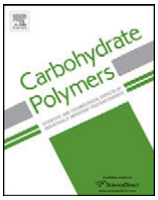
Carbohydrate Polymers 83 (2011) 659–664

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Plasticization of corn starch by polyol mixtures

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ARTICLE INFO

Article history:
Received 10 May 2010
Received in revised form 13 August 2010
Accepted 15 August 2010
Available online 21 August 2010

Keywords:
Starch
Glycerol
Polyol
Composite
Biodegradable

ABSTRACT

Polyol mixtures including mixture of conventional plasticizer glycerol and higher molecular weight polyol (HP) such as xylitol, sorbitol and maltitol were used to plasticize corn starch by melt-blending method, and effect of the polyol mixture on the pocessibility, microstructures, thermal stability and mechanical properties of these starch composites (SC) were investigated. The introduction of HP providing greater processing torque can dramatically reduce the strong molecular chain interaction in starch without obvious residual starch granules in the starch composites. The increasing of the molecular weight and content of HP in polyol mixture is beneficial for the significant enhancement of the thermal stability and mechanical strength of the starch composite. Meanwhile, the addition of HP besides conventional glycerol increases the modulus and phase transition temperature of the starch composite too.

1. Introduction

In recent years, increasing concern about the environmental pollution problem resulted from petroleum-derived plastics has promoted the development and rapid advance of the biodegradable materials. Among these biodegradable materials, natural starch-based plastics have drawn more and more attentions of researchers due to its availability, renewability and low cost (Averous & Fringant, 2001; Matzinos, Tserki, Kontoyiannis, & Panayiotou, 2002; Souza & Andrade, 2001). However, possessing higher decomposition temperature than melting temperature, native starch can not be considered as a typical thermoplastic polymer, and merely after the plasticization under the action of adequate temperature and mechanical shear force can native starch be processed like common plastics (Mathew & Dufresne, 2002; Myllarinen, Partanen, Seppala, & Forssell, 2002; Stepto, 2000).

Various plasticizers such as glycerol, water, urea and formamide have been tried for starch to decrease its strong molecular chain interactions and improve its processability and mechanical strengths. As a small molecule, water is not stable and evaporates into the environment when starch composites are stored in low relative humidity conditions. Besides water, glycerol is another common plasticizer for preparing the starch composites, but its remarkable sensitivity to moisture content still causes a great limit for the wide application of starch composites as plastics (Liu, Yi, & Feng, 2001; Lorcks, 1998; Ma, Yu, & Jin, 2004). The addition of formamide in glycerol-water plasticized starch can alleviate the destructurization of the polysaccharide chain due to the removal of water and dramatically improve the fluidity and elongation of starch composites without sacrificing the tensile strength, with the formation of stronger hydrogen-bond interactions of formamide with starch (Wang, Yu, Ma, & Han, 2009; Wang, Zhang, Liu, & Wang, 2009). During the preparation of bidegradable starch/clay nanocomposites, plasticizer mixture of urea and ethanolamine is demonstrated to be a better plasticizer than glycerol for improving the compatibility of starch with clay and enhancing the barrier property of the starch composties (Zeppa, Gouanve, & Espuche, 2009), and plasticizer mixture of sorbitol and formamide is also verified to be able to effectively intercalate clay layers to improve the thermal stability and mechanical property of the starch composite (Ma, Yu, & Wang, 2007). It is also reported that the usage of mixture of formamide and water together with glycerol as starch plasticizer can enhance the dispersion and the interfacial affinity in the starch/poly(lactic acid) composites (Wang, Yu, Chang, & Ma, 2008). Moreover, monosaccharide, other amino compounds (such as ethylenebisformamide, N,N-bis(2-hydroxyethyl)formamide, N-(2-hydroxypropyl)formamide, N-(2-hydroxyethyl)-N-methylformamide, formamide mixture, etc.), ionic liquid, N,N-dimethylacetamide combined with lithium chloride have also been utilized as the novel plasticizers for starch. Comparable with the polyol-plasticized starch films in tensile test, monosaccharide-plasticized starch films were more resistant in moisture permeation, which should be attributed to the denser polymer-plasticizer complex, smaller size of free volume, and less segmental motions of starch chains resulting from the structural compatibility of monosaccharides with starch (Zhang & Han, 2006).

