a swelling equilibrium. The swollen specimens were taken out, wiped and weighted to an accuracy of 0.1 mg at a given time (M_1). The swollen specimens were then dried in a vacuum oven at 60 °C until the mass change of less than 0.1 mg. The dried residuals, defined as “gel” in this work, were then weighted to an accuracy of 0.1 mg (M_2). The gel content (W_R) of the TPV was calculated via $W_R = M_2 / M_0 \times 100\%$. Three specimens of each sample were measured and an average value was presented. All the experiments were performed at 30℃.

With an assumption of volume additivity of gel and absorbed solvent during swelling, the gel swelling ratio (S) of the TPV was calculated using the equation 1,[28] i.e.

$$S = \frac{\frac{a\times M_2}{\rho_{PLA}}+\frac{b\times M_2}{\rho_{EVA}}+\frac{M_S}{\rho_S}}{\frac{a\times M_2}{\rho_{PLA}}+\frac{b\times M_2}{\rho_{EVA}}} \qquad (1)$$

where ρ_{PLA} and ρ_{EVA} are the density of PLA and the solvent, respectively, while a and b are the mass fraction of PLA and EVA in the gel, respectively. M_s is the weight of absorbed solvent, i.e. $M_s = M_1 - M_2$.

Thermal gravimetric analysis (TGA): TGA (1100SF, Meteler-Toledo International Trade Co., Ltd. Switzerland) was used to evaluate the thermal decomposition behavior and the composition of the TPV gel. The TGA measurements were performed from 20 to 600 ℃ at 10 ℃/min in nitrogen atmosphere.

Rheological behavior: Dynamic rheological experiments were carried out on a DHR-2 rheometer (TA Instruments, USA) in a plate-plate configuration (25 mm in diameter and 1 mm in gap) at 170 °C. The samples were tested in a frequency-sweep mode (from 100 to 0.01 Hz) with an optimal strain of 1%. The optimal strain was pre-determined from a strain-sweep experiment to make sure the measurements were performed in the linear viscoelastic strain range.

Dynamic mechanical analysis (DMA): DMA (Q800, TA Instruments, USA) was carried out in a tensile-film mode to measure the dynamic mechanical properties and thermal behavior of the TPV. The specimens ($15 \times 5.3 \times 0.5$ mm^3) were tested under a nitrogen atmosphere from -60 ℃ to 120 ℃ at a temperature ramp of 3 ℃/min. The frequency and amplitude were set as 1 Hz and 20 μm, respectively. The storage modulus and loss modulus were recorded as a function of temperature.

Atomic force microscope (AFM): AFM (Nanonavi E-Sweep SPM, Seiko Instruments, Japan) was used to study the phase morphology and phase inversion of the TPV as a function of DCP content. The AFM was operated in a tapping mode under an air atmosphere. The TPV samples were cryo-microtomed and the resulting ultrasmooth surfaces were subjected to AFM characterization.

Mechanical properties: Tensile properties of the TPV were measured by using a universal tensile tester (Instron 5967, USA) according to GBT529-2008 standard at a tensile speed of 200 mm/min. The dimension of the parallel section of the tensile bar is $25 \times 4 \times 1$ mm^3. Five specimens of each sample were tested and the averaged results were presented. The tensile permanent set (S_p) of each specimen was measured according to $S_p = (L_1\text{-}L_0)/L_0 \times 100\%$, where L_0 is the original length of the parallel section, while L_1 is the final length of the stretched parallel section which was measured 24 hours after fracture. The hardness was measured by using a Shore D hardness tester (LX-D, Qianzhou Measuring Instrument, Wuxi, China) according to GB/T 531.1-2008 standard. All the mechanical tests were performed at room temperature.

3. Results and discussion

3.1. Crosslink-structure analysis of the PLA/EVA-based TPV

Crosslink network, gel, was generated after addition of dycumyl peroxide (DCP) in the PLA/EVA blends, i.e. TPV. The structure and composition of the gel are so important to phase morphology and mechanical properties of the TPV, thus it was first studied by using swelling equilibrium experiments, as described in Section 2.3.

The gel swelling ratios (*S*) of the TPV were measured as a function of DCP content and the results are shown in Figure 1. The *S* values were gradually decreased from 42 to 23 with increasing the DCP content from 0.5 wt% to 3.0 wt%. These results indicate an increase in crosslink density of the gel with DCP content, which is more pronounced at low DCP contents (0.5 - 1.0 wt%). On the other hand, the crosslink density of the gel is low since the *S* values are larger than 20 even at DCP content of 3.0 wt%.

