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Thermal and viscoelastic properties of alginate/poly(vinyl alcohol) blends cross-linked with calcium tetraborate

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Abstract

Binary blends of alginate (Alg) with poly(vinyl alcohol) (PVA) were cast in film form from mixed aqueous polymer solutions by solvent evaporation. The thermal transition and viscoelastic behavior of the Alg/PVA blends were investigated by differential scanning calorimetry and dynamic mechanical analysis. Irrespective of composition, blend samples gave a single glass transition temperature (T_g) situated between the T_gs of PVA and alginate per se. The melting point of the PVA component was depressed systematically with increasing alginate content in the blends. These observations indicate that the polymer blend of Alg/PVA is capable of forming a thermodynamically miscible phase in the amorphous state. An additional treatment of as-cast samples with calcium tetraborate solution gave rise to a marked elevation of their T_gs. This may be ascribed to the possible, simultaneous occurrence of a chelate complexation of alginates with Ca^{2+} cation and a borate ion-aided cross-links between PVA chains, resulting in the formation of an 'IPN' structure. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Alginate; Poly(vinyl alcohol); Blends; Calcium tetraborate; Cross-linking; Thermal transitions; Viscoelasticity

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1. Introduction

As it is currently well established, polymer blending is an important method for modification or improvement of the physical properties of polymeric materials, and a number of fundamental studies of blends have been carried out in parallel with investigations on their practical applications. Amongst them, microscopic hybridization of natural polymers including polysaccharides may be of great significance, in view of the wider utilization and new functionalization of abundant biomass. Alginate employed in this present work is an abundant polysaccharide, which can be supplied in plenty from marine algae. It is well known that alginate is a copolymer composed of β-D-mannuronate (M) and α-L-guluronate (G) residues in various M/G ratios; these residues are arranged in a blockwise fashion, constructed not only of homopolymer blocks (MM or GG) but also alternating blocks (MG) (Fischer and Dörfel, 1955; Haug et al., 1966). This carbohydrate polymer has been re-evaluated recently as an attractive natural resource, possessing a potential to be further developed for medical, pharmaceutical, and bio- and other industrial applications.

One of the useful characteristics of alginate is the ability to form hydrogels (Atkins, 1985; Clark and Ross-Murphy, 1987). An aqueous solution of alginate is readily transformed into a hydrogel on addition of metallic divalent cations such as Ca^{2+} (Grant et al., 1973; Smidsrød and Haug, 1972). The gelation behaviour of alginate has been investigated so far in various ways (Ross-Murphy, 1994), e.g., by a thermodynamical model treatment (Nilsson, 1992) and by ^{13}C NMR spectroscopy (Wang et al., 1993). It has been generally accepted that in the gelation mechanism cross-links are formed by coordination of divalent metal cation to the interchain cavities made up of guluronate blocks, resulting in development of a so-called 'egg-box' junction zone. In contrast to the numerous studies performed on the physical properties and industrial applications of alginate gels, there have been only a few examples of studies dealing with alginate/synthetic polymer blends (Nagura et al., 1991; Yonese et al., 1992).

In the present work, miscibility characterization was performed on binary blends of alginate/poly(vinyl alcohol) (Alg/PVA) prepared from mixed polymer solutions by solvent evaporation. An attempt was also made to introduce

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cross-links into the cast blends by treatment of the films with a calcium tetraborate (CaB_4O_7) aqueous solution. There are already two reports concerning the same system of polymer blends, accomplished by Nagura et al. (1991) and Yonese et al., (1992). However, these studies were directed mainly to properties of the blended hydrogels prepared via gelation of the PVA component by repeating freeze-thaw cycles. As an alternative process of PVA gelation, it is well known that this polymer forms hydrogels by cross-linking owing to complexation with borate ions (Deuel and Neukom, 1949; Kurokawa et al., 1992; Sano et al., 1992), whereupon boric acid/sodium hydroxide mixtures or sodium tetraborate has been commonly utilized to induce gelation. It can be expected that in the present study the adopted post-treatment with CaB_4O_7 will allow the production of cross-links in both components simultaneously; i.e., borate ion-aided cross-links between PVA chains and chelate complexing of alginate chains with Ca^{2+} would occur at the same time. The thermal transition behaviour and the viscoelastic properties of Alg/PVA blends have been characterized through the use of differential scanning calorimetry and dynamic mechanical analysis. The data has been discussed with regard to blend miscibility of the polymers and the effect of cross-linking on the thermal and mechanical properties of the films.