In our research work, polyol mixtures including mixture of conventional plasticizer glycerol and higher molecular weight polyol

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doi:10.1016/j.carbpol.2010.08.035

Table 1
The formulation of the starch composites plasticized by polyol mixtures.

Sample	Starch (phr)	Glycerol (phr)	Sorbitol (phr)	Xylitol (phr)	Maltitol (phr)
SC-G40	100	40			
SC-G45	100	45			
SC-G50	100	50			
SC-G55	100	55			
SC-G60	100	60			
SC-GS5	100	45	5		
SC-GS10	100	40	10		
SC-GS15	100	35	15		
SC-GS20	100	30	20		
SC-GS25	100	25	25		
SC-GX20	100	30		20	
SC-GM20	100	30			20

(HP) such as xylitol, sorbitol and maltitol were utilized to plasticize corn starch to reduce the moisture sensitivity and improve the thermal stability and mechanical strength of the starch composite, and effects of the molecular weight and content of HP on the pocessibility, microstructures, thermal property and mechanical properties of the starch composites were investigated through the characterization and analysis of processing torque, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), tensile test and dynamic mechanical thermal analysis (DMTA).

2. Experimental

2.1. Materials

Cornstarch was purchased from Shanghai Lu Yuan Starch Co. Ltd., and the plasticizers of glycerol, xylitol, sorbitol and maltitol were purchased from Sinopharm Group Chemical Reagent Co. Ltd.

2.2. Preparation of starch composites

Before the preparation of the starch composites (CS), starch and plasticizer of glycerol or polyol mixture were premixed by hand and sealed for 12 h to make plasticizer to swell the starch granule to enhance the molecular interactions between plasticizer and starch. During processing, the premixtures were melt blended in a Rheocord 900 HAAKE roller mixer at 150 °C for 10 min with a constant screw rotation speed of 100 rpm, and the torque and melt temperature were monitored. The obtained starch composites were then hot pressed at 160 °C to achieve sample sheets of 1 mm thickness and cut into different shapes for measurements. After that, the samples for testing were placed in tightly sealed polyethylene bags to prevent moisture absorption and reserved for 3 days before testing to make the material equilibrated and stable. The formulation of these starch composites is listed in Table 1. Just as shown in Table 1, SC-G series represent the starch composites plasticized by different content of glycerol, and the following number describes the amount of glycerol used. SC-GS, SC-GX and SC-GM series represent the starch composites plasticized by mixture of glycerol and sorbitol, mixture of glycerol and xylitol and mixture of glycerol and maltitol respectively, and the following numbers describes the amount of sorbitol, xylitol and maltitol used. In each above polyol mixture-plasticized starch composite, the amount of plasticizer is fixed to be half that of starch. In Table 1, the component amount is represented by phr, which means parts per hundreds of starch.

2.3. Structure and property characterization

An S-2150 scanning electron microscope (SEM) (Hitachi, Japan) was used to observe the microstructure and morphology of the starch and starch composites. Before SEM observation, the test specimens of starch and cold-fractured starch composites in liquid nitrogen were coated with a thin layer of gold. The measurements were operated with an acceleration voltage of 20 kV.

Thermal property test was carried out in a TGA 2050 Thermogravimetric analysis unit (TA, USA) with a heating rate of 10 °C/min from room temperature to 800 °C under an atmosphere of flowing nitrogen. Dynamic Mechanical Thermal Analysis system DMTA IV (TA, USA) was also used to estimate the thermal stability of specimens by creep sweep. The samples, sheets of 10 mm length gap similar to those used in dynamic mechanical properties test, were loaded in tension geometry at a force of 10 g and measured in a temperature range from −30 to 160 °C at a scanning rate of 3 °C/min.

Tensile properties were measured by the use of an Instron 4465 Universal Tensile Tester (Instron, USA) for dumbbell specimens of 4 mm width with a scalar distance of 20 mm and a crosshead speed of 10 mm/min, and five bars were tested and averaged for each sample to obtain the tensile strength and elongation at break. These measurement were conducted at 23 °C and a humidity of 50%.