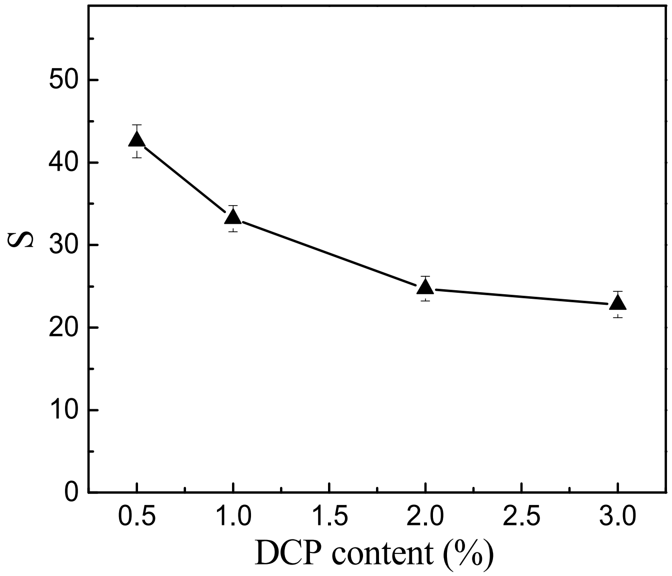


Figure 1. The swelling ratio (*S*) of the PLA/EVA-based TPV as a function of DCP content.

Although the DCP was premixed in EVA, a certain amount of DCP still can migrate into the PLA phase during subsequent compounding. It is known that both EVA and PLA are crosslinkable with peroxide following a free-radical reaction mechanism.[29,30] Such reaction at the interface would increase the compatibility of polymer blends resulting in enhanced mechanical properties of TPV.[31-33] Therefore, the gel of the TPV likely consist of both PLA and EVA components. The composition of gel not only affected the morphology and properties but also the processability of the TPV.

The decomposition behavior and composition of the gel were characterized by using thermal gravimetric analysis (TGA), as shown in Figure 2. EVA exhibited two-step decomposition behavior relating to the side chain (CH3COO-, around 335 °C) and the main chain (-CH2-CH2-, around 445 °C) respectively,[32] while PLA decomposed in a single step (around 340 °C). It is observed from Figure 2 that the mass residual of gel at 400 °C decreased monotonically with increasing the DCP content, which demonstrated an increase in PLA fraction in the gel.

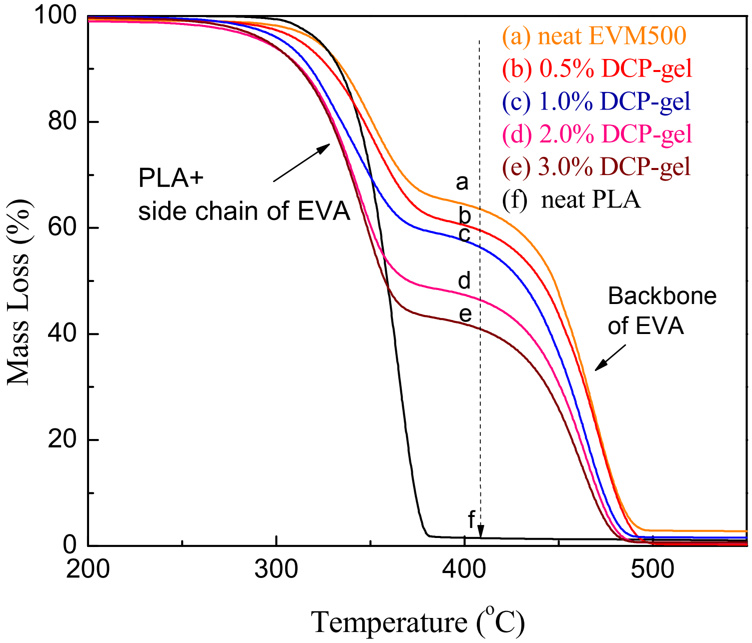


Figure 2. TGA curves of EVA, PLA and gel of the TPV.

