Cellulose/poly(2-hydroxyethyl methacrylate) composites prepared via solution coagulation and subsequent bulk polymerization

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Conditions are described for the preparation of cellulose/poly(2-hydroxyethyl methacrylate) (CELL/PHEMA) composites from solutions of cellulose in dimethylacetamide–lithium chloride (DMAc–LiCl) by coagulation with 2-hydroxyethyl methacrylate monomer and subsequent bulk polymerization of the coagulated films. The CELL/PHEMA composites obtained over a wide composition range were characterized mainly through measurements of the temperature dependence of the dynamic storage modulus (E') and loss modulus (E''). For compositions rich in PHEMA (PHEMA > 80 wt%), it was assumed that an original structure of 'as-coagulated' cellulose gels was successfully perpetuated into the PHEMA matrix and, concurrently, an 'IPN'-type organization resulted. These samples gave a T_g value higher than that of PHEMA (~75°C), and the degree of lowering of their modulus E' in the glass transition region became extremely small with increasing CELL content. The E'' *versus* temperature curves for cellulose-rich compositions (PHEMA < 30 wt%) yielded a single, broad dispersion peak, the maximum position of which was located above 150°C and shifted to the side of higher temperature along with the decrease in PHEMA component. This dispersion was interpreted as due to a molecular relaxation in the abundant amorphous regions of cellulose into which PHEMA constituent was intimately incorporated. Other samples with intermediate CELL/PHEMA compositions showed a dual transition behaviour, due to phase separation into two distinct amorphous mixtures of both polymers.

(**Keywords: cellulose; poly(2-hydroxyethyl methacrylate); composites; solution coagulation; bulk polymerization; IPN**)

INTRODUCTION

A naturally occurring polysaccharide, cellulose, has been re-evaluated recently as a renewable resource. Its potential to develop further as a new, functional chemical or high-performance material has been studied by many workers[1–3]. The study of cellulose-based hybrid materials falls within this vital research field, relating to the utilization of an inexhaustible natural product.

Multicomponent polymer materials with unmodified cellulose may be grouped for convenience into three classes: wood/plastic combinations; mechanical mixtures in the form of fibres; and blends or microcomposites at a hyperfine structural level. In particular, the sequence of findings[4–8] of a variety of new non-aqueous solvents for dissolution of cellulose has motivated recent investigations[9–17] on blends and microcomposites.

Considerable efforts have been devoted to the preparation of intimate blends of cellulose with various polymers including vinyl polymers[3,9,11–13,17], polyesters[10,14], polyamides[14], polyethers[2,15], and other polysaccharides[16], using a suitable solvent and procedure for each individual case. The preparation methods adopted at present include: casting from solutions by evaporation of solvent; and coagulation of solutions with a non-solvent, followed by drying. Both processes involve mixing of two polymers in a common solvent. For example, one of the authors (Y.N.) demonstrated that cellulose blends with several important polymers such as polyacrylonitrile[12], poly(vinyl alcohol)[13,18], poly(ethylene oxide)[2,15,19], poly(ε-caprolactone)[14], and nylon 6 (ref. 14), can be obtained easily in film form over the entire composition range from solutions in *N*,*N*-dimethylacetamide (DMAc)–LiCl by a solution coagulation method. It was revealed that polyacrylonitrile, poly(vinyl alcohol) and poly(ethylene oxide) are able to form an amorphous mixture with cellulose showing fairly good miscibility. Recently, Masson *et al.*[20] showed that cellulose/poly(vinyl pyrrolidone) blends are miscible at every composition, when the films are cast from mixed polymer solutions in dimethylsulphoxide–paraformaldehyde (DMSO–PF) by solvent evaporation.

In this paper, we propose an alternative route to a new combination of cellulose/synthetic polymer materials,

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which have been mixed intimately with each other at a fine structural level. *In-situ* polymerization of a vinyl solvent as coagulant and impregnant used to form cellulose gels, is an essential part of the preparation. This technique is based on the combined use of the solution coagulation method reported previously[12–15] and one of the methods used for synthesis of IPNs[21], which are chemical blends with an interpenetrating network structure. The thermal and mechanical characterization of cellulose/poly(2-hydroxyethyl methacrylate) (CELL/PHEMA) composites prepared according to the 'solution coagulation/ bulk polymerization' method is described in detail.

EXPERIMENTAL

Original materials

The cellulose sample used was a wood pulp with a degree of polymerization of 935, which was treated by a solvent exchange technique[7,12,13] with water, methanol, and *N,N*-DMAc before preparation of solutions. 2-Hydroxyethyl methacrylate (HEMA) was purified by distillation at 60°C in a reduced pressure nitrogen atmosphere. Reagent-grade *N,N*-DMAc was stored for 1 week over potassium hydroxide before use. Lithium chloride was dried at 100°C overnight in a vacuum oven. Guaranteed reagent-grade α,α'-azobisisobutyronitrile (AIBN) was used without further purification as a radical initiator of the polymerization.

Sample preparation

A viscous solution of cellulose in DMAc–LiCl was prepared at a polymer concentration of 1.4 wt% in a similar manner as has been described previously[12,13]. The solvent DMAc–LiCl was used at a salt concentration of 4% with respect to DMAc. A weighed amount of the cellulose solution was poured into a rectangular Teflon tray with a flat bottom. An adequate quantity of HEMA was carefully applied onto the spread solution, whereupon the cellulose solution was transformed into a gelatinous film. After washing the coagulated cellulose gel with fresh HEMA several times, it was steeped for about 1 h in HEMA containing a radical initiator AIBN at a concentration of 0.98%. In the coagulation step, we made an attempt to use ethanol or acetone as coagulant instead of HEMA. As long as the sample was soaked with HEMA, all the cellulose gels obtained were almost the same in shape and size.

The composition of the swollen gel films thus prepared was controlled by removing an appropriate amount of the impregnating agent HEMA with filter papers. Following this, the cellulose/HEMA samples were allowed to solidify via *in-situ* polymerization of the monomer solvent by heating or ultraviolet (u.v.) irradiation. Thermal polymerization was carried out at 50°C for ~19 h in a thermostat. The photopolymerization was conducted at 27°C for 30 min on the swollen samples inserted into a u.v. curing chamber that was equipped with a 15 W u.v. lamp, which gave an intensity maximum at 352 nm. The distance between the sample and the light source was 40 mm. The CELL/PHEMA samples thus synthesized were washed with ethanol in order to extract residual monomer solvent, then dried at 30°C overnight *in vacuo*.

PHEMA homopolymer films were also synthesized by both photo- and thermal polymerization methods under the same conditions as those specified above. In this case, the monomer was charged between parallel quartz plates spaced by a Teflon tape. Cellulose homopolymer films were prepared solely by drying the gel samples, which were obtained from solutions in DMAc–LiCl by precipitation in acetone followed by washing with ethanol.

Measurements

The characterization of CELL/PHEMA composites and the corresponding homopolymer samples was performed mainly through dynamic mechanical measurements with a Rheovibron model DDV-II-C. The oscillatory frequency of the dynamic test was 11 Hz, and the temperature was raised at a rate of 1.5°C min^{-1}, usually in the range −90 to 220°C. Film strips 4 × 35 mm were employed, which were heat treated in an oven at ~140°C for 5 min prior to the measurement.

D.s.c. was carried out on 6 mg samples with a Seiko DSC-200 apparatus equipped with a thermal analysis station SSC-5000. The temperature readings were calibrated with an indium standard. In the d.s.c. apparatus, the samples were first heated up to 150°C and subsequently quenched to −20°C. The second heating scans were run up to 220°C at a rate of 10°C min^{-1}, to record stable thermograms. Only the T_g data obtained for plain PHEMA and PHEMA-rich compositions are presented in this paper; no clear glass transition was discernible in the d.s.c. thermograms of cellulose and cellulose-rich composites, and no sample examined gave an endothermic melting peak.

The tensile behaviour of CELL/PHEMA composites was examined with a Shimadzu tensile tester (Auto-graph IM-100) at room temperature. Stress–strain curves were recorded by elongating the specimens at a crosshead speed of 5 mm min^{-1}.

RESULTS AND DISCUSSION

In the case of bulk polymerization of HEMA, the monomer is liable to undergo a cross-linking reaction to form a network system. In fact, PHEMAs and CELL/PHEMA composites synthesized in this work were found to swell but did not flow or dissolve in water/organic solvents. A simple test of swelling was made with water and a highly aprotic solvent, dimethylsulphoxide (DMSO), for films of a few CELL/PHEMA composites and the corresponding homopolymers. The degree of swelling, S, estimated here was defined as a percentage of the weight of absorbed solvent to that of the original dried films. The following values of S were obtained for six samples steeped in DMSO for 24 h at room temperature: $S = 470\%$ (*L*-100), 430% (*H*-100), 360% (*L*-93), 330% (*H*-95), 270% (*H*-30), and 225% (cellulose), where L and H indicate whether the specimens tested were polymerized by u.v.-exposure (L) or by heating (H), and the numbers in parentheses denote wt% PHEMA content to represent the polymer composition of the specimens. Several per cent of cellulose embedded in the PHEMA matrix in a gelatinous form causes appreciable diminution of the degree of swelling. If a simple rule of additivity was applicable to the swelling behaviour of this binary system, the degree of swelling for the composites tested here would be evaluated in the following way: $S_c = 453\%$ (*L*-93), 420% (*H*-95), and 287% (*H*-30), which were calculated from $S_c = xS(\text{PHEMA}) +$

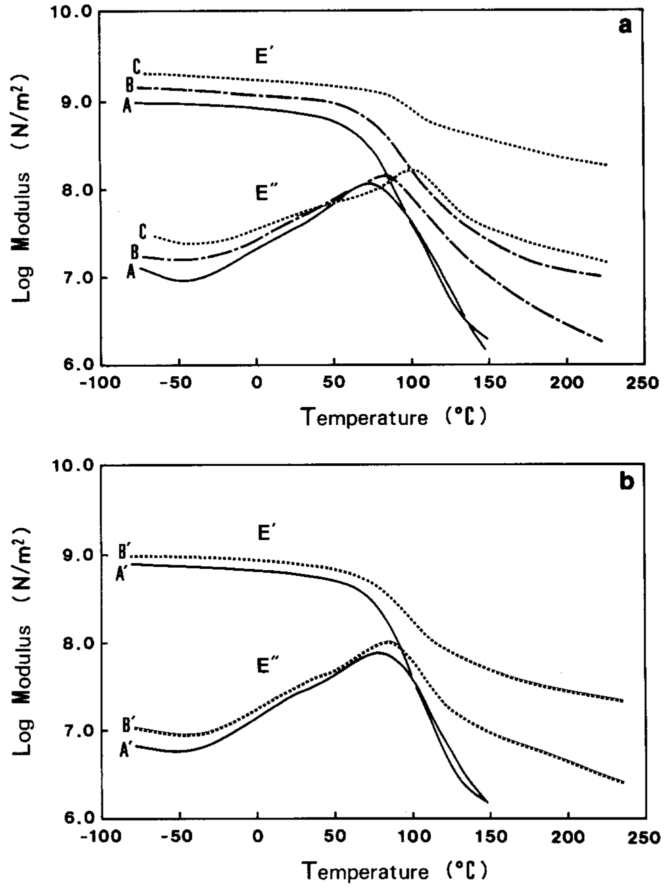

Figure 1 Temperature dependence of the dynamic storage modulus (E') and loss modulus (E'') for CELL/PHEMA samples prepared at PHEMA-rich concentrations by (a) photopolymerization and (b) thermal polymerization. PHEMA content: A, 100 wt%; B, 93 wt%; C, 84 wt%; A′, 100 wt%; B′, 96 wt%

$(1 - x)$ S(cellulose), where x is the weight fraction of PHEMA. Thus the S_c value calculated for each composite sample is larger than the corresponding S value observed. The negative deviation, i.e., $S - S_c < 0$, implies that the network structure developed in the polymer composites possesses an apparently higher density of cross-linking, in comparison with the situation expected by the law of additivity. This synergistic effect may be ascribed to the formation of molecular interpenetration of the two constituent polymers, anticipated to occur via *in-situ* polymerization and cross-linking of HEMA monomers penetrating the cellulose gels. In the case in which water was used as a swelling agent, there was less of a difference in the degree of swelling; i.e., all the samples gave a small S value of ~50%. Qualitatively, however, wet films of PHEMA homopolymer were more flexible and elastic, compared with wet CELL/PHEMA composites.

More explicit characterization of CELL/PHEMA composites was made by dynamic mechanical measurements with a Rheovibron viscoelastometer. In what follows, the composition-dependent viscoelastic properties are described in detail.

The variation of the storage modulus, E', and of the loss modulus, E'', as a function of temperature, are shown in *Figure 1* for samples containing 100–84 wt% PHEMA. The data in *Figure 1a* refer to photopolymerized samples, and *Figure 1b* shows results obtained for heat-polymerized samples. A PHEMA homopolymer obtained by photopolymerization exhibits a primary dispersion peak centred at 74°C in the E'' *versus* temperature curve, this dispersion being associated with the glass transition of the PHEMA sample. The presence of a secondary dispersion due to a local relaxation mode, is also noted at about 25°C as a faint shoulder in the E'' curve. Another PHEMA film obtained by thermally initiated polymerization gives much the same E' and E'' data as those for the photopolymerized PHEMA, but with an E'' peak maximum at a somewhat higher temperature (79°C). This difference of 5°C in the E'' peak position may be attributable to a slight difference between the two PHEMAs in the density of cross-linking, as suggested by the swelling test with DMSO. The rapid and intense decrease of the dynamic modulus E' in the glass transition region is of importance in the case of PHEMA homopolymers. After onset of the transition on heating, the micro-Brownian motion of PHEMA molecules appears to become more and more conspicuous with increasing temperature, and above 145°C the values of E' and E'' were actually out of the measurement range. It was checked visually that the homopolymer samples exhibited a rubbery property of expansion and contraction in an oven heated to ~150°C.

The bulk polymerization of 'as-coagulated' CELL/HEMA samples with avoidance of intemperate pretreatment, for example, compression into a thin film, gave rise to the formation of clear, hard films of PHEMA-rich composites containing >80 wt% PHEMA. Visual inspection of the CELL/PHEMA composites indicated complete retention of the starting gel form. In the dynamic mechanical measurements, such PHEMA-rich samples exhibited a principal dispersion located at a temperature position higher than that in the case of plain PHEMAs. For the two examples shown in *Figure 1a*, whose CELL/PHEMA compositions are 7/93 and 16/84, the T_g values were estimated to be 83 and 99°C, respectively, from precise readings of the temperature position of the E'' peak maximum. It is clear that the magnitude of an E'-drop occurring in the glass transition region becomes extremely small with an increase in cellulose content. Also, above T_g the loss modulus E'' of the composites does not fall so remarkably as the reference sample of PHEMA, resulting in broadening of the E'' *versus* temperature plots. Similar dynamic mechanical behaviour was observed for PHEMA-rich samples obtained by thermal polymerization. As demonstrated in *Figure 1b*, a heat-polymerized sample with a composition of 4/96 shows a rather broad E'' peak centred at 84°C. It should be stressed that the chemical blending of PHEMA with only 4 wt% cellulose leads to a marked suppression of the E'-drop in the glass transition region. These observations suggest that a more tight network structure was formed in the composites, compared with the PHEMA homopolymer films, in accordance with the swelling test result discussed previously.

The elevation of the T_g of PHEMA due to addition of cellulose, was also ascertained by d.s.c. measurements. *Figure 2* shows thermograms measured for the same CELL/PHEMA compositions as those used in *Figure 1*. As can be seen from the d.s.c. data, the T_g of PHEMA shifts to higher temperatures as it is blended with various amounts of cellulose ($\leqslant 16$ wt%), corresponding to the peak shift in E'' described previously.

Judging from the several significant effects of the blending observed for compositions rich in PHEMA, it

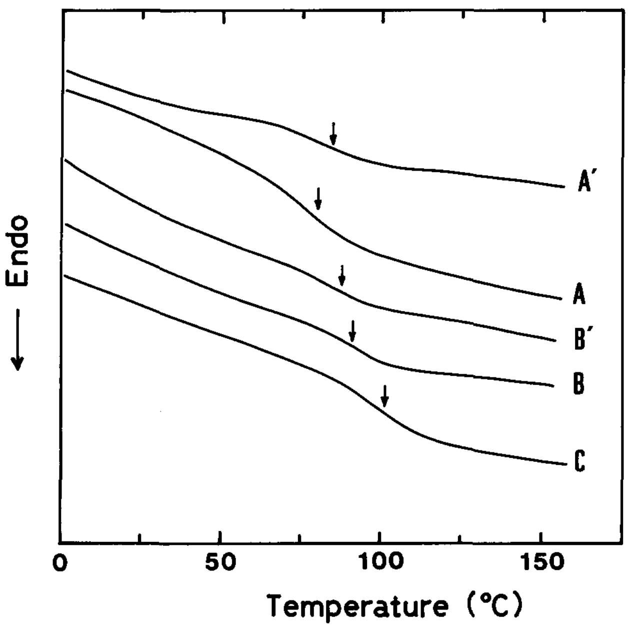

Figure 2 Differential scanning calorimetric thermograms of CELL/PHEMA samples with PHEMA-rich compositions. The notations to designate samples are the same as used for *Figure 1*. Arrows indicate a T_g position taken as the midpoint of the discontinuity in heat flow

seems natural to assume that an initial structure of swollen cellulose gels was sufficiently fixed into the composites by polymerization of HEMA, accompanied by the formation of an interpenetrating polymer network. In the present case, the products may be called 'semi-IPN' according to the IPN nomenclature[21], since the PHEMA component is cross-linked and cellulose is essentially linear. With regard to the facility of preparation of such semi-IPN composites, polymerization with u.v.-irradiation was of greater advantage than thermal polymerization. This is due to the speed of photo-induced reactions under mild conditions.

The result of dynamic mechanical tests performed on the CELL/PHEMA samples containing 0–20 wt% PHEMA is shown in *Figure 3*. In *Figure 3b*, solid-line curves represent the E' and E'' data obtained for cellulose homopolymer film that was prepared by solution coagulation and drying. As has been stated[12,13], cellulose regenerated from DMAc–LiCl solutions via coagulation in non-aqueous media show an extremely low degree of crystallinity. Nevertheless, no clear amorphous relaxation reflecting the glass transition of cellulose could be detected in the viscoelastic measurement, before appreciable thermal degradation began to occur above ~230°C. The cellulose T_g was, however, predicted to lie at ~250°C, from our previous blend studies[12,13]. In contrast to the monotonous variation in the viscoelastic behaviour of pure cellulose, CELL/PHEMA composites with PHEMA concentrations <30 wt% exhibited a single transition peak above 150°C in the E'' curves, in spite of the lack of a sharp break in the storage modulus *versus* temperature plots. As demonstrated in *Figure 3a* for three CELL/PHEMA compositions of 95/5, 91.5/8.5 and 87/13, the respective E'' yields a maximum at 185, 173 and 162°C. Thus the E'' peak position shifts towards lower temperature with an increase in PHEMA component. A similar composition dependence of the transition peak temperature was noted in the data for heat-polymerized cellulose-rich composites, as illustrated in *Figure 3b*. However, the E'' peak positions are located at somewhat higher temperatures, in comparison with the E'' data given in *Figure 3a*, taking account of the difference in composition.

The mechanical dispersions observed for the cellulose-rich composites can be taken to originate from a molecular relaxation in the cellulose amorphous regions in which PHEMA molecules are incorporated intimately. With this interpretation, however, attention should be given to the following point: in the preparation of the cellulose-rich composites, it was necessary to extract a large amount of HEMA monomers from the 'as-coagulated' gels before polymerization. For this purpose, the original samples were sandwiched between filter papers and covered with slide glasses under slight pressure. Inevitably, the samples were depressed into considerably thinner films, whereupon part of the constituent cellulose might have cohered exclusively to form agglomerates within the films. Therefore, discrete amorphous domains of pure cellulose may be present in cellulose-rich products.

In *Figure 4* the temperature dependence of E' and E'' values is depicted for other samples with intermediate CELL/PHEMA compositions. An example illustrated in *Figure 4a* gives data for a photopolymerized sample containing 71 wt% PHEMA, and *Figure 4b* includes two examples measured for heat-polymerized samples the PHEMA concentrations of which were 68 and 54 wt%. These data of viscoelasticity are decidedly far from linear combinations of the corresponding data for the two

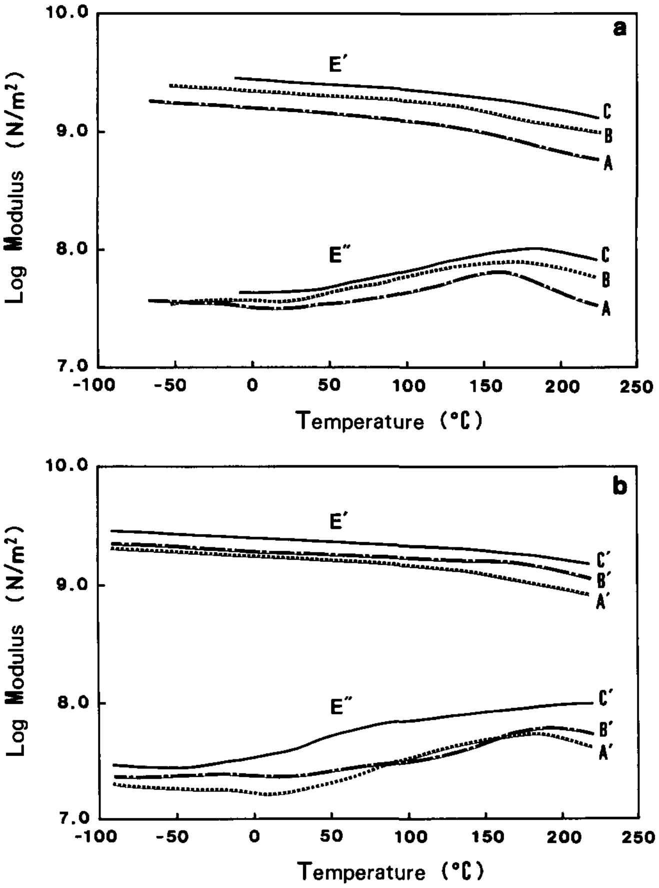

Figure 3 Temperature dependence of E' and E'' for CELL/PHEMA samples prepared at CELL-rich concentrations by (a) photopolymerization and (b) thermal polymerization. PHEMA content: A, 13 wt%; B, 8.5 wt%; C, 5 wt%; A', 20 wt%; B', 9.5 wt%; C', 0 wt% (a solution-coagulated CELL homopolymer)

