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Transition behaviour of cellulose/poly(*N*-vinylpyrrolidone-*co*-glycidyl methacrylate) composites synthesized by a solution coagulation/bulk polymerization method

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Cellulose/poly(*N*-vinylpyrrolidone-*co*-glycidyl methacrylate) (CELL/P(VP-*co*-GMA)) composites were synthesized via photopolymerization in the gel state of cellulose swollen in a mixture of VP and GMA monomers as reactive impregnant. The cellulose gels were formed from homogeneous solutions in *N,N*-dimethylacetamide/lithium chloride by coagulation in ethanol, followed by exchange of the coagulant for the monomer mixture. The thermal transition behaviour and phase construction of the (CELL/P(VP-*co*-GMA) composites obtained in film form over a wide composition range were investigated. For compositions containing less than 20 wt% CELL, it was reasonably assumed that the original network structure of cellulose gels was sufficiently perpetuated into the polymerized bulk. Dynamic mechanical analysis revealed that the lowering of the storage modulus (E') of the copolymer-rich composites in the glass transition temperature (T_g) region was extremely suppressed, compared with the corresponding E' drop observed for plain P(VP-*co*-GMA) samples. The additional treatment of as-polymerized composites with aqueous formic acid or sodium hydroxide solution gave rise to a marked elevation of their T_g values, due to a certain crosslinking reaction in the copolymer constituent. A similar T_g elevation phenomenon was noted in the case where CELL/P(VP-*co*-GMA) samples were subjected to a prolonged heat treatment at temperatures higher than ca. 175°C. This may be ascribed to the prominence of crosslinking between the cellulose and copolymer components through reaction of GMA epoxides with cellulose hydroxyls. Copyright © 1996 Elsevier Science Ltd.

(Keywords: cellulose; P(VP-*co*-GMA); composites; IPN)

INTRODUCTION

In recent years considerable efforts have been devoted to the microscopic incorporation of cellulose with various synthetic polymers, against the generally believed intractability of the natural fibrous polysaccharide showing poor solubility in most organic solvents. It is worth noting that a highly compatible blend has been shown to be attainable for some pairs of cellulose/synthetic polymers by using a suitable, non-aqueous solvent and procedure for each individual case[1–6]. Marked synergistic effects in physical and physicochemical properties, including thermal and tensile behaviour, swelling, vapour absorption, etc., have been demonstrated[7], in the achievement of desirable preparation of intimate polyblends or microcomposites of cellulose. Two methods have been mainly adopted to prepare cellulose-based hybrid samples: one is casting from solutions by evaporation of solvent, and the other is coagulation of solutions in a non-solvent, followed by drying. Both processes involve dissolution and mixing of two polymer components in a common solvent.

Quite recently, the authors have proposed an alternative route leading to unique composites made up of cellulose/synthetic polymer networks[8]. *In situ* polymerization of a vinyl solvent as coagulant and/or impregnant used to form cellulose gels is an essential part of the preparation. Actually, an 'interpenetrating network' (IPN) type of organization was realized in cellulose/poly(2-hydroxyethyl methacrylate) (CELL/PHEMA)[8] and cellulose/poly(*N*-vinylpyrrolidone) (CELL/PVP)[9] composites obtained via bulk polymerization in the gel state of cellulose impregnated with 2-hydroxyethyl methacrylate or *N*-vinylpyrrolidone monomer. Appropriate modification of this preparation technique, termed a 'solution coagulation/bulk polymerization' method, would enable us to design a variety of microcomposites based on cellulose.

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In the present work, we made an attempt to synthesize an IPN type of cellulosic composite with a copolymer comprising hydrophilic–hydrophobic monomer residues. Cellulose/poly(*N*-vinylpyrrolidone-*co*-glycidyl methacrylate) (CELL/P(VP-*co*-GMA)) composites were prepared successfully in film form from homogeneous solutions of cellulose by coagulation and subsequent polymerization of the resulting gels swollen in a VP/GMA monomer mixture as reactive impregnant. The thermal transition behaviour and phase structure of the composites thus obtained were characterized mainly through differential scanning calorimetry and dynamic viscoelastic analysis. Furthermore, some chemical and thermal post-treatments were applied to as-polymerized CELL/P(VP-*co*-GMA) samples for the purpose of introducing different types of intermolecular crosslinks thereinto. Discussion is given on the observation of a marked elevation in the glass transition temperature (T_g) of the composites.

EXPERIMENTAL

Materials

The cellulose sample used was a wood pulp with a degree of polymerization of 1040. *N*-vinylpyrrolidone (VP) (Nacalai Tesque Inc.) and glycidyl methacrylate (GMA) (Junsei Chemical Co. Inc.) were purified by distillation under reduced pressure. Reagent-grade *N,N*-dimethylacetamide (DMAc) was stored for more than 5 days over potassium hydroxide before use. Lithium chloride (LiCl) was dried at 120°C for 12 h in a vacuum oven. Guaranteed reagent-grade α,α'-azobisisobutyronitrile (AIBN) was used without further purification.

Sample preparation

The original cellulose sample was treated by a solvent exchange technique[1,2] successively with water, methanol and DMAc, before addition to the solvent system DMAc/LiCl, which was used at a salt concentration of 4.5 wt%. A viscous solution of cellulose in DMAc/LiCl was prepared at a polymer concentration of 0.9–1.2 wt% in a similar manner as described in the previous papers[1,2,8]. The actual concentration of cellulose was determined by weighing the solid film regenerated from a portion of the solution.