The quantity of each component in the gel and the gel fraction of each component can be calculated base on the overall gel fraction and the TGA analysis. The results are shown in Figure 3. Apparently, the gel fraction of EVA phase is always higher than that of PLA phase at the examined DCP range due to the premixing technique, while the overall gel fraction of the TPV is in between. Interestingly, a two-stage curing behavior as a function of DCP content was observed. In stage I (DCP ≤ 1 wt%), the gel fraction of EVA phase increased linearly with DCP content, whereas the gel fraction of PLA phase kept at a low level (< 10 wt%). On the contrary, the gel fraction of EVA leveled off in stage II (DCP ≥ 1.5 wt%), while the gel fraction of PLA phase increased linearly with the DCP content. These results clearly indicate that it is mainly the EVA phase crosslinked at low DCP content. DCP is “saturated” in the EVA phase when it exceeds 1 wt%, and the excess amount of DCP could migrate into the PLA phase in mixing, leading to the undesirable crosslink of PLA phase. To serve as a commodity TPV material, the higher gel fraction of rubber phase (EVA) and the lower gel fraction of the plastic phase (PLA) the better.[24] Thus, the ideal DCP content should be around 1 wt%.

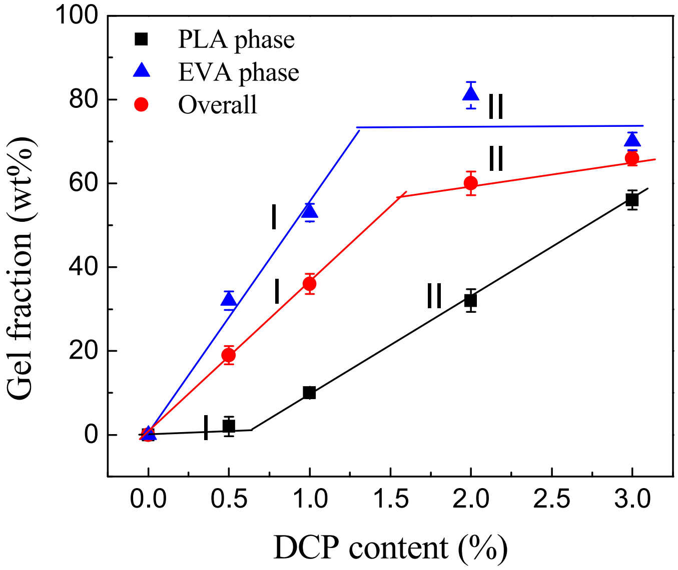
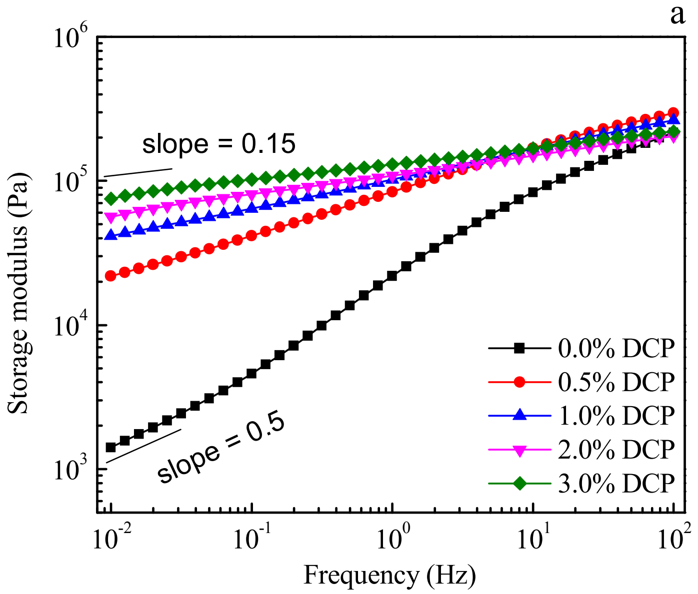


Figure 3. Gel fraction of each component in the PLA/EVA-based TPV as a function of DCP content.

3.2 Rheological behavior of the PLA/EVA-based TPV

Rheology has been proven a powerful technique to investigate structures of polymer and polymer blends. The storage modulus (G') and complex viscosity (η^*) of the PLA/EVA-based TPV are shown as a function of DCP content and frequency (Figures 4a and b). The G' and η^* are affected by the three dimensional network that resulted from dynamic crosslinking. Consequently, it leads to a sharp rise in both G' and η^* with DCP content at the frequency (ω) less than 1 Hz, indicating an increased melt elasticity of the TPV. When the frequency approaches to 0.01 Hz, the slope of log(G') versus log(ω) was decreased from 0.5 to 0.15 with DCP content up to 3.0 wt% (Figure 4a), meanwhile the slope of log(η^*) vs log(ω) was reduced from -0.45 to -0.85 (Figure 4b). Apparently, the TPV showed solid-like behavior at low frequency zone due to the presence of network. These results are well consistent with the gel analysis. It has to be remarked that all samples show similar viscosity at high frequency zone, which means the TPV remain processability after the dynamic crosslinking.