2. Experimental

2.1. Materials

The alginate material used was a commercial product of sodium alginate (NaAlg), Duck Algin 350 purchased from Kibun Food Chemifa Co. (Japan). The fraction of guluronate was 0.57, which was determined by ^{13}C NMR spectroscopy, following the peak assignments given in the literature (Grasdalen et al., 1977, Grasdalen et al., 1981). Poly(vinyl alcohol) (PVA) was also of commercial origin, PVA 117-H of Kuraray Co.; the nominal degree of polymerization was 1750 and the saponification value was 99.9 mol%. Calcium tetraborate (CaB_4O_7) (Soekawa Chemicals Co. Ltd.) was used without further purification.

2.2. Preparation of blend films

Aqueous solutions of alginate and PVA were prepared separately at concentrations of 2.0 wt% and 6.0 wt%, respectively. The powder materials were dissolved in water at room temperature (~20°C) for alginate and at ~75°C for PVA, with continuous stirring. The two polymer solutions were mixed in the desired proportions at room temperature and then stirred overnight. The resulting viscous solutions were optically clear and showed no visible separation into bilayers nor any precipitation on standing. The relative composition of the two polymers in the mixed solutions ranged from 10/90–90/10 in Alg/PVA weight percent ratio. An appropriate amount of each solution was poured into a glass tray with a flat bottom and cast in film form by solvent evaporation at room temperature. The blend and homopolymer films thus obtained were dried at 50°C for ~ 12h in vacuo and stored in a desiccator.

Intermolecular cross-links were introduced into the cast films by subjecting them to a post-treatment with calcium tetraborate (CaB_4O_7), in the following way: a 0.4 wt% CaB_4O_7 aqueous solution was prepared and the desired amount was poured into a Teflon tray. Then a dried Alg/PVA film, which was weighed previously, was immersed in the solution, so that the film swelled gradually and, eventually, absorbed almost the whole quantity of CaB_4O_7 solution. The gelatinous films thus obtained were dried once again at 50°C for more than 12 h in vacuo. For a given Alg/PVA composition, three different concentrations of the cross-linking agent were selected: 2.0%, 4.0%, and 8.0% CaB_4O_7 relative to the total polymer weight of the film sample. Corresponding to this selection, three series of post-treated samples are designated as Alg/PVA[W], Alg/PVA[M] and Alg/PVA[S], where notations [W], [M], and [S] serve to indicate that the respective series of samples are cross-linked comparatively weakly, moderately, and strongly. Untreated samples are designated as Alg/PVA[O] for convenience.

2.3. Measurements

Differential scanning calorimetry (DSC) was carried out on ca. 6 mg samples with a Seiko DSC210/SSC5000 apparatus. Temperature readings were calibrated with an indium standard. The samples were first heated up to 245°C and subsequently quenched to -20°C. The second heating scans were run from this temperature to 250°C, to record stable thermograms. All the measurements were performed at a heating rate of 20°C min^{-1} under a nitrogen atmosphere.

Dynamic mechanical properties were examined with a Rheovibron Model DDV-II-C viscoelastometer (Orientec Co., Tokyo, Japan). The oscillatory frequency of the dynamic test was 11 Hz, and the temperature was raised at a rate of 1.5°C min^{-1} in the range -50°C-240°C. Film strips 5 mm × 30 mm were employed, which were heated in an oven at 150°C for 7 min prior to the measurement in order to remove trace amounts of water and for the relaxation of possible stresses.

3. Results and discussion

3.1. Thermal transition behaviour and viscoelastic properties of Alg/PVA[O] blends

Alg/PVA films cast from the stable, mixed polymer solutions, i.e., O-series of samples, showed good transparency to the naked eye over the whole range of the composition. Thus visual inspection gave no indication of phase separation in any of the blends.