A weighed amount of the cellulose solution was poured into a glass tray, and then the proper amount of ethanol as coagulant was carefully applied onto the spread solution. The resulting gelatinous film of cellulose was washed with ethanol several times, followed by exchange of the impregnant for a VP/GMA monomer mixture containing the radical initiator AIBN at a concentration of ca. 2%. The cellulose content in the gel films thus obtained was controlled by removing an appropriate amount of the impregnating agent VP/GMA with filter papers. In the next step, the cellulose gel samples were allowed to solidify by bulk copolymerization of VP and GMA monomers at ca. 30°C for 90 min under irradiation with ultra-violet (u.v.) light. The photopolymerization was conducted in a curing chamber equipped with a 15 W u.v. lamp that gave an intensity maximum at 352 nm. The cellulose/poly(*N*-vinylpyrrolidone-*co*-glycidyl methacrylate) (CELL/P(VP-*co*-GMA)) composites thus synthesized were washed with ethyl acetate to extract monomer traces, and then dried at 50°C for 24 h *in vacuo*. The products are termed the O-series of composite samples and designated as CELL/P(VP-*co*-GMA)[O] for convenience.

Film specimens of PVP and PGMA homopolymers and those of P(VP-*co*-GMA) copolymers were also prepared by photopolymerization under the same conditions as described above; in this case, the monomer fluid was charged between thin polyethylene sheets. Cellulose homopolymer films were made solely by drying the gels obtained from solutions in DMAc/LiCl by coagulation with ethanol.

The O-series of composites were subjected to three different post-treatments, for the purpose of introducing different types of intermolecular crosslinks thereinto:

(a) Composites were dipped in aqueous alkaline solution of 3% sodium hydroxide. After 50 min immersion, they were taken out of the solution and then warmed, usually at 60°C for 90 min in an atmosphere of nitrogen. Following this, the samples were washed with water, then dried at 45–50°C *in vacuo*.

(b) Composites were exposed to 50% aqueous formic acid at 90°C for 60 min. The acid-treated samples were washed with water thoroughly, then dried at 45–50°C *in vacuo*.

(c) Composites were heat treated, usually at 180°C for ~6 h under vacuum, without exposure to any reagent.

The three series of samples thus post-treated are designated as CELL/P(VP-*co*-GMA)[S], CELL/P(VP-*co*-GMA)[F] and CELL/P(VP-*co*-GMA)[H], where notations [S], [F] and [H] serve to indicate the sodium hydroxide, formic acid and prolonged heat treatment, respectively, each specified above.

Measurements

Differential scanning calorimetry (d.s.c.) was carried out on ca. 7 mg samples with a Seiko DSC210 apparatus equipped with a thermal analysis station SSC5000. The measurements were performed at a scanning rate of 20°C min^{-1} under a nitrogen atmosphere, after calibration of the temperature readings with an indium standard. Usually, the samples were first heated up to 180°C and then immediately quenched to −30°C. The second heating scans were run from −30°C up to 220°C, to record stable thermograms.

Dynamic mechanical measurements were carried out with a Rheovibron model DDV-II-C viscoelastometer (Orientec Corp.) at an oscillatory frequency of 11 Hz. The temperature was raised at a rate of 1.2°C min^{-1} in the range −60 to 240°C. Film strips 3 × 30 mm^2 were employed, which were heated in an oven at 155–160°C for 5 min prior to the measurement, for removal of trace amounts of solvents and/or moisture and relaxation of possible stresses.

Fourier transform infra-red (*FT*i.r.) spectra were recorded with a Shimadzu spectrophotometer FTIR-8100M equipped with a diffuse reflectance instrument (DRS-8000).

A swelling test was made with water for film strips of CELL/P(VP-*co*-GMA)[O] samples. The degree of swelling, *S*, estimated in this examination was defined as follows:

$$S = [(W - W_0)/W_0] \times 100(\%)$$

where W is the weight of test specimens at swelling equilibrium, and W_0 the weight of the original dried specimens.

RESULTS AND DISCUSSION

*Transition behaviour of CELL/P(VP-*co*-GMA)[O] composites*

Figure 1 depicts d.s.c. thermograms obtained for CELL/P(VP-*co*-GMA)[O] composites containing < 20 wt% cellulose and a reference sample of P(VP-*co*-GMA) copolymer, all synthesized at a monomer ratio of VP/GMA = 7/3 via bulk polymerization with the same u.v. irradiation. In the d.s.c. curve of the P(VP-*co*-GMA) sample, we can see a single, clear baseline gap reflecting the glass transition of the copolymer. From the midpoint of the discontinuity in heat flow, the T_g of this sample was evaluated to be 123°C, which was situated between the two T_g values of the corresponding homopolymers, i.e. 63°C (for PGMA) and 136°C (for PVP). On the other hand, the T_g values of copolymer-rich composites with cellulose tended to be rather lower than that of the copolymer alone, as can be seen in *Figure 1*; here, the T_g values of the composites containing 5 and 10 wt% cellulose were estimated to be 102 and 97°C, respectively. At cellulose concentrations of $\gtrsim$20 wt%, the change in slope of the d.s.c. baseline became so broad that their T_g values could not be estimated precisely.