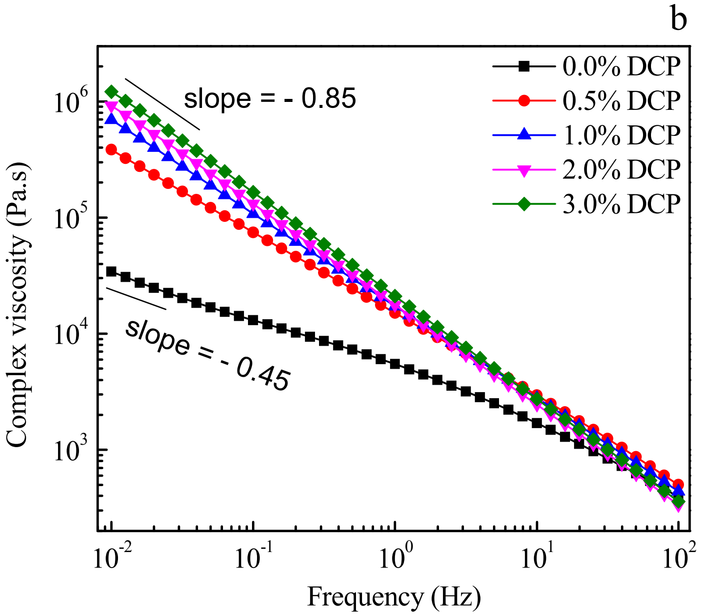


Figure 4. (a) storage modulus and (b) complex viscosity of the PLA/EVA-based TPV as a function of frequency and DCP content.

3.4. Phase morphology of the PLA/EVA-based TPV

It is well known that the mechanical properties of multiphase polymer blends depend largely upon morphology, thus AFM was used to identify the phase structure of the dynamically vulcanized EVA/PLA blends with different DCP content, as shown in Figure 5. The dark region in the phase-angle images (Figure 5a, b and c) corresponds to the EVA phase while the bright region corresponds to the PLA phase. A contrast inversion occurred in the height images (Figure 5a', b' and c')

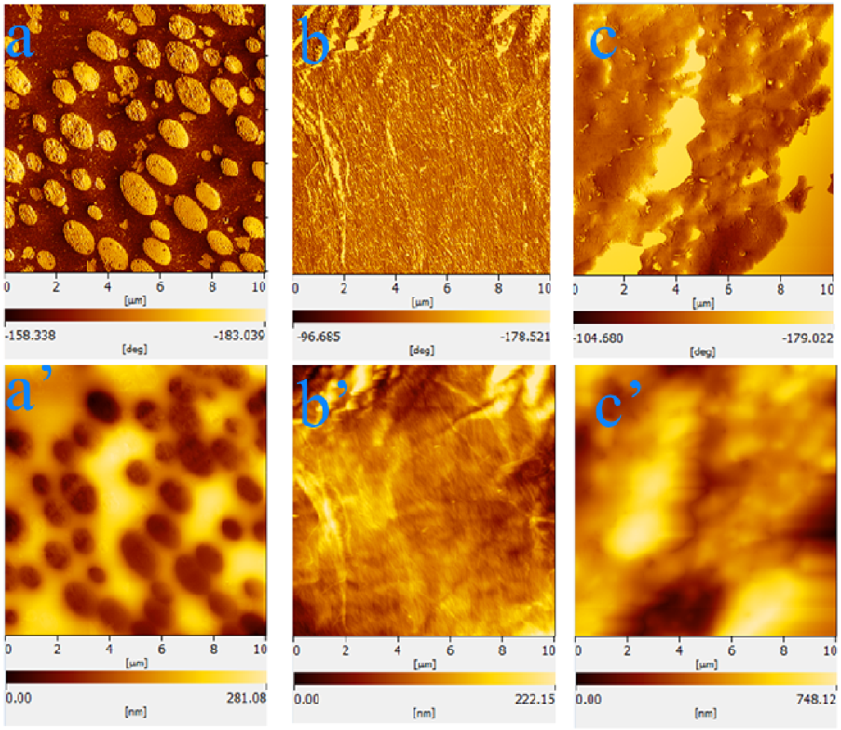
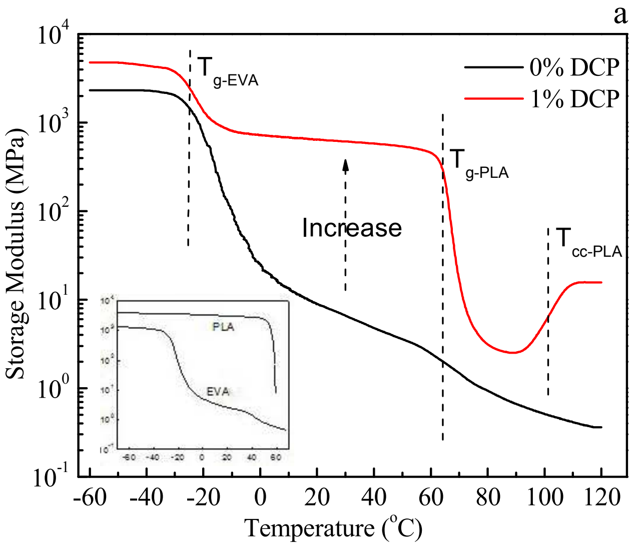