Dynamic mechanical properties were also evaluated with the DMTA IV for the 20 mm × 4 mm × 1 mm sample sheets. The measurements were performed at a frequency of 1 Hz and a heating rate of 3 °C/min from −90 to 120 °C in a single cantilever mode, and the dynamic mechanical property parameters of the storage modulus (E'), loss modulus E'' and loss factor $\tan\delta$ ($\tan\delta = E''/E'$) were obtained as a function of temperature.

3. Results and discussion

3.1. Processing property

Fig. 1 illustrates the torque–time curves of the starch composites prepared with different plasticizers. It can be seen from Fig. 1 that during processing all of these starch composites show similar change tendency of torque with time, increasing rapidly to maximum torque and decreasing gradually and then level off to equilibrium torque. Before the breakage of the strong hydrogen-bond interaction between the starch molecules the processing torque increases rapidly, but after the addition of small molecule plasticizer, with the weakening of starch molecular interaction and the melting of starch microcrystals under the action of mechanical shear force and heat atmosphere, the processing torque decreases greatly and tends to equilibrium 10 min later. With the introduction of HP into glycerol, the torque–time curve becomes broader in shape and stronger in intensity. The greater amount of HP is used and the higher molecular weight HP possesses, the broader the plasticizing peak is and the greater the processing torque is. As it can be seen, the decrease of plasticizer content and the increase of the molecular weight and content of HP in polyol mixture will prolong the time to attain equilibrium torque and enhance the processing torque, whether for maximum torque or equilibrium torque. When the glycerol content is decreased from 60 to 40 phr or 20 phr