Figure 2 shows the temperature dependence of the dynamic storage modulus (E') and loss modulus (E'') for CELL/P(VP-*co*-GMA)[O] samples containing 0–19 wt% cellulose (VP/GMA = 7/3 in feed). The E'' *versus* temperature curve of the reference copolymer sample exhibits a dispersion peak with a maximum value at ca. 60°C. This dispersion signal may also be associated with the glass transition of the copolymer; however, the E'' peak is located at a considerably lower temperature, compared with the T_g estimated by d.s.c. It is presumed that the two tests respond somewhat differently to the same relaxation process[10]. In the dynamic mechanical data for the P(VP-*co*-GMA) copolymer, it is of importance to observe a rapid and intense decrease of the dynamic modulus E' following onset of the glass transition on heating; the micro-Brownian motions of copolymer chains appear to become more and more conspicuous with increasing temperature, and above 140°C the values of E' and E'' were actually out of the measurement range due to the prominence of plastic flow of the film specimen. Such a striking drop in both E' and E'' was a common feature in the viscoelastic property of unblended P(VP-*co*-GMA) samples, irrespective of VP/GMA ratio. In contrast to this behaviour, the chemical blending of the copolymer with cellulose led to a marked suppression of the lowering of E' and E'' after onset of the glass transition, as demonstrated in *Figure 2* for two composites containing 5 and 19 wt% cellulose. It should be stressed here that the cellulose component incorporated at only 5 wt% plays the role of effective reinforcement for the copolymer matrix at high temperatures above T_g. These composite films were optically clear, and visual inspection indicated complete retention of the starting gel form of cellulose. Thus, for such composites with copolymer-rich compositions, it can be assumed that the physical network of cellulose was successfully fixed into the copolymerized bulk, and, concurrently, a semi-IPN-like organization resulted. This is also confirmed by a swelling test described below.

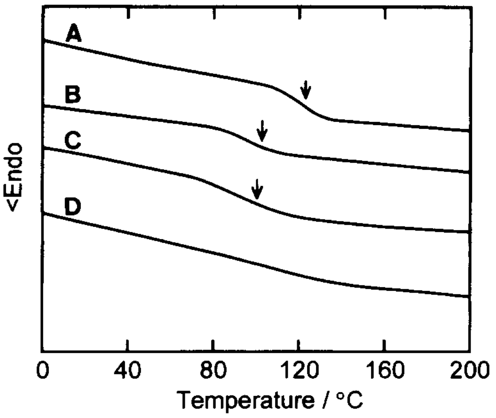


Figure 1 D.s.c. thermograms of CELL/P(VP-*co*-GMA)[O] composites with copolymer-rich compositions. CELL content: (A) 0 wt%; (B) 5 wt%; (C) 10 wt%; (D) 19 wt%. VP/GMA (in feed): 7/3. Arrows indicate a T_g position

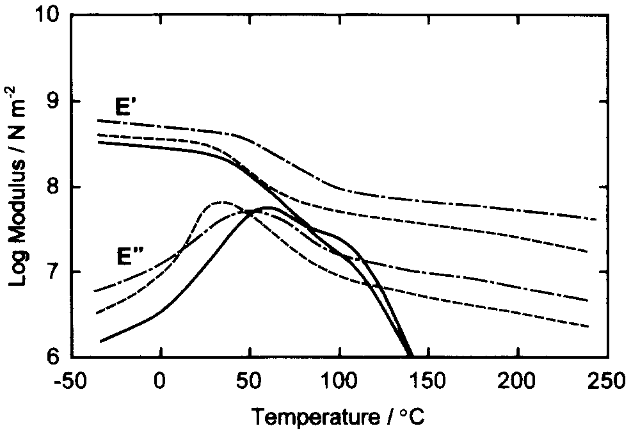


Figure 2 Temperature dependence of the dynamic storage modulus (E') and loss modulus (E'') for CELL/P(VP-*co*-GMA)[O] composites with copolymer-rich compositions. CELL content: (—) 0 wt%; (- - -) 5 wt%; (– · –) 19 wt%. VP/GMA (in feed): 7/3

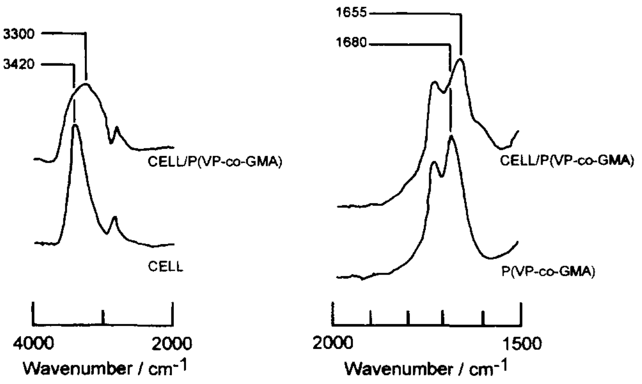
In spite of the indication of development of such a network structure in the cellulosic composites (CELL < 20 wt%), those samples gave a T_g value lower than that of copolymer alone in the d.s.c. measurements. The dynamic mechanical data are also consistent with the d.s.c. result, as is apparent in *Figure 2*; i.e. there occurs a clear shift in the E'' peak of P(VP-*co*-GMA) to the lower-temperature side on introducing cellulose thereinto. These observations form a strange contrast to the glass transition behaviour of a similar IPN type of composite of cellulose with poly(2-hydroxyethyl methacrylate) (PHEMA)[8], which was also prepared by the solution coagulation/bulk polymerization method. In the CELL/PHEMA system, the presence of even a few per cent of the cellulose component gave rise to a distinct elevation of the T_g of PHEMA.

A T_g depression phenomenon similar to that observed for the present system was noted in a previous study[9] of cellulose/poly(*N*-vinylpyrrolidone) (CELL/PVP) composites synthesized by the same method as adopted in this work. In interpretation of this peculiar phenomenon perceived for the two composite systems, it may be instructive to consider some potential effects due to a specific interaction between cellulose and VP components in the process of photopolymerization of the starting gel samples. There are at least two possibilities:

(1) One is concerned with a possible diminution in molecular chain length of the P(VP-*co*-GMA) (or PVP) component. Owing to a hydrogen-bond type of interaction between cellulose hydroxyls and VP carbonyls, the growth of copolymer (or PVP homopolymer) chains during polymerization may be considerably restrained, and consequently the molecular weight and therefore the T_g of the copolymer (or PVP) component in the resulting composite would be smaller than those of P(VP-*co*-GMA) (or PVP) alone synthesized under the same conditions.

(2) The other is concerned with a partial modification of cellulose molecules. In the starting gel state, cellulose chains may be solvated by coordination preferentially to VP monomers with a proton-accepting carbonyl group. In the course of polymerization of the gel, the cellulose molecules would be transformed into a pseudo-graft-derivative form, which should give a T_g value much lower than that of cellulose *per se* ($T_g \simeq$ 220–250°C[1,2,11-13]).

In any case, the participation of a specific interaction between cellulose hydroxyls and VP carbonyls is suggested. In order to ascertain the presence of this attractive interaction, *FT*i.r. spectra were measured for three different specimens: regenerated cellulose; P(VP-*co*-GMA) copolymer (VP/GMA = 7/3); and their composite (CELL $\simeq$ 10 wt%). *Figure 3a* shows a comparison of the O–H stretching band between the cellulose homopolymer and composite samples. The hydroxyl absorption of the composite yields a considerably broad peak, and its maximum position is situated at ~ 3300 cm^{-1}, which is much lower than the corresponding wavenumber (3420 cm^{-1}) for the cellulose sample. In the C=O stretching frequency region (*Figure 3b*), too, the CELL/P(VP-*co*-GMA) composite gives an absorbance maximum at a somewhat lower frequency, compared with a spectrum of the unblended copolymer, exhibiting the corresponding peak centred at around 1680 cm^{-1}.



(a) OH band

(b) C=O band

Figure 3 *FT*i.r. spectra of CELL, P(VP-*co*-GMA) and a CELL/P(VP-*co*-GMA)[O] composite containing 10 wt% cellulose (VP/GMA = 7/3)

The shift in frequency of both hydroxyl and carbonyl signals, observed for the CELL/P(VP-*co*-GMA) sample, can be explained as due to the hydrogen bonding of O–H···O=C[14-16]. It is conceivable that this attractive interaction existing in the polymer composite was formed already in the state of gel impregnated with VP/GMA monomers, and sustained even in the process of the polymerization reaction. This specific interaction may be responsible for the production of a copolymer with a relatively low molecular weight and/or a partially modified cellulose, each giving a lower T_g value, as described previously. No other lucid explanation of the T_g depression phenomenon is known at present.

The copolymer-rich samples described above were synthesized by the bulk polymerization of as-coagulated gels with avoidance of intemperate pretreatment, e.g. compression into a thin film. To prepare samples with CELL-rich compositions, however, it was necessary to extract a large amount of VP/GMA monomers from the as-coagulated cellulose gels before polymerization, by compressing them into a considerably thinner film form. In this process, part of the cellulose constituent might have cohered, to form agglomerates within the thin films. It is therefore plausible that the resulting CELL-rich composites would have less IPN character.

In *Figure 4*, the dynamic viscoelastic behaviour characteristic of CELL-rich samples (CELL $\gtrsim$ 70 wt%) is illustrated with two selected CELL/P(VP-*co*-GMA) compositions of 70/30 and 82/18, and compared with that for a cellulose homopolymer prepared by solution coagulation and drying. The ratio of VP/GMA monomer residues making up the copolymer component is 7/3 again here. As can be seen from the E' and E'' data depicted by full curves in the figure, the pure cellulose sample exhibited no clear amorphous relaxation, reflecting the glass transition in this measurement, before thermal degradation began to manifest itself above 230°C. In our previous blend studies[1,2,7], however, the T_g of cellulose was predicted to lie in the neighbourhood of 250°C. In contrast to the less temperature-dependent viscoelasticity of cellulose *per se*, the two examples of CELL-rich composites show a single but broad dispersion peak in their respective curves, with the maximum position centred at ~ 135°C (for 70/30) and ~ 185°C

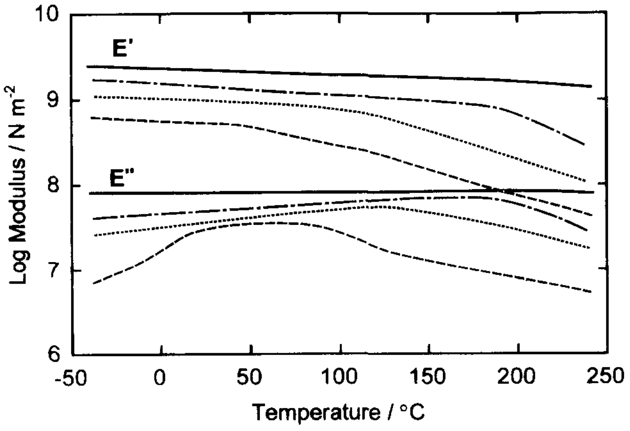


Figure 4 Temperature dependence of the dynamic storage modulus (E') and loss modulus (E'') for CELL/P(VP-*co*-GMA)[O] composites with CELL-rich compositions. CELL content: (- - -) 47 wt%; (· · · · ·) 70 wt%; (— · —) 82 wt%; (——) 100 wt%. VP/GMA (in feed): 7/3

(for 82/18). The shift in location of the E'' peak towards higher temperature with increasing cellulose content was also ascertained by using other CELL/P(VP-*co*-GMA) compositions ranging from ca. 70/30 to 95/5. These observations suggest that a large amount of molecules of the copolymer component are incorporated intimately in the cellulose amorphous regions, instead of making discrete domains, even though the CELL-rich products are poor in IPN architecture.

Figure 4 includes further data of the temperature dependence of E' and E'' examined for a CELL/P(VP-*co*-GMA) sample with a just intermediate composition (47/53). The E'' curve yields a plateau-like dispersion signal over a very wide temperature range of ca. 20–120°C. This signal is probably composed of a mixture of plural dispersion peaks laid to partially overlap each other, originating from the coexistence of multiple phases having different polymer compositions in the bulk composite. However, it may be admitted to assume that a certain degree of interpenetration of the two component molecules is realized in each phase, taking into consideration the chemical blending procedure adopted. The appearance of such a plateau region in an E'' *versus* temperature curve was familiar at CELL/P(VP-*co*-GMA) compositions containing ca. 30–60 wt% cellulose. With an increase in the cellulose content in this composition range, the location of the plateau tended to shift to the higher-temperature side. When the cellulose content reached ~ 60 wt%, however, the characteristic feature was no longer discernible.

The dynamic mechanical measurements were also performed on the other O-series of composites prepared at VP/GMA ratios of 5/5 and 3/7 in the feed. The viscoelastic profile of those composites varied depending on the cellulose/copolymer composition in almost the same manner as that observed for the series of samples synthesized at a VP/GMA ratio of 7/3, except for the following two points: (i) At copolymer-rich compositions (CELL < 20 wt%) where a semi-IPN organization was embedded in the products successfully, the increase in GMA residues in the copolymer component led to less prominence of the T_g depression phenomenon mentioned above. (ii) The samples prepared at a ratio of VP/GMA = 3/7 so as to contain 10–30 wt% cellulose, in particular, exhibited an abnormal dispersion signal above 170°C in addition to the major dispersion situated ordinarily below 100°C. This observation will be discussed in a later part of the text, in relation to a possible crosslinking reaction between the cellulose and copolymer components.

For the three O-series of composites characterized above, a swelling test as a complementary examination was made with water on film strips of various cellulose/copolymer compositions. The degree of swelling, S, defined in the 'Experimental' section, was determined on each specimen and plotted as a function of cellulose content. The result is shown in *Figure 5*; here, data obtained previously[9] for the CELL/PVP system with a network structure are also compiled for reference. As is evident from this figure, a simple rule of additivity is not applicable to the composition dependence of the swellability for any series of composites; i.e. the degree of swelling does not change monotonically with polymer composition, but shows a distinct minimum peak at a CELL fraction of less than 0.2. This striking negative deviation may be ascribed to the formation of molecular interpenetration of the two constituent polymers, which is realized well especially at compositions of CELL < 20 wt%, as has been indicated by the dynamic mechanical study.

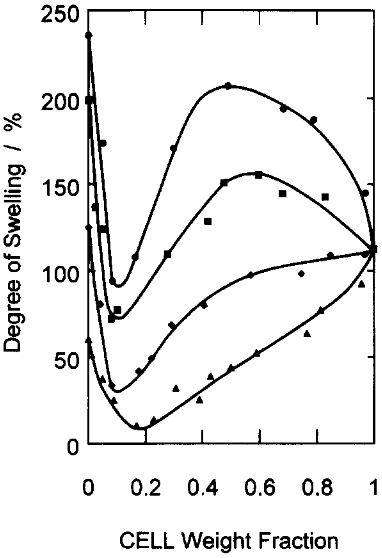


Figure 5 Plots of the degree of swelling (S) *versus* CELL weight fraction of CELL/P(VP-*co*-GMA)[O] samples. VP/GMA (in feed): (●) 10/0 (data from ref. 9); (■) 7/3; (◆) 5/5; (▲) 3/7

Another point of significance in the swelling data is a large difference in the water absorbance among the three series of composites having different proportions of VP/GMA units in the copolymer component. Cellulose composites with a VP-rich copolymer give a relatively higher degree of swelling over the whole range of CELL/copolymer composition, while composites with a GMA-rich copolymer show a rather poor swellability, reflecting clearly the difference in affinity for water between VP and GMA residues. Thus the water absorption property of the present system is of widely variable degree, by changing the binary polymer composition (CELL/copolymer) and the proportion of hydrophilic/hydrophobic (VP/GMA) residues in the copolymer.

Post-treatment effect

The post-treatments with aqueous formic acid and sodium hydroxide solutions were conducted on semi-IPN-type composites in which a cellulose gel was immobilized at a concentration of 4–5 wt%. Both chemical treatments gave rise to a drastic change in the thermal property of the composites. Examples of d.s.c. thermograms measured before and after the treatments are displayed in *Figure 6*, where notations [F] and [S] indicate the treatment method defined in the 'Experimental' section. The data are presented separately for two cases different from each other in the monomer composition of the copolymer component: (a) VP/GMA = 7/3 and (b) VP/GMA = 3/7. In the respective cases, we can see a remarkable elevation in T_g for the relevant sample following the post treatments. In the case using a cellulose composite with a VP-rich copolymer (*Figure 6a*), the sodium hydroxide treatment is more effective than the treatment with formic acid, concerning the extent of shift in T_g. In contrast with this, if the same experiment is carried out for a composite

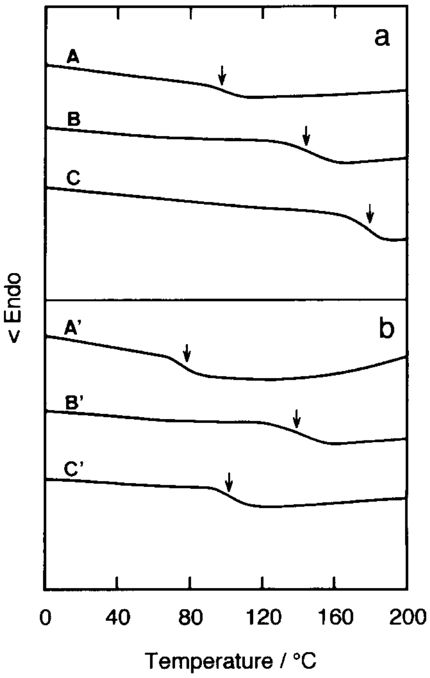


Figure 6 D.s.c. thermograms of cellulose composites synthesized with two different monomer feed compositions: (a) VP/GMA = 7/3 and (b) VP/GMA = 3/7. Data were obtained before and after the treatment with aqueous formic acid or sodium hydroxide solution (see text for discussion): (A, A′) CELL/P(VP-*co*-GMA)[O]; (B, B′) CELL/P(VP-*co*-GMA)[F]; (C, C′) CELL/P(VP-*co*-GMA)[S]. The cellulose content of all the samples is 4 wt%

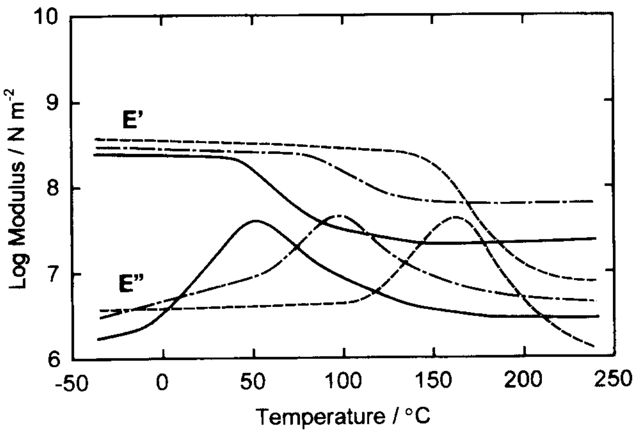


Figure 7 Temperature dependence of E' and E'' for different film species of a cellulose composite synthesized at a monomer ratio of VP/GMA = 3/7: (——) CELL/P(VP-*co*-GMA)[O]; (- - -) CELL/P(VP-*co*-GMA)[F]; (– · –) CELL/P(VP-*co*-GMA)[S]. CELL content = 4.5 wt%

synthesized at a ratio of VP/GMA = 3/7 (*Figure 6b*), the formic acid treatment exerts a greater effect on the glass transition behaviour, compared with the other treatment.

The post-treatment effect revealed by d.s.c. was also ascertained by measurements of dynamic viscoelasticity. *Figure 7* illustrates the temperature dependence of E' and E'' for a cellulose composite (CELL = 4.5 wt%) with a copolymer of VP/GMA = 3/7, examined before and after the chemical treatments. As is clearly demonstrated here, the principal dispersions of both post-treated samples (S-series and F-series) are located in an extremely high temperature region, compared with that of the untreated one (O-series). The observation of a difference in the shift of the E'' peak position between the two samples treated differently is in qualitative accordance with the d.s.c. result shown in *Figure 6b*.

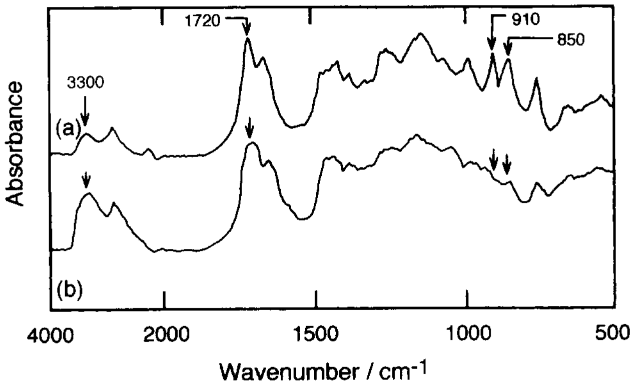
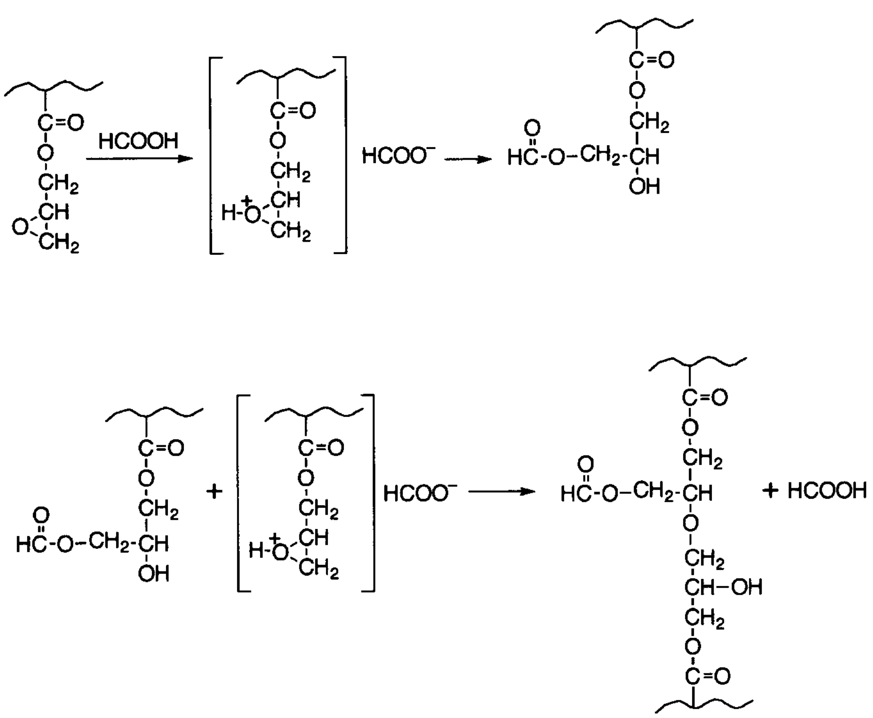


Figure 8 *FT*i.r. spectra of (a) CELL/P(VP-*co*-GMA)[O] and (b) CELL/P(VP-*co*-GMA)[F]. CELL content: 4 wt%. VP/GMA (in feed): 3/7

Such a striking T_g shift is presumably due to a specific crosslinking reaction of the copolymer component caused by the post-treatments. *Figure 8* shows *FT*i.r. absorption spectra measured for a composite (VP/GMA = 3/7) before and after the treatment with aqueous formic acid. It is found that two absorption peaks characteristic of the epoxide ring disappear after the acid treatment, which are present at 850 and 910 cm^{-1} in the spectrum of the untreated sample. Furthermore, the carbonyl peak of GMA around 1720 cm^{-1} is broadened and the OH signal near 3300 cm^{-1} is also enlarged, after the treatment. These spectral changes indicate that the copolymer component was crosslinked between GMA units via a ring-opening reaction[17] of the epoxide group with carboxylic acid, according to *Scheme 1*. The first step of the sequence of reactions is an addition-type esterification of the GMA epoxide with formic acid accompanied by the ring opening, and the second one is a crosslinking etherification. The bridge formation between GMA residues in copolymer chains would develop a tighter IPN structure in the composite material, resulting in elevation of the T_g.

In the other case where as-polymerized composites were treated with an aqueous solution of sodium hydroxide, a different type of crosslinking prevailed therein. *Figure 9* shows a comparison of *FT*i.r. data between an NaOH-treated sample and the corresponding untreated one. The monomer feed composition for synthesizing the composite was VP/GMA = 7/3 in this example. In the spectrum measured after the treatment, a novel absorption peak emerges around 1580 cm^{-1}, while the epoxide signals of GMA remain as they were in the untreated state. The appearance of the new peak probably originates from the occurrence of both carboxylate ion and secondary amide group, the two corresponding i.r. signals merging into an apparently single peak in the spectrum. Thus we can propose the reaction scheme as in *Scheme 2*. The treatment with NaOH solution first induces hydrolysis of the amide linkage in VP moieties of the copolymer component. Following the cleavage of some pyrrolidone rings, carboxylate anions are produced in the side chain of the copolymer and a couple of them interact with a sodium



Scheme 1

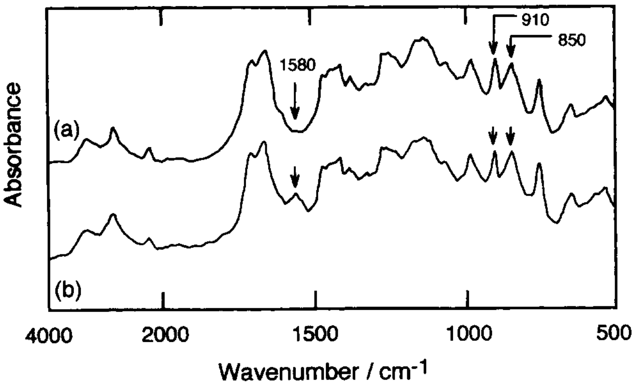
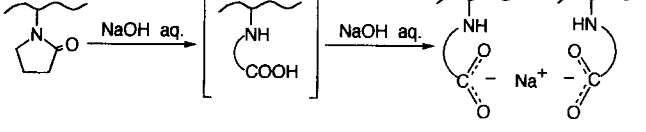


Figure 9 *FT*i.r. spectra of (a) CELL/P(VP-*co*-GMA)[O] and (b) CELL/P(VP-*co*-GMA)[S]. CELL content: 4 wt%. VP/GMA (in feed): 7/3



Scheme 2

cation to form an ionic junction. Such a transformation of the copolymer component into a kind of 'ionomer'[18] should also lead to the development of a tighter network structure in the composite material. This may be regarded as responsible for the T_g elevation observed in the d.s.c. and dynamic mechanical measurements.

Thus it has been shown that the semi-IPNs made up of cellulose/P(VP-*co*-GMA) can be converted into 'full-IPNs' through the post-treatments with aqueous formic acid and sodium hydroxide solutions, under the conditions imposed in the present study. Here, however, caution should be exercised because of the susceptibility of cellulose to degradation in a concentrated acid or alkali solution. Actually, in *Figure 7*, we notice an unusual viscoelastic behaviour for the formic acid-treated sample, i.e. a relatively large magnitude of the E' drop in the glass transition region, despite the remarkable shift of the E'' peak position due to the attainment of a full-IPN-type organization. This observation may be attributable to some extent to degradation of the cellulose component, elicited by the treatment with highly concentrated (50%) formic acid solution. On the other hand, the NaOH-treated sample seems to have avoided heavy degradation of the cellulose constituent via the use of a relatively low concentration (3%) for the caustic alkaline solution.

The phenomenon of marked elevation in T_g as a post-treatment effect was also noted in a comparative study of thermal analysis between the O-series and H-series of composites. The latter underwent heat treatment at 175–180°C over a period of ~ 6 h under vacuum. *Figure 10* shows dynamic viscoelastic data for a composite (CELL = 11 wt%) synthesized at a monomer ratio of VP/GMA = 3/7, demonstrating the difference in the transition behaviour before [O] and after [H] prolonged heat treatment. As can be seen from the data depicted by full curves, the untreated sample exhibits two dispersion signals: a primary dispersion centred at ca. 70°C, which is associated with the glass transition of this sample; and a secondary dispersion located around 190°C, with an abnormal increase of the storage modulus E'. In the other data obtained for the heat-treated sample, there appears a definitely single transition signal with an E'' peak maximum at 140°C, this being higher by as much as 70°C compared with the corresponding peak position for the original sample.

The observation of such a T_g shift following the prolonged heating of CELL/P(VP-*co*-GMA) composites can be interpreted as due to an intermolecular crosslinking

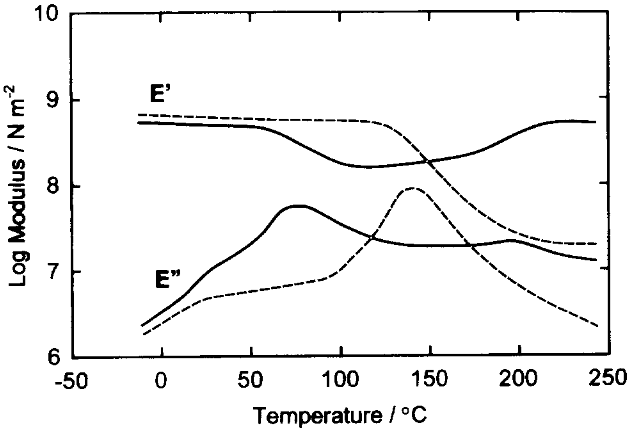
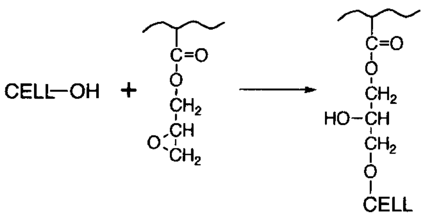


Figure 10 Temperature dependence of E' and E'' for two different film species of a cellulose composite synthesized at a monomer ratio of VP/GMA = 3/7: (——) CELL/P(VP-*co*-GMA)[O]; (- - -) CELL/P(VP-*co*-GMA)[H]. CELL content = 11 wt%

between the cellulose and copolymer components through etherification of GMA epoxides with cellulose hydroxyls, as shown schematically in *Scheme 3*. As evidence of this intercomponent bridging, *FT*i.r. measurements revealed that the absorption peaks at 850 and 910 cm^{-1} characteristic of the epoxide ring were suppressed considerably in spectra recorded for the H-series of samples. Thus it turns out that the heat treatment imposed above 170°C transformed the original semi-IPN of CELL/P(VP-*co*-GMA) into a 'joined-IPN' type of composite in which two polymer components are partially bound covalently. In this regard, it is reasonable to assume that the secondary dispersion observed in *Figure 10* for the untreated sample is not a relaxation signal essential to the original phase structure, but a transient signal occurring due to the crosslinking etherification described above, which proceeded markedly above ~ 170°C during the measurement.



Scheme 3

CONCLUSIONS

Cellulose/poly(*N*-vinylpyrrolidone-*co*-glycidyl methacrylate) (CELL/P(VP-*co*-GMA)) composites were synthesized successfully via photopolymerization in the gel state of cellulose impregnated with a reactive monomer mixture of VP and GMA. For the compositions containing < 20 wt% cellulose, it was reasonably assumed from swelling and dynamic viscoelastic data that the original network structure of cellulose gels was sufficiently perpetuated into the copolymerized bulk, accompanied by the formation of a semi-IPN-type organization. The dynamic mechanical analysis revealed that the lowering of the modulus E' of the copolymer-rich composites in the glass transition region was extremely suppressed, compared with the corresponding E' drop observed for plain copolymer samples. However, these composites gave a T_g value lower than that of P(VP-*co*-GMA) copolymer alone. This T_g depression phenomenon, which was quite prominent for samples synthesized with a VP-rich monomer mixture, was explained by taking into consideration two potential effects due to a specific interaction between cellulose and VP monomers in the process of photopolymerization, i.e. the possibility of producing a copolymer with a relatively low degree of polymerization and/or a partially modified cellulose was considered.

CELL-rich composites containing $\gtrsim$70 wt% cellulose exhibited a single, broad dispersion centred at a temperature higher than 130°C in the viscoelastic measurements. The position shifted systematically to the higher-temperature side with increase in cellulose content. Therefore the dispersion was interpreted as due to a molecular relaxation in the cellulose amorphous regions into which copolymer molecules were intimately incorporated. Other samples with intermediate CELL/P(VP-*co*-GMA) compositions usually showed a plateau-like dispersion signal in their E'' curve over a wide temperature range, probably originating from the coexistence of multiple phases having different polymer compositions in the composites.

Chemical and thermal post-treatments were applied to as-polymerized samples with copolymer-rich compositions, acting on the possibility of introducing different types of intermolecular crosslinks thereinto. Both of the treatments with aqueous formic acid (~ 50%) and sodium hydroxide (~ 3%) solutions gave rise to a drastic elevation of the T_g of the sample used, owing to the formation of a tighter network (full-IPN) structure. In the formic acid treatment, a ring-opening reaction of the epoxide group of GMA with the carboxylic acid was involved in the bridge occurrence between copolymer chains; while the sodium hydroxide treatment transformed the copolymer component into a kind of ionomer as a result of hydrolysis of the amide linkage in pyrrolidone rings. A similar T_g elevation was noted when cellulose composites with a GMA-rich copolymer were subjected to prolonged heating at ~ 180°C over a period of several hours. This may be ascribed to the development of a joined-IPN organization containing some amount of intercomponent crosslinks, in consequence of the etherification possible between GMA epoxides and cellulose hydroxyls.

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