Figure 5. AFM images of the PLA/EVA-based TPV with different DCP content. (a, a') 0.0, (b, b') 0.5 and (c, c') 1.0 wt%. (a, b, c) are phase images while (a', b', c') are height images.

Apparently, a typical sea-island structure is observed in the blend without DCP, where PLA is the fine dispersed phase (Figure 5a and a'). As designed, a phase inversion occurred when 1.0 wt% of DCP was added (Figure 5c and c'). A cocontinuous-like morphology seems to be present in the image 5b and b' which is regarded as a transition state of the phase inversion with DCP content. The phase inversion is mainly due to the increased viscosity of EVA phase caused by dynamic crosslinking. During dynamic vulcanization, the EVA rubber phase was dominantly crosslinked and immobilized, hence they could be further broken into micron-sized particles under the applied shear field.[35] The particle size is associated with the crosslink extent, the viscosity ratio of the two phases, shear rate and processing time.[36] In addition, no significant interfacial debonding is observed from the AFM images, showing fine wetting and interactions between the EVA and PLA phases.

3.3 Dynamic mechanical properties of the PLA/EVA-based TPV

The dynamic mechanical properties of the PLA/EVA blends with and without DCP were studied by using dynamic mechanical analysis (DMA). The storage modulus (*E'*) and loss modulus (*E''*) as a function of temperature are shown in Figure 6. The peak temperatures of *E''* are referred to as glass transition temperatures (T_g) in this work.