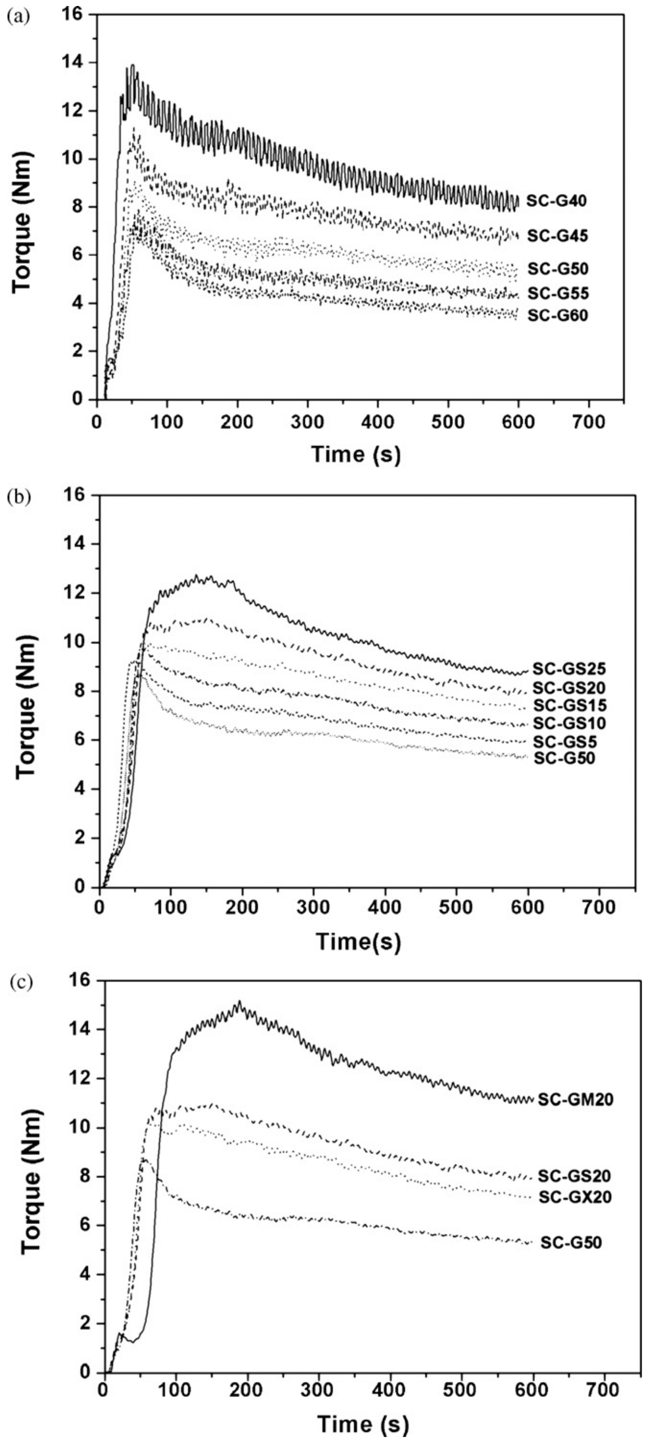

Fig. 1. The torque–time curves of the starch composites prepared with different plasticizers: (a) glycerol; (b) mixture of glycerol and sorbitol; (c) polyol mixtures.

glycerol is substituted by maltitol in polyol mixture, the processing torque of the starch composite is doubled significantly. Thus it can be seen, higher plasticizer content and lower molecular weight plasticizer are beneficial for the improvement of processibility with both the reduction of the processing torque and the shortening of the time to attain the equilibrium.

In fact, the increasing of processing torque can provide greater shear force and facilitate the destruction of the starch crystalline structure, but dissipate more power during processing on the other hand. Equilibrium torque is related to the viscosity of the gelatinous starch during melting processing, while viscosity is related to the mobility of the starch molecular chains under shear force and adequate temperature. It is the plasticizer that decreases the starch molecular chain interaction and destructs the starch crystalline structure (Myllarinen et al., 2002; Smits, Hulleman, Van Soest, Feil, & Vliegenthart, 1999; Stepto, 2000). In general, the less the high molecular weight plasticizer content is and the lower the plasticizer molecular weight is, the better the mobility of plasticizer molecules is and the greater plasticizing effect is. Therefore, with the increasing of the content and molecular weight of HP, it is more difficult for polyol molecules to penetrate between starch molecular chains, thus resulting in the increasing of the melt viscosity and equilibrium torque. More plasticizer molecules and smaller plasticizer molecules are advantageous for the increasing of the molecular chain mobility of starch and the decreasing of the melt viscosity and processing torque of the starch composite.

3.2. Microstructure

The SEM photographs of starch and starch composites plasticized by glycerol and polyol mixture of glycerol and sorbitol are given in Fig. 2. It can be observed from Fig. 2 that the starch granules appear nearly spherical with a diameter of 15 μm and very easy to aggregate due to the strong interaction of intermolecular and intramolecular hydrogen bonds of starch molecules. After plasticizer is added, the starch granule aggregate structures are broken during processing, and the effect of polyol mixture is superior to that of glycerol, showing uniform morphology without obvious remaining starch granules. As for the starch composite plasticized by glycerol, these is still a few smaller starch granules with a diameter of 5 μm remained, which implies that single addition of glycerol can not obtain enough torque to wholly break the strong hydrogen bonds between the starch molecules (Myllarinen et al., 2002; Wang, Yu, et al., 2009; Wang, Zhang, 2009). However, after the blending of sorbitol, higher molecular weight polyol, the resultant higher processing torque and corresponding greater mechanical shear force facilitate the penetration of plasticizers into the starch chains, destroying the starch granule aggregates completely, accelerating the plasticizing process of starch and leading to an even continous phase in the starch composite, just as reflected in Fig. 2.

Actually, the microcrystals of starch granules can not melt when being heated due to the existence of their strong molecular interactions, but merely degrade with the loss of balance water, thus making the starch having no thermoplastic availability and corresponding processibility. However, the addition of small molecules of plasticizer can weaken the hydrogen-bond interactions of starch molecules, and the starch granule aggregates can be destroyed under the action of mechanical shear force and heat atmosphere with the melting of microcrystals and the structure transition from order to random form, thus providing the starch thermoplastic ability and processibility as normal plastics.