One of the most commonly used methods to estimate

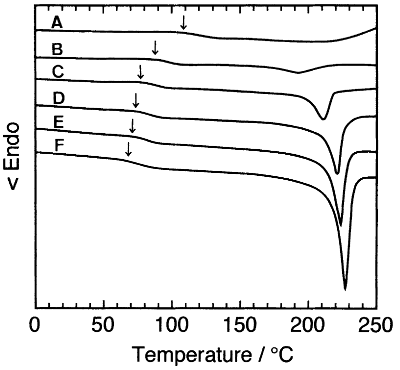

Fig. 1. DSC thermograms of Alg/PVA[O] blends. Alg/PVA composition: A, 100/0 (Alg); B, 80/20; C, 60/40; D, 40/60; E, 20/80; F, 0/100 (PVA). Arrows indicate a T_g position taken as the onset point of the discontinuity in heat flow.

polymer–polymer miscibility is the determination of the T_g of the blend compared with the T_gs of the two components separately. In the case where one component is crystalline, observation of a melting point depression of this polymer may also be used as evidence to support the miscibility of the polymer pair (Nishi and Wang, 1975; Imken et al., 1976). Fig. 1 compiles selected data of DSC thermograms obtained for a series of Alg/PVA[O] samples. The PVA homopolymer (curve F in Fig. 1) exhibits a sharp melting endotherm with a peak maximum at 227°C and a clear baseline gap reflecting the glass transition in a temperature range ca. 65°C–80°C. From precise analysis of the discontinuity in heat flow on an enlarged scale, the T_g of the PVA was found to be 69°C at the onset point of the transition and 75°C at the midpoint. The other polymer, alginate, showed no melting signal in this thermal analysis (curve A in Fig. 1), and its T_g was estimated to be 110°C at the onset point and 119°C at the midpoint of the DSC base-line change. Concerning the blends of the two polymers, a single glass transition was detected for all the compositions investigated, the location shifting to the higher temperature side as the alginate concentration was increased. As can be seen from Fig. 1, the melting temperature T_m of the PVA component was depressed systematically to lower temperatures with increasing alginate content. In addition, the magnitude of the endothermic peak area reduced disproportionately with Alg/PVA ratio, and when the alginate content exceeded 60 wt%, the development of crystallinity of the PVA component became less prominent. Such effects in thermal transition behaviour observed for the present system, i.e., the composition-dependent shift in T_g of blends, the depression in T_m and the repression in the degree of crystallinity of the crystallizable component (i.e. PVA), owing to the addition of the second component (i.e. Alg), are common features which are shared with other crystalline/amorphous polymer pairs that are capable of forming a miscible phase in their blends (MacKnight et al., 1978; Olabishi et al., 1979.

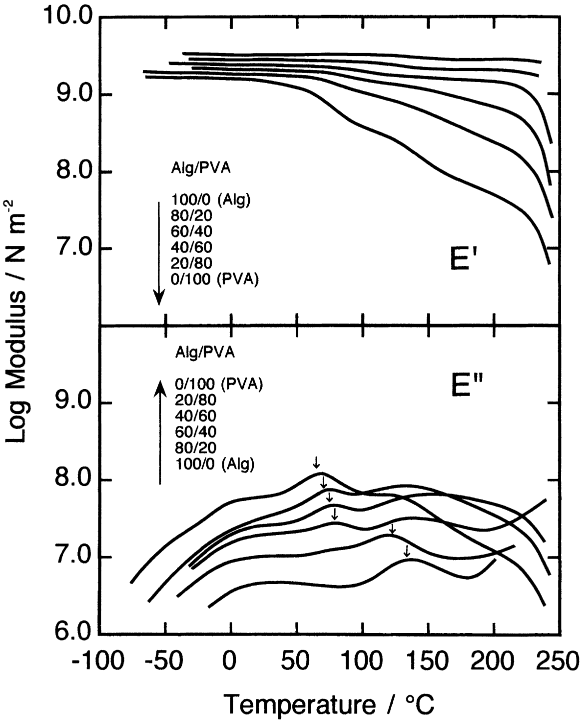

Fig. 2. Temperature dependence of the dynamic storage modulus (E′) and loss modulus (E″) for Alg/PVA[O] blends. Arrows indicate a peak maximum position of the α_a dispersion.

Fig. 2 shows the variation of the dynamic storage modulus E′ and loss modulus E″ as a function of temperature, measured for film specimens of Alg and PVA, and Alg/PVA[O] blends. In the data for the PVA homopolymer sample, three mechanical dispersions are observable above − 50°C, each designated as the following, based on literature data (Takayanagi, 1963; Nishio and Manley, 1988). A relatively sharp peak in E″ with the maximum at around 70°C can be assigned to the primary dispersion α_a associated with the glass transition of this polymer. In this transition temperature region, the dynamic modulus E′ decreases markedly from the ‘frozen modulus’ value, indicating that micro-Brownian motions of the main chains of PVA molecules become conspicuous in the amorphous regions. The presence of the secondary dispersion β_a owing to the local relaxation mode of the PVA main chains is also noted as a broad shoulder ranging from 0°C to 30°C in the E″ curve. The sample gives another dispersion signal above 100°C; this is concerned with a relaxation in the PVA crystalline phase. The other homopolymer sample, an alginate film cast from aqueous solution, exhibits a dispersion peak centering at ca. 130°C in the E″ versus temperature curve. This signal may be attributed to the amorphous relaxation corresponding to the glass transition, i.e. α_a, of the alginate, although the lowering of the modulus E′ in the transition temperature region is small, possibly owing to the semi-rigidity of the carbohydrate backbone chains. The E″-peak is, however, situated at a somewhat higher temperature, compared with the T_g(midpoint) of 119°C estimated by the DSC measurement. This discrepancy may be ascribed to

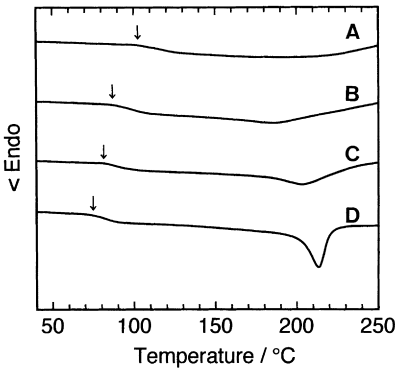

Fig. 3. DSC thermograms of Alg/PVA samples with a 60/40 composition, measured before and after the treatment with CaB_4O_7 aqueous solution: A, Alg/PVA[S]; B, Alg/PVA[M]; C, Alg/PVA[W]; D, Alg/PVA[O]. Notations [S], [M] and [W] serve to distinguish the difference in the extent of cross-linking (see the Experimental section (Section 2)).

differences in the responses for the same relaxation process between the two analytical methods (MacKnight et al., 1978).

The dynamic viscoelastic data depicted in Fig. 2 suggests a general trend of elevation in the position of the α_a peak with an increase in alginate content, as indicated by arrows (Fig. 2). This observation is consistent with the systematic T_g-shift revealed in the DSC study. It should also be noted here that the amplitude of the drop in E' occurring in the glass transition region becomes extremely small with increasing amount of alginate, and concomitantly the β_a dispersion of PVA tends to lose its prominence with a slight displacement to the higher temperature side. These effects suggest a serious restraint of the amorphous relaxation of PVA main chains, arising from the intimate incorporation with the alginate component. Thus, the result of the dynamic viscoelastic measurements supports strongly the conclusion that the two constituent polymers are coexistent in a fairly good state of miscibility in the blend materials.

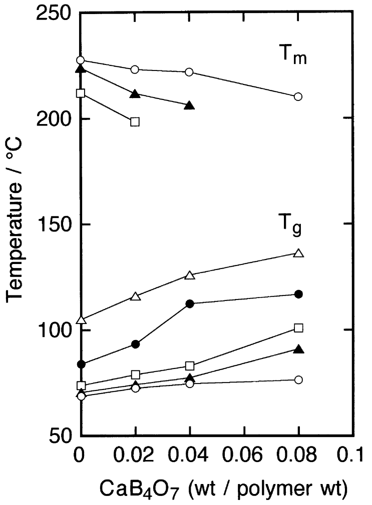

Fig. 4. Plots of the transition temperatures T_g and T_m versus CaB_4O_7 concentration for different Alg/PVA compositions. Alg/PVA: ○, 0/100 (PVA); ▲, 20/80; □, 60/40; ●, 80/20; △, 100/0 (Alg).

3.2. Effect of post-treatment with calcium tetraborate solution

The post-treatment with aqueous calcium tetraborate solution (0.4 wt% CaB_4O_7) was conducted on as-cast Alg/PVA films, into which the cross-linker was introduced at a concentration of 2%–8% (per total polymer weight). All the samples remained transparent and visually homogeneous after the treatment.

Chemical cross-linking gave rise to an appreciable change in the thermal and viscoelastic properties of the cast blends. Fig. 3 displays DSC thermograms measured before and after the treatment, for a blend composition of Alg/PVA = 60/40. Four curves are presented, referring to the relevant samples of the O-, W-, M-, and S- series defined in the Experimental section (Section 2). As shown by curve D (Fig. 3), an untreated 60/40 sample gives a T_g of 74°C, when evaluated from the onset point of a base-line gap, and a T_m of 212°C, when read as the peak maximum of a melting endotherm. Following post-treatment, there is an elevation in T_g, relatable to the concentration of cross-linking agent in the following manner: 80°C for Alg/PVA[W] (curve C); 85°C for Alg/PVA[M] (curve B); and 102°C for Alg/PVA[S] (curve A), each value corresponding to the onset point of the transition. Another striking effect of the treatment is that the PVA crystallinity decreases with an accompanying depression in the melting temperature, as soon as 2.0% CaB_4O_7 was introduced into the sample. When the CaB_4O_7 concentration reached 4.0% (M-series), the melting endotherm became vanishingly small so that the T_m value could not be estimated exactly. Ultimately the melting signal was no longer discernible for the corresponding sample of the S-series, as can be seen from curve A (Fig. 3).

In Fig. 4, the T_g and T_m data obtained by DSC for different polymer compositions are plotted against cross-linker concentration, to clarify the effect of the post-treatment on the thermal property of the present system. The elevation in T_g, and the depression in T_m attended by diminution of the crystallinity (if any), with an increase of the CaB_4O_7 concentration, are evident for all of the polymer compositions investigated. These changes in thermal transition behaviour are undoubtedly owing to specific cross-linking reactions of the component polymers caused by the post-treatment. Alginate is known to be readily cross-linked in the presence of divalent metallic ions such as Ca^{2+}, by chelate complexation between carboxylate anions of this polysaccharide and the metallic cations. In the presence of borate compounds, PVA chains having abundant hydroxyl groups can also form a network through a borate-ion-aided complexing reaction. Accordingly, the treatment with CaB_4O_7 solution, adopted in this study, should make it possible for the two constituent polymers to undergo their respective, specific cross-linking reactions simultaneously.

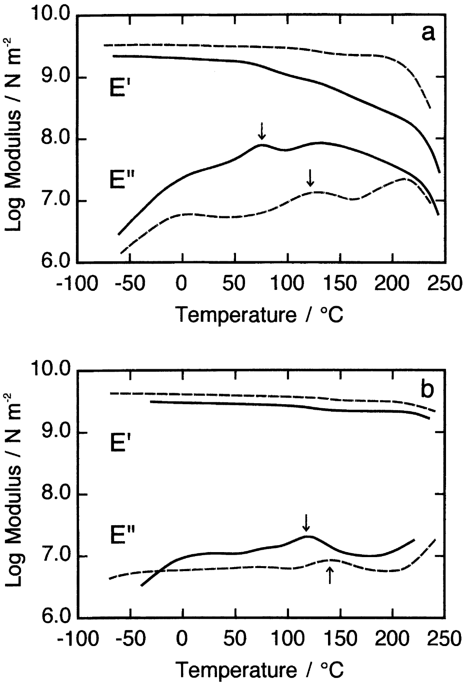

Fig. 5. Temperature dependence of E′ and E″ for Alg/PVA blends, measured before and after the treatment with CaB_4O_7 solution. Data in (a) refer to Alg/PVA[O] (—) and Alg/PVA[S] (---), both having a 20/80 composition. Data in (b) refer to Alg/PVA[O] (—) and Alg/PVA[W] (---), both having a 80/20 composition.