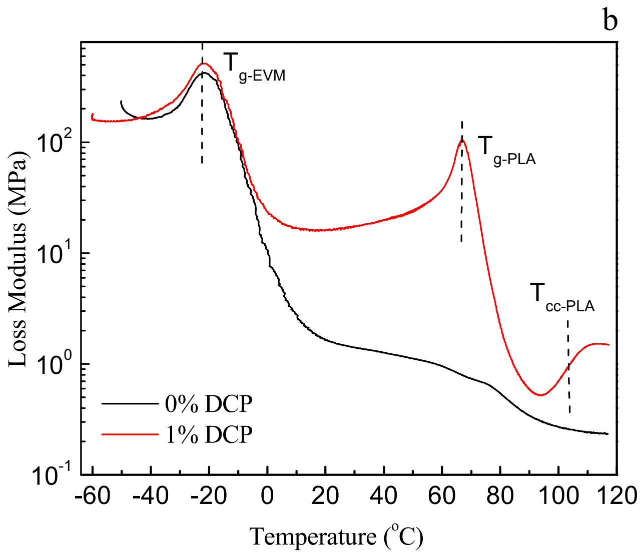


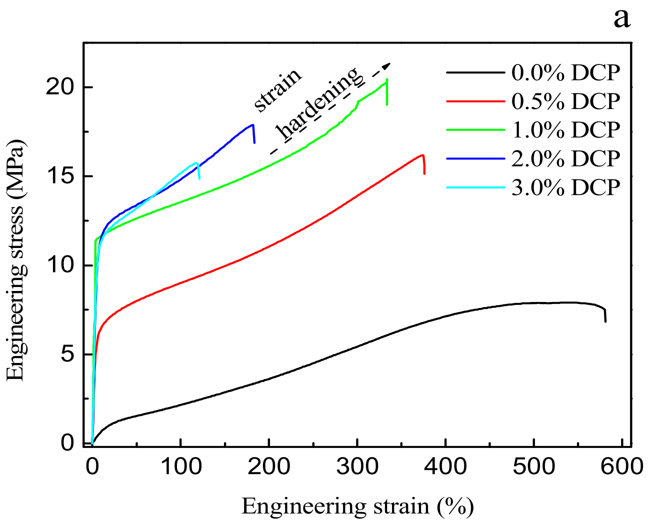
Figure 6. (a) storage modulus (*E'*) and (b) loss modulus (*E"*) of the PLA/EVA-based TPV as a function of temperature and DCP.

In general, polymer chains and segments are rigid below its T_g, thus both the two samples show high *E'* values (> 2000 MPa) at low temperatures (< $T_{g\text{-}EVA}$≈ −28 ℃), as shown in Figure 6a. The *E'* of the physical PLA/EVA blend (0 wt% DCP) was dropped by 2 orders of magnitudes with increasing the temperature up to $T_{g\text{-}EVA}$. This result indicates that EVA is the matrix while PLA is the dispersed phase. In contrast, the *E'* of the PLA/EVA-based TPV (cured with 1 wt% of DCP) remained above 500 MPa up to the $T_{g\text{-}PLA}$ (≈ 65 ℃), indicating a continued PLA phase in the PLA/EVA-based TPV. Evidently, a phase inversion of the PLA/EVA blends occurred after the dynamic crosslinking, which is consistent with the morphology observation (AFM images). It was also noticed that the *E'* of the PLA/EVA-based TPV increased at around 100 ℃ which is due to cold crystallization (T_{cc}) of the PLA phase.[37] The loss modulus as a function of temperature is shown in Figure 6b. Only one *E"* peak (corresponding to the $T_{g\text{-}EVA}$) is observed in the physical PLA/EVA blend, showing that the fine dispersed PLA domains have less effect on the *E"* in comparison with the EVA matrix. On the other hand, the $T_{g\text{-}PLA}$ response is clearly visible in the PLA/EVA-based TPV due to the phase inversion.

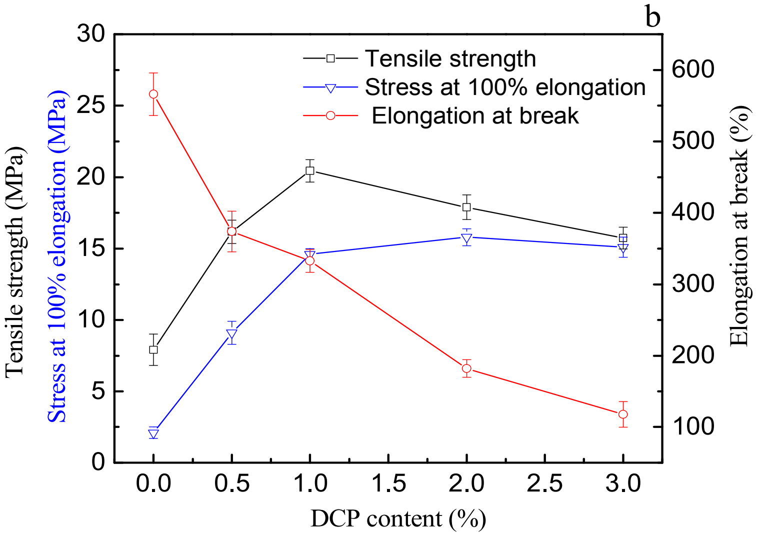
3.5. Mechanical properties

3.5.1. Effect of crosslink agent

The stress-strain curves and mechanical properties of the EVA/PLA-based TPV, as a function of DCP content, are presented in Figures 7 a, b and c, respectively. PLA is a brittle polymeric material with low elongation at break ($\varepsilon_b \approx 4\%$) and high strength ($\sigma_t \approx 60$ - 70 MPa),[6] while the σ_t and ε_b of the EVA rubber are around 5 MPa and 800% respectively. The PLA/EVA (40/60) blend in which EVA is the matrix showed typical tensile behavior of an uncured rubber, i.e. high ε_b (≈ 600%) but low σ_t (8 MPa) and tensile modulus (Figure 7a). After addition of DCP, the stress-strain behavior changed obviously. Notably, much higher tensile modulus and more pronounced strain hardening were observed for the TPV in comparison with the physical PLA/EVA blend. It can be seen from Figure 7b that the σ_t was gradually increased from 8 MPa to 20 MPa with DCP up to 1 wt%, and decreased with a further increase in DCP content. The stress at 100% elongation ($\sigma_{100\%}$) exhibited similar trend as the σ_t. Meanwhile the ε_b decreased monotonically with the DCP content which is in agreement with the mechanical behavior of cured rubber.[26] Tensile set (T_S) and hardness are important for TPV. Low T_S indicate high elastic recovery of a rubbery material. The tensile set of the PLA/EVA blend is 90% which is reduced to around 30% after addition of 0.5 - 3.0 wt%. On the other hand, the hardness of the PLA/EVA blend was enhanced from 14 Shore D to around 50 Shore D after addition of DCP due to the phase inversion. Apparently, the mechanical behavior is well associate with the above discussed crosslink structure and the phase morphology of the PLA/EVA-based TPV.


a
Engineering stress (MPa)
Engineering strain (%)
0
5
10
15
20
0
100
200
300
400
500
600
strain
hardening
0.0% DCP
0.5% DCP
1.0% DCP
2.0% DCP
3.0% DCP

1


b
Tensile strength (MPa)
Stress at 100% elongation (MPa)
Elongation at break (%)
DCP content (%)
0
5
10
15
20
25
30
100
200
300
400
500
600
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Tensile strength
Stress at 100% elongation
Elongation at break

2

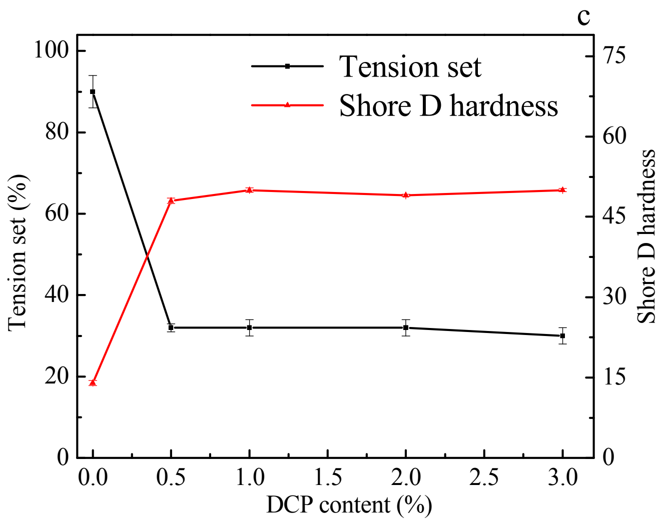


Figure 7. Mechanical behavior of the PLA/EVA-based TPV as a function of DCP content: (a) stress-strain curves, (b) tensile strength, stress at 100% elongation and elongation at break and (c) tensile set and hardness.

3.5.2. Effect of plasticization

As discussed above, good mechanical properties of the PLA/EVA-based TPV were obtained at the DCP content of 1.0 wt% such as high tensile strength, reasonable elongation at break and relatively low tensile set. In order to enhance the flexibility and reduce the hardness of the TPV (1.0 wt% DCP), a plasticizer, i.e. acetyl tributyl citrate (ATBC) was incorporated into the TPV. The mechanical properties of the TPV with varying amount of ATBC are shown in Figure 8. As expected the tensile strength and hardness of the TPV decreased gradually with increasing the ATBC content. Meanwhile, the elongation at break was increased from 330% to 500%. It has to be remarked that larger tensile set is obtained as well due to the higher elongation at break and plasticization of the PLA matrix.

To summarize, the mechanical properties of the PLA/EVA-based TPV can be tuned by the DCP content and the utilization of plasticizer.

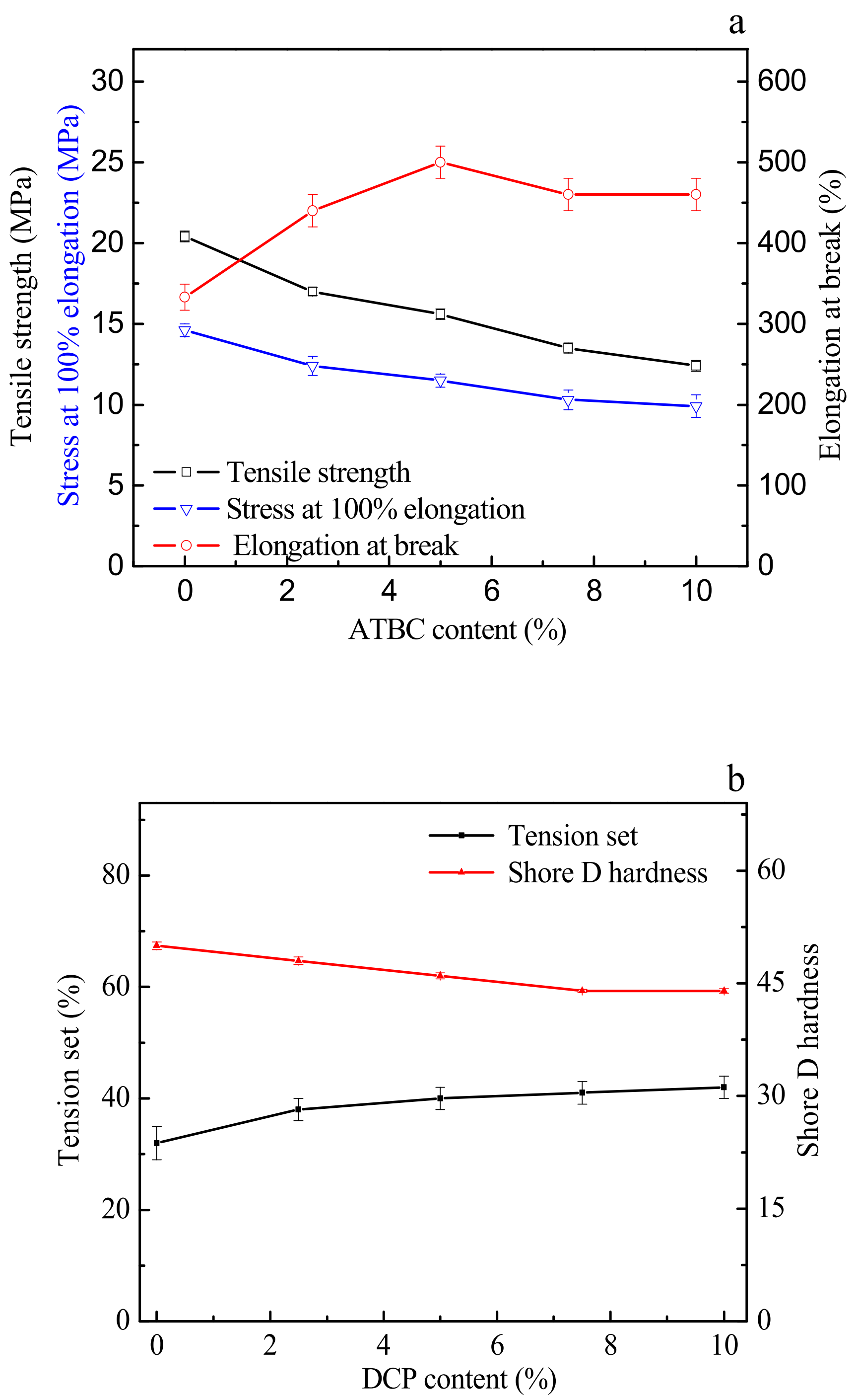


Figure 8. Mechanical properties of the PLA/EVA-based TPV with varying amount of ATBC: (a) tensile strength, stress at 100% elongation and elongation at break and (b) tensile set and hardness.

4. Conclusions

A series of PLA/EVA-based TPV were successfully prepared via two-step mixing and dynamic vulcanization in the presence of dicumyl peroxide (DCP). Due to the two-step mixing technique, the gel fraction of EVA phase is always higher than that of the PLA. Crosslink of the EVA is dominantly when the DCP content is lower than 1 wt% while the gel fraction of PLA phase increased linearly when the DCP content exceeds 1 wt%. A desirable phase inversion occurred in the PLA/EVA(40/60) blend after addition of a small amount of DCP (0.5 - 3.0 wt%), which is confirmed by the AFM observation and dynamical mechanical analysis. The mechanical properties reveal that PLA/EVA-based TPV with high strength, high elongation at break, intermediate hardness and relatively low tensile set are obtained by tuning the DCP concentration. The optimum DCP content, in terms of mechanical properties, is proposed at around 1.0 wt%. In addition, the mechanical properties of the TPV can be tuned further by plasticization. The development of the new bio-based PLA/EVA-based TPV may broaden the application range of both PLA and EVA rubber.

Acknowledgments

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