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Melt processing of poly(vinyl alcohol) through blending with sugar pendant polymer

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Abstract

Poly(vinyl alcohol) (PVA) was blended with the sugar pendant polymer, poly(glucosyloxyethyl methacrylate) (poly(GEMA)), through the reprecipitation from the mixed aqueous solution. By blending a small amount (1–25%, w/w) of poly(GEMA) with PVA, the thermal decomposition temperature abruptly increased above 300 °C. This is attributed to the strong hydrogen bonds between PVA and poly(GEMA) molecules. The increase in the difference between the thermal decomposition temperature and the melting point ($\Delta T \sim 100$ °C) enabled the melt processing of PVA. Blending of poly(GEMA) with PVA was also found to be effective for the suppression of the thermal decomposition of PVA in an aqueous solution. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl alcohol); Melt processing; Thermal decomposition

1. Introduction

Poly(vinyl alcohol) (PVA) is one of the most popular water-soluble polymers. PVA has been utilized in the shapes of fibers, films, hydrogels, glue because of its high mechanical properties, gas barrier properties and so on [1,2]. PVA has been processed mainly from an aqueous solution even though the melt processing is economically favored. For example, the fibers are wet-spun, and the films are obtained by casting a solution. This is because the melting point (T_m, typically 226 °C) and the decomposition temperature of PVA are close to each other. The thermal degradation also undergoes simultaneously during melting. A gel spinning of PVA has been reported recently [3–5], as stimulated by the development of the gel spinning process of ultra high molecular weight polyethylene [6,7]. Melt spinning of PVA has been tried from the water swollen state [8], by a rapid processing [9], and for PVA/boronic acid complex [10]. In these processes, thermal decompositions were avoided by the decrease of T_m of PVA and/or the shortening of processing time [11]. Consequently, the melt processing of PVA has not been succeeded industrially.

Poly(glucosyloxyethyl methacrylate) (poly(GEMA)) is a polymer composed of a methacrylate backbone and sugar residues in its side chains as shown in Fig. 1. We have utilized this polymer as functional materials for a glucose sensor [12], and a glucose sensitive gel [13], where the complexation/dissociation between the sugar residue and a lectin were used. Poly(GEMA) and its copolymers possess very hydrophilic surface. It was found that this is quite effective for a good biocompatibility [14–17], and a production of a pressure sensitive adhesive in water [18]. The addition of poly(GEMA) was also reported to be effective for the stabilization of enzyme [19].

Poly(GEMA) possesses a lot of sugar residues in its side chains, so a novel functionality will be expected through hydrogen bonds with other compounds. In this study, poly(GEMA) was blended with PVA, and a possibility of melt processability of PVA was investigated. The thermal, optical properties of the melt pressed PVA film were also studied.

2. Experimental

2.1. PVA/poly(GEMA), poly(HEMA), and D-glucose blends

The PVA used in this study was supplied by Nippon Synthetic Chemical Industry, Co. Ltd, commercial named Gohsenol NH-18. The degree of polymerization was 1800, and the degree of saponification was more than 99%. The poly(GEMA) was supplied by Nippon Fine Chemicals Co. Ltd. The weight averaged molecular weight was 108×10^4. The 5% (w/w) aqueous solution of each polymers was mixed in a flask and gently stirred for 12 h at room

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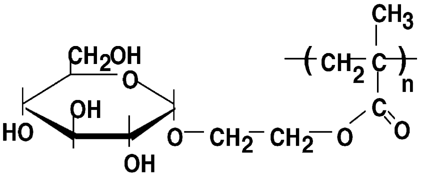


Fig. 1. Chemical formula of poly(2-glucosyloxyethyl methacrylate).

temperature. Subsequently, the mixed solution was poured into methanol followed by drying under vacuum at 60 °C.

The dried blend powder was melt pressed at 260 °C, 6 MPa for 4 min, then quenched into room temperature by air cooling.

Poly(2-hydroxyethyl methacrylate) (poly(HEMA)) was synthesized by a radical polymerization in dimethyl sulfoxide (DMSO) solution with 4,4′-azobisisobutylonitrile as an initiator. After reprecipitation into acetone, poly(HEMA) was dissolved into DMSO (5%, w/w). This solution was mixed with PVA in the DMSO solution followed by reprecipitating into acetone, and drying.