An additional point of significance in the DSC data shown in Fig. 3 is the finding of a single, composition-dependent T_g for all of the three series of cross-linked blends, indicating that high miscibility in the original blends (O-series) was retained in the cross-linked series. Thus the occurrence of the two kinds of cross-links in both polymer components never leads to a phase segregation under the mild conditions imposed in the present treatment, where a relatively low concentration (0.4 wt%) of CaB_4O_7 solution was used.

The elevation in T_g as a post-treatment effect was also ascertained by measurements of dynamic viscoelasticity. Fig. 5 illustrates the temperature dependence of E′ and E″ for two representative samples of Alg/PVA blends: one is a PVA-rich blend with a 20/80 Alg/PVA composition (Fig. 5(a)) and the other is an alginate-rich blend with an 80/20 Alg/PVA composition (Fig. 5(b)), each examined before and after the chemical treatment. As can be seen from the data depicted by full curves in Fig. 5(a), the untreated 20/80 sample exhibits the principal dispersion α_a centered at ca. 75°C, reflecting the glass transition. In data obtained for the post-treated 20/80 sample (S-series), the corresponding dispersion signal appears with an E″ peak maximum at 117°C, which is higher by as much as 40°C compared with the α_a peak position for the original sample (O-series). As is also demonstrated for the other Alg/PVA composition in Fig. 5(b), a primary dispersion associated with the glass transition of the post-treated 80/20 sample (W-series) is located in a higher temperature region, compared with the case of the untreated blend. The observation of a shift in α_a peak position following the CaB_4O_7 treatment is in qualitative accordance with the elevation of T_g revealed by DSC.

Another important observation in the dynamic mechanical measurements was as follows: the treatment with CaB_4O_7 solution led not only to a more gradual and a smaller decrease of the storage modulus E′ with increasing temperature in the glass transition region, but also to an augmentation of the glassy-state modulus at temperatures lower than T_g, in comparison with the behaviour of untreated blend materials. These effects were more pronounced when PVA-rich blends were employed for the comparative experiment, as is readily perceptible from the data in Fig. 5(a); here, note that the modulus data are represented in a logarithmic scale. An observation similar to the previous was made for several blend systems of cellulose or chitin/vinyl polymers having an interpenetrating network (IPN)-type organization (Nishio, 1994; Miyashita et al., 1997, Miyashita et al., 1998), which were synthesized via bulk polymerization in a gel state of cellulose or chitin impregnated with the corresponding monomers of the blending partners of the polysaccharides. In the present system, both alginate and PVA components are cross-linked between the respective polymer chains with the aid of calcium tetraborate, fortunately with retention of the good miscibility state of the original blends, as discussed previously. The construction of such a double network architecture implies the occurrence of a full IPN organization in the polymeric blends. This may be regarded as responsible for the significant changes in viscoelastic properties as well as thermal transition behaviour caused by the post-treatment.

4. Conclusions

Binary blend films composed of alginate (Alg) and poly(vinyl alcohol) (PVA) were prepared from mixed aqueous polymer solutions by solvent evaporation. Thermal and viscoelastic properties of the blends were characterized by DSC and dynamic mechanical analysis. Judging from the observations of a single, composition-dependent T_g and a systematic depression in the melting point of PVA, it is reasonable to conclude that the polymer mixtures of Alg/PVA form a thermodynamically miscible phase in their blends. By the post-treatment of as-cast samples with an aqueous calcium tetraborate solution, two kinds of polymer networks were introduced into the blend films, without giving rise to a definite phase-separation: one of the networks is based on the borate-ion aided cross-links formed between PVA molecular chains and the other is owing to cross-links of alginate chains via chelate complexing with Ca^{2+} ions. It is plausible that the concurrent cross-linking reactions perpetuated an IPN-type organization in the post-treated blends, resulting in a marked elevation of T_g and an augmentation of E′ making the materials stiffer.

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