3.3. Thermal stability

The thermal stability of the starch composites plasticized by different polyol mixtures was evaluated by thermogravimetric analysis (TGA) and creep experiment, just as shown in Figs. 3 and 4. From Fig. 3 it can be seen clearly that the TGA curves of these starch composites are very similar to each other with the loss of water and plasticizer and the degradation of starch (Ma, Jian, Chang, & Yu, 2008; Teixeira et al., 2009). However, the introduction of HP, especially maltitol, obviously increases the thermal stability of the starch composite, and when 50% weight is lost the corresponding temperature of the starch composite is 316.0, 315.9, 318.0 and 321.0 °C for SC-G50, SC-GX20, SC-GS20 and SC-GM20, respectively.

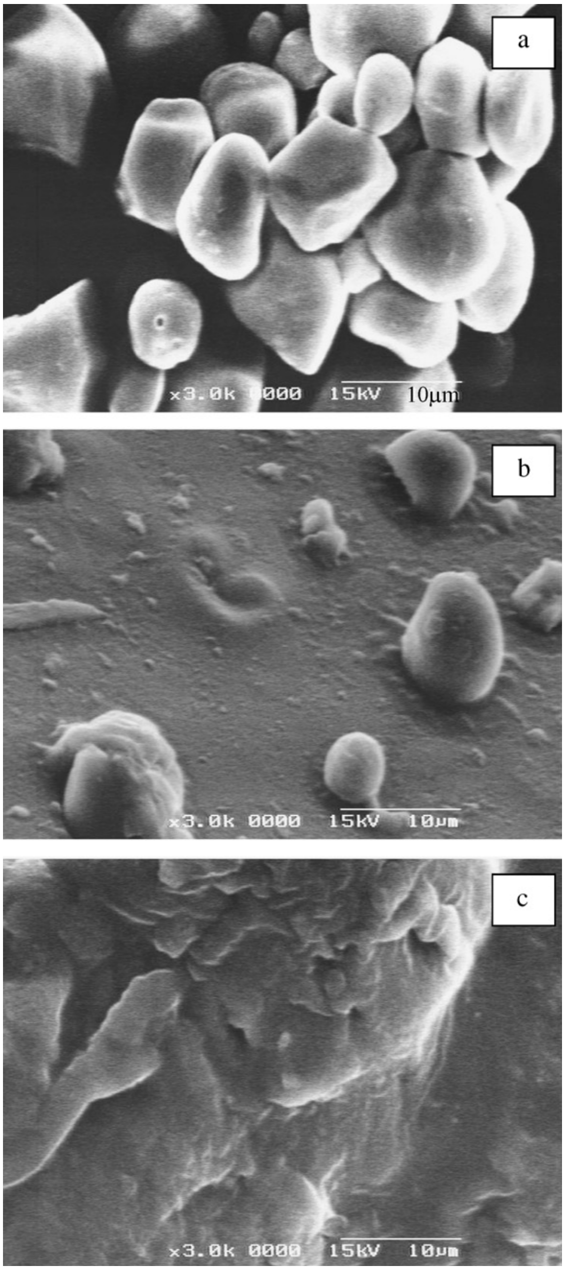

Fig. 2. The scanning electron micrographs of starch (a) and starch composites plasticized by glycerol (b) and mixture of glycerol and sorbitol (c).

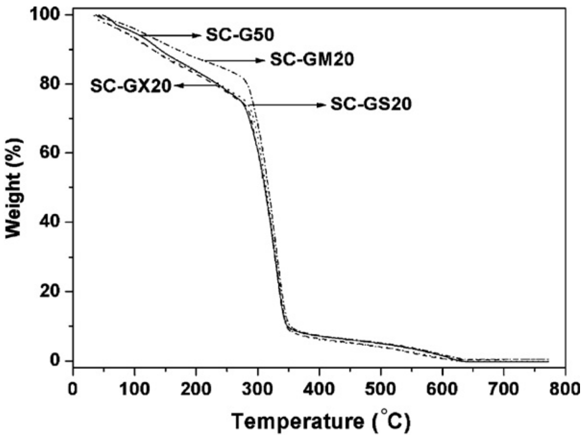

Fig. 3. TGA curves of the starch composites plasticized by polyol mixtures.

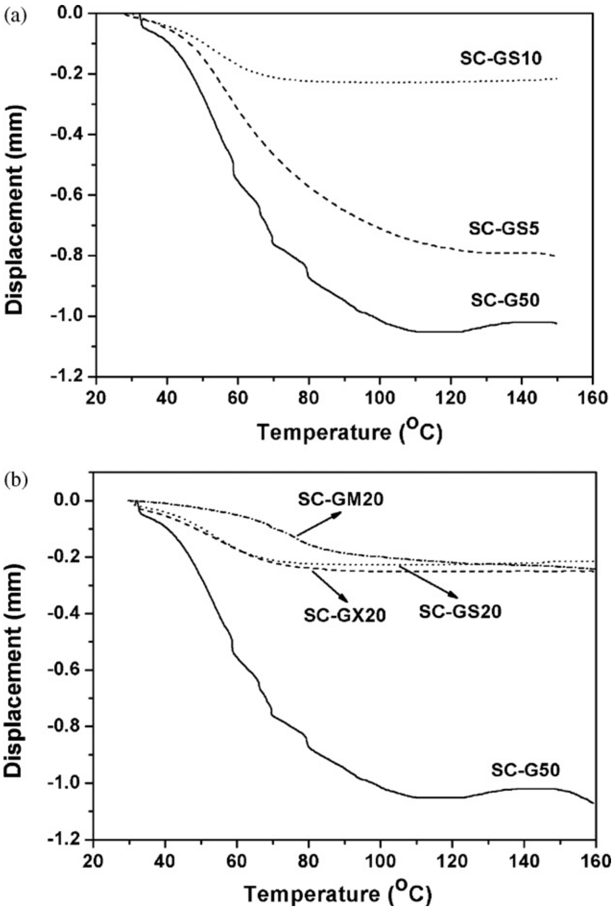

Fig. 4. Creep curves of the starch composites prepared with different plasticizers at 10 g force (a) glycerol and mixture of glycerol and sorbitol; (b) polyol mixtures.

Compared with TGA results, creep curves in Fig. 4 show more obvious advantageous effects of HP on the thermal stability of the starch composite. Creep curves are very sensitive to temperature with rapid deformation initially and then level off as a plateau after a certain temperature. With the increase of the molecular weight and content of the introduced HP, the creep deformation of the starch composite decreases and the plateau appears earlier. Under the tension of 10 g force, the starch composite plasticized by glycerol exhibits the greatest equilibrium creep deformation of 1.1 mm at 140 °C, while after 20 phr glycerol is substituted by HP such as xylitol, sorbitol and maltitol, the equilibrium creep deformation of the starch composite is reduced remarkably to be less than 0.2 mm at 70 °C. Similar to TGA results, the effects of xylitol and sorbitol are nearly the same, but the effect of maltitol has much greater effects on the improvement of the thermal stability of the starch composite. Moreover, the thermal stability of the starch composite increases with the HP content, but for sorbitol after its content exceeds 10 phr its effect seems similar without obvious decrement of the creep deformation. Thus it can be seen, the introduction of HP can obviously improve the thermal stability and increase the work temperature of the starch composites.

3.4. Mechanical property

The tensile property parameters of the starch composites prepared with different plasticizers are given in Fig. 5. It can be found from Fig. 5 that with the decrease of plasticizer content, the increase of HP content or the rising of polyol molecular weight from xylitol to maltitol, the tensile strength is significantly improved to be

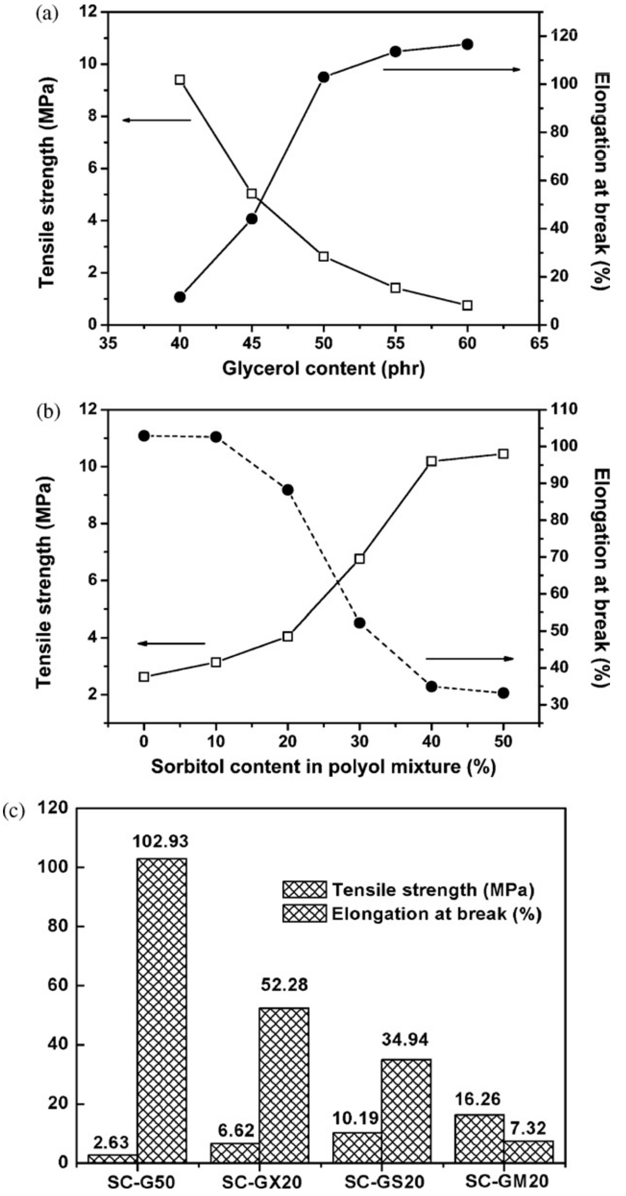

Fig. 5. The tensile property of the starch composites prepared with different plasticizers: (a) glycerol; (b) mixture of glycerol and sorbitol; (c) polyol mixtures.

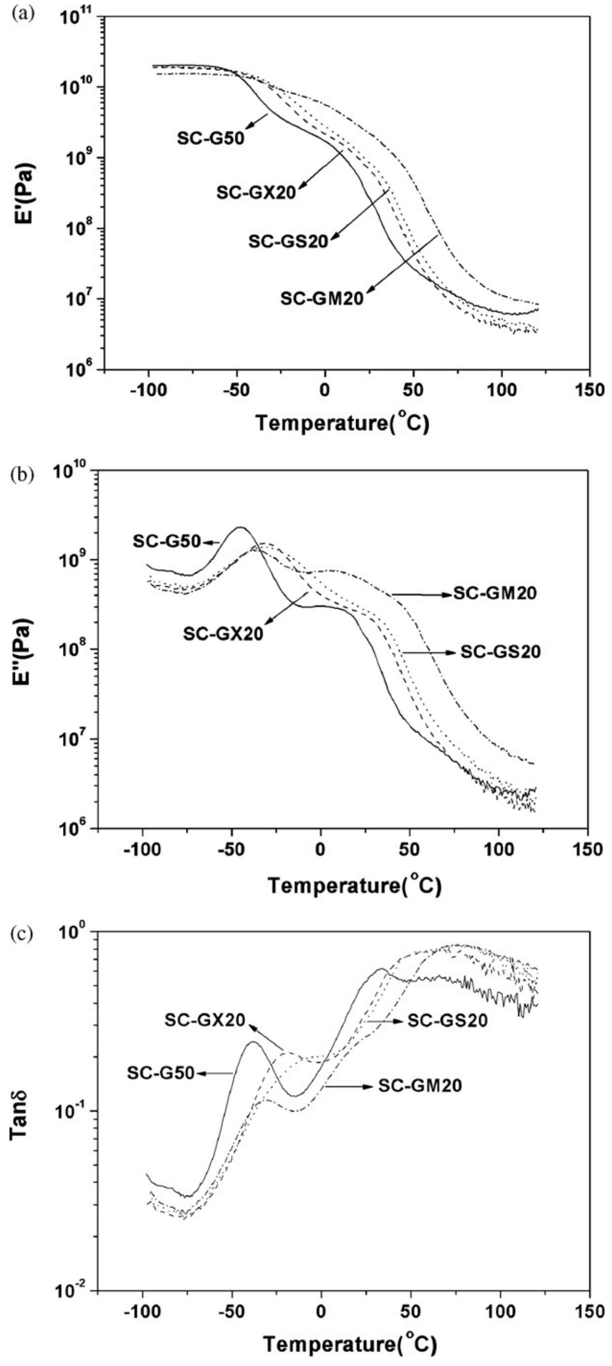

Fig. 6. DMTA curves of the starch composites plasticized by glycerol and polyol mixtures: (a) storage modulus; (b) loss modulus; (c) loss factor.

nearly six times for the maximum, while the elongation at break decreases correspondingly. Although the small molecule plasticizer is helpful for the reduction of the molecular interaction of starch with the increase of the free volume and the improvement of the processibility and toughness due to its higher mobility, more plasticizer molecules will cause negative effect for the mechanical strength of the starch composite. Compared with the starch composite plasticized by glycerol, the starch composites plasticized by polyol mixtures show greater mechanical strength because of the existence of high molecular weight plasticizer and the formation of the uniform morphology without the defect of starch granules. This reinforcement effect is elevated with the increase of the content and molecular weight of HP. Suitable choice of plasticizer mixtures with different content and molecular weight of polyol can help to control the mechanical property of the starch composites for application.

3.5. Dynamic mechanical thermal analysis

Fig. 6 presents the dynamic mechanical property curves of the starch composites plasticized by different polyol mixtures. It can be seen from Fig. 6 that after HP is added, the storage modulus is notably raised for the starch composite, and the increment turns greater with the rising of HP molecular weight. The addition of HP is beneficial for the improvement of the modulus and strength of the starch composite, which should be attributed to the reinforcement effect of HP with higher strength, very similar to the tensile strength results. In general, the region of rapid decrease of storage modulus corresponds to maximum loss factor (tan δ), and the loss factor is very sensitive to molecular mobility, thus leading to the usage of its peak as a representative of glass transition temperature (T_g) (Ma et al., 2008). Due to the existence of two phases originating from the partial miscibility of plasticizer and starch, two relaxation peaks occurs in tan δ curves (Teixeira et al., 2009; Wang, Yu, et al., 2009; Wang, Zhang, 2009). Meanwhile, with the specific interaction of glycerol with other polyols owing to their chemical similarity, the starch composites plasticized by polyol mixtures with different glass transition temperatures exhibit merely one glass transition process of plasticizer-rich domains below 0 °C. The relaxation process of the starch composites at about 50 °C corresponds to the glassy state transition of starch-rich phase, and this relaxation appears broader with greater intensity and shifts towards higher temperature from xylitol, sorbitol to maltitol. In general, smaller molecules relaxes more easily with higher mobility, and the starch molecular chains plasticized by lower molecular weight polyol can move more easily without much energy loss, thus causing the sharpening and weakening of the tan δ peak of the starch composite at lower temperature. It is the strengthening of H-bonding interaction of starch and HP with more –OH group that increases the transition temperature. The lower relaxation resulting from the glass transition of plasticizer-rich phase exhibits similar change tendency as the above upper relaxation with the replacement of glycerol by HP, except for a litter lower transition temperature of the starch composite plasticized by maltitol than those by xylitol and sorbitol.

4. Conclusions

Effects of polyol mixture plasticizers on the pocessibility, microstructures, thermal stability and mechanical properties of the corn starch composites were investigated in this paper. As for these starch composites, the increase of the molecular weight and content of HP mixed with glycerol prolongs the time to attain equilibrium torque and enhances the processing torque, but the resultant increasing of the shear force can facilitate the destruction of the starch crystalline structure with the formation of even continous phase in the starch composite. With the extra addition of HP in glycerol plasticizer, the thermal stability and mechanical strength of the starch composite are significantly improved, and the modulus and phase transition temperature of the starch composite are obviously increased too.

Acknowledgement

The authors thank Instrumental Analysis Center of Shanghai Jiao Tong University for the assistance with the measurements.

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