In order for a blending of D-glucose with PVA, D-glucose was added to PVA aqueous solution, then cast at room temperature.

2.2. Measurements

The melting point (T_m) and the glass transition temperature (T_g) were measured by a differential scanning calorimeter (Seiko Instruments, Co., DSC-220CU). Heating was performed under a flow of nitrogen at a rate of 10 °C/min. A sample weight was 5 mg. T_m was determined as a peak temperature of the melting endotherm. Temperature was calibrated by using In and Sn as standards.

The thermal decomposition temperature (T_d) was measured by a thermogravimeter (Seiko Instruments, Co., TG/DTA-220U) at the heating rate of 10 °C/min under a flow of nitrogen with a sample weight of 5 mg. T_d was determined as a temperature of 5% thermal weight loss.

Infrared spectra were measured with a Fourier transform infrared spectrophotometer (Perkin Elmer, Spectrum GX). The measurement was carried out with KBr method at 2 cm^{-1} resolution and 10 scans.

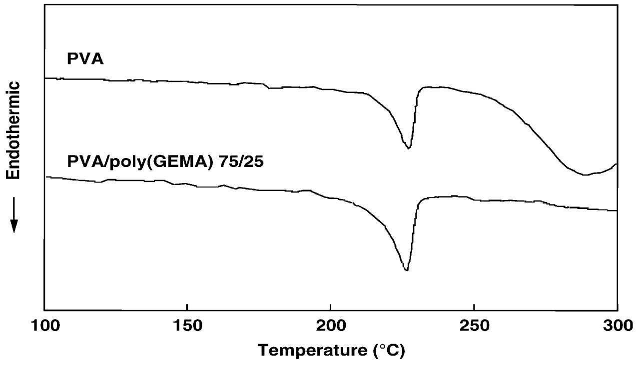


Fig. 2. DSC thermograms of PVA, PVA/poly(GEMA) blend (75/25 w/w).

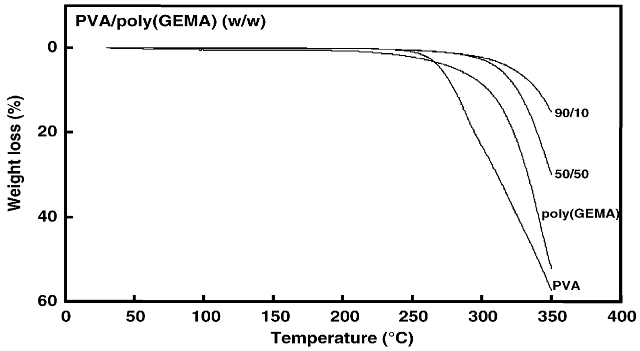


Fig. 3. TG traces of PVA, poly(GEMA), and PVA/poly(GEMA) blends.

All these experiments were performed for the sample dried under vacuum for 2 days at 60 °C followed by storing in a desiccator.

Decomposition in the aqueous solution was observed using a UV/Vis spectrophotometer (Hitachi U-2000). PVA or PVA/poly(GEMA) mixed aqueous solutions were boiled under air atmosphere, then their ultraviolet absorption from 300 to 350 nm was measured at room temperature. The polymer concentration was 0.5% (w/w).

3. Results and discussion

Fig. 2 shows the DSC thermograms of PVA and PVA/poly(GEMA) blend (75/25 w/w). PVA showed a melting endotherm at 226 °C followed by another gradual endotherm at a higher temperature. The latter endotherm corresponds to the thermal decomposition of PVA, which brought a difficulty in the melt processing of PVA as described earlier. On the other hand, PVA/poly(GEMA) blend showed a straight base line after melting endotherm, and no further endotherm was observed at the higher temperature. This implies that a thermal decomposition of PVA was suppressed by the blending of poly(GEMA). Same phenomena were observed for the PVA–boronic acid complex by Nishimura et al. [10] and for the PVA/cericin blend by Wang et al. [20]. However, a significant depression of T_m was observed for the former case.

Fig. 3 shows the TG traces of PVA, poly(GEMA), and their blends. PVA started to decompose just above T_m, and T_d (temperature at the 5% weight loss) was 270 °C. Comparing with the TG curves of homopolymers of PVA and poly(GEMA), those of blends shifted to a high temperature. T_d increased above 300 °C for PVA/poly(GEMA) blends.

Fig. 4 shows the relationship between T_d, T_m, T_g and the poly(GEMA) weight fraction in PVA/poly(GEMA) blends. T_m decreased slightly with the amount of poly(GEMA) in the blends. The enthalpy of fusion did not change by blending as shown in Fig. 2. These indicate that the crystalline future of PVA was not intrinsically sacrificed by the

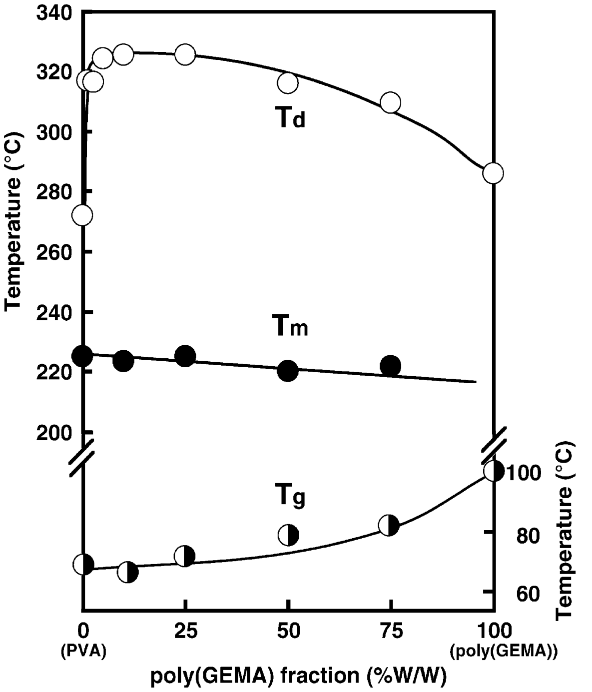


Fig. 4. Relationship between the poly(GEMA) weight fraction and (○) the thermal decomposition temperature (T_d), (●) the melting temperature (T_m) and (○) the glass transition temperature T_g of the PVA/poly(GEMA) blends.

blending of poly(GEMA). Only single glass transition was observed on each DSC thermogram, and T_g increased monotonously with the amount of poly(GEMA) in the blends. Both these polymers are found to be phase separated each other after annealing at high temperature. This suggests that this is not completely miscible, but partially miscible system in the equilibrium state. Thus, the results shown in Fig. 4 revealed that both polymers are apparently miscible in the amorphous region when the mixed solutions were reprecipitated rapidly. Further details on the phase behavior will be reported elsewhere. The most drastic change was observed for the thermal decomposition temperature. T_d increased to 320 °C by blending even a small amount (1%, w/w) of poly(GEMA). T_d reached at the maximum of 326 °C for 5–25% (w/w) poly(GEMA) blend with PVA. This indicates that the temperature difference between T_m and T_d increased to 100 °C by blending, which is in contrast with the case of original PVA ($T_d - T_m = 50$ °C). T_d decreased above the poly(GEMA) fraction of more than 25% (w/w). The increases of T_d for PVA/poly(GEMA) blends compared with those of both homopolymers suggest the intermolecular interaction between both polymers.

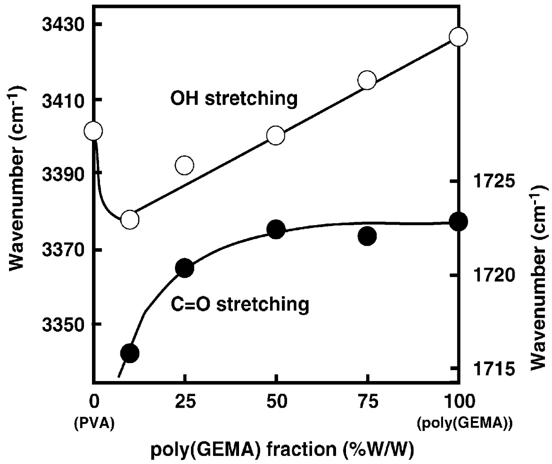


Fig. 5. Relationship between the poly(GEMA) weight fraction in PVA/poly(GEMA) blends and the wavenumber of the infrared absorption band of (○) hydroxyl stretching and (●) carbonyl stretching.

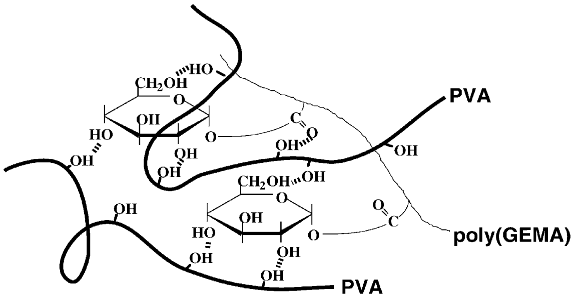
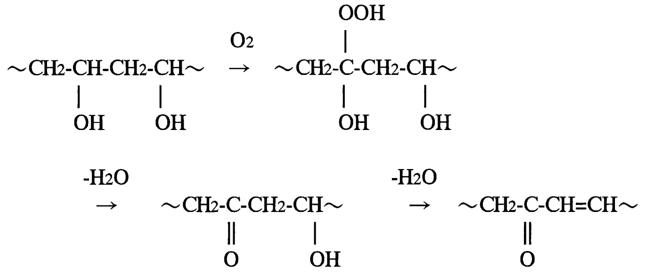


Fig. 6. Schematic representation of PVA/poly(GEMA) blend.

Fig. 5 shows the relationship between the wavenumber of the infrared absorption bands of the hydroxyl, carbonyl stretchings and the poly(GEMA) weight fraction in PVA/poly(GEMA) blends. Both polymers have hydroxyl groups, and the wavenumber of its stretching shifted to the lowest value around poly(GEMA) fraction of 10% (w/w). This indicates that the intermolecular hydrogen bonds were strengthened by the blending, which corresponds to the change in T_d. The wavenumber for the carbonyl stretching also shifted around poly(GEMA) content of 10% (w/w).

The thermal decomposition of PVA was reported to be progressed as follows [21]:



$$\sim CH_2\text{-}\underset{\overset{|}{OH}}{CH}\text{-}CH_2\text{-}\underset{\overset{|}{OH}}{CH}\sim \xrightarrow{O_2} \sim CH_2\text{-}\overset{\underset{|}{OOH}}{\underset{\overset{|}{OH}}{C}}\text{-}CH_2\text{-}\underset{\overset{|}{OH}}{CH}\sim$$

$$\xrightarrow{-H_2O} \sim CH_2\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH_2\text{-}\underset{\overset{|}{OH}}{CH}\sim \xrightarrow{-H_2O} \sim CH_2\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH{=}CH\sim$$

Here, the hydroxyl groups were converted into the carbonyl groups with the existence of oxygen. Then, the production of the double bonds followed by the chain scission [22–25]. These indicate that at least the hydroxyl groups take part in the oxidative decomposition of PVA. Thus, the intermolecular hydrogen bonds between PVA and poly(GEMA) molecules, as schematically illustrated in Fig. 6, suppress these decomposition reactions, which is considered to result in the increase of T_d by blending poly(GEMA) with PVA.

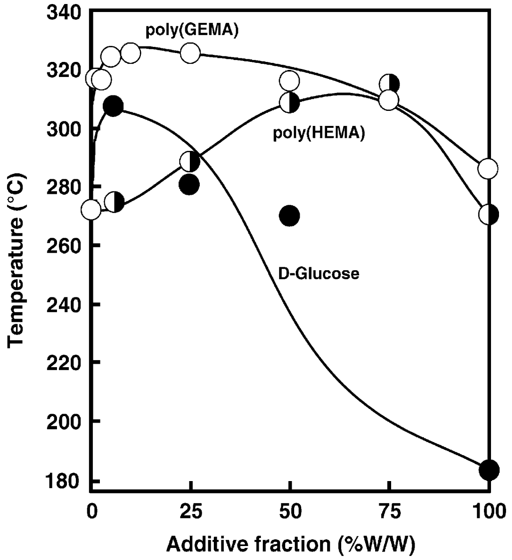


Fig. 7. Relationship between the thermal decomposition temperature (T_d) and the additive fraction of (○) the PVA/poly(GEMA) blend, (●) PVA/D-glucose blend, and (○) PVA/poly(HEMA) blend.

The chemical formula of poly(GEMA) is composed of glucose residues and a methacrylate backbone. Thus, next, D-glucose and poly(HEMA), model compounds for the sugar residue and the methacrylate backbone, respectively, were blended with PVA, and the decomposition phenomena were investigated.

Fig. 7 shows the relationship between T_d and the blended weight fraction of poly(HEMA), and D-glucose with PVA. Blending of poly(HEMA) and D-glucose was also effective for the increase of T_d of PVA. However, more than 50% (w/w) of poly(HEMA) is needed for the sufficient increase of T_d. A small amount of D-glucose brought a significant increase of T_d, however, sample color turned brown considerably. The results is in contrast with PVA/poly(GEMA) blends, where the color of the blend powder remained white even when heated up to 300 °C.

Fig. 8 shows the relationship between the weight loss of PVA, poly(GEMA), and PVA/poly(GEMA) (90/10 w/w) blend and the holding time at 280 °C under a flow of nitrogen. All the samples were in the molten state. PVA showed a significant weight loss, which reached more than 40% after 2 h. Comparing with those of original PVA and poly(GEMA), the weight loss of PVA/poly(GEMA) blend was suppressed remarkably. This indicates that the thermal stability of PVA was improved significantly by blending of poly(GEMA), which brings the possibility of the melt processing of PVA.

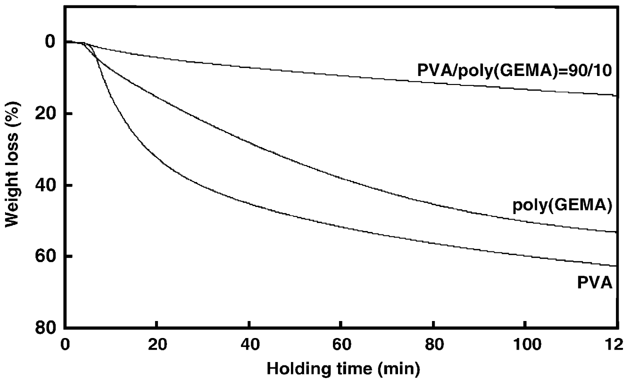


Fig. 8. Relationship between the holding time at 280 °C and the weight loss of PVA, poly(GEMA), and PVA/poly(GEMA) = 90/10 w/w blend.

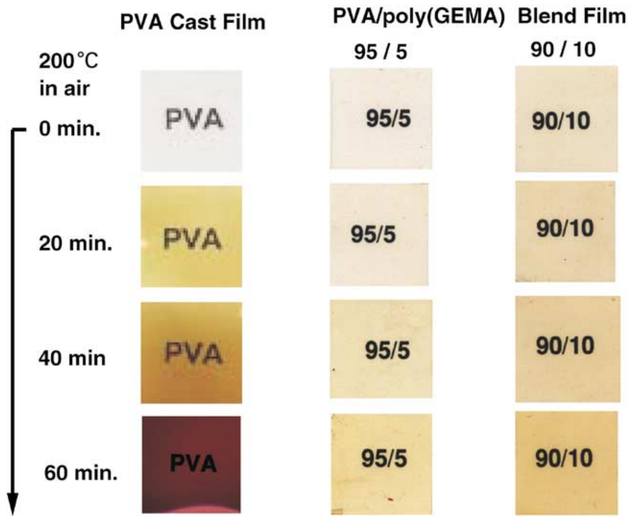


Fig. 9. Relationship between the annealing time at 200 °C and the coloring degree of PVA cast film and PVA/poly(GEMA) blend films.

Fig. 9 shows the relationship between the annealing time at 200 °C and the coloring degree of PVA cast film and PVA/poly(GEMA) blend melt pressed film. The annealing was performed under air. PVA could be melt pressed by blending of poly(GEMA). PVA film was optically transparent in its as-cast stage. However, it turned yellow to brown, and finally transparency was diminished by annealing at 200 °C. This corresponds to the formation of double

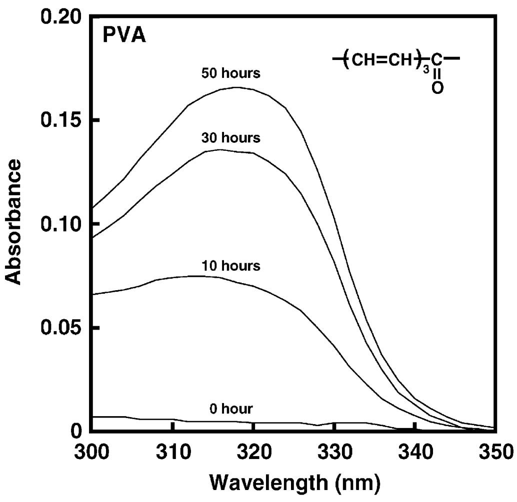


Fig. 10. Absorbance of PVA aqueous solution after boiling under air atmosphere.

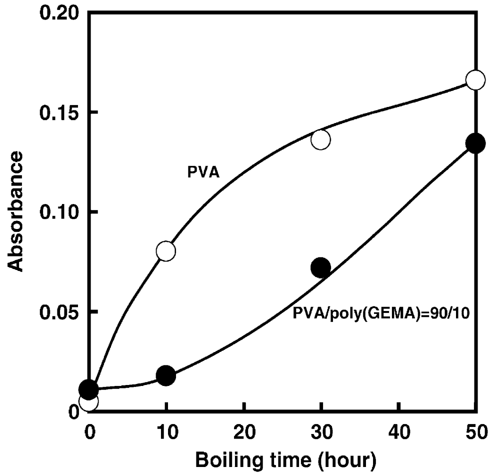


Fig. 11. Relationship between the boiling time at 100 °C and the absorbance at 317 nm of (○) PVA, (●) PVA/poly(GEMA) = 90/10 w/w aqueous solution.

bonds, and the subsequent increase of the conjugation of the double bonds along the PVA chains. The PVA/poly(GEMA) blend films showed a little bit yellowish color just after melt press. However, the color did not change by annealing for a long time. This shows that the melt pressed films of the blends are thermally stable in the viewpoint of coloring.

Next, the thermal stability of PVA in an aqueous solution was investigated.

Fig. 10 shows the absorbance of PVA aqueous solution after boiling under air atmosphere. The absorption around 317 nm was reported to be assigned as $-(CH{=}CH)_3-(C{=}O)-$ sequence along the chain [26]. The double bonds and the carbonyl groups were produced even in boiling water for PVA, which coincides with the oxidative decomposition mechanism as shown earlier. It was reported that the conjugated sequence, $-(CH{=}CH)_3-(C{=}O)-$, is the longest in aqueous solution [27]. This corresponds to the results in Fig. 10, where no adsorption shift was observed.

Fig. 11 shows the relationship between the boiling time at 100 °C and the absorbance at 317 nm of (○) PVA, and (●) PVA/poly(GEMA) (90/10 w/w) mixed aqueous solution. The absorbance increased by boiling, where the decomposition was clearly suppressed by the blending of poly(GEMA). Thus, the existence of poly(GEMA) is effective for the decrease in the oxidative decomposition of PVA both in the solid state and in the aqueous solution.

4. Conclusions

By blending a small amount of poly(GEMA) with PVA, the thermal stability of PVA was significantly improved without decreasing the melting point. This was considered to be due to the strong intermolecular hydrogen bonds between hydroxyl and carbonyl groups, which suppressed the oxidative decomposition of PVA. The increase in the difference between T_m and T_d enabled the melt processing of PVA. The melt pressed PVA film showed excellent properties both from thermal and optical viewpoints. Blending of poly(GEMA) with PVA was also found to be effective for the suppression of the thermal decomposition of PVA in the aqueous solution. The structure and the mechanical properties of the melt pressed PVA will be discussed elsewhere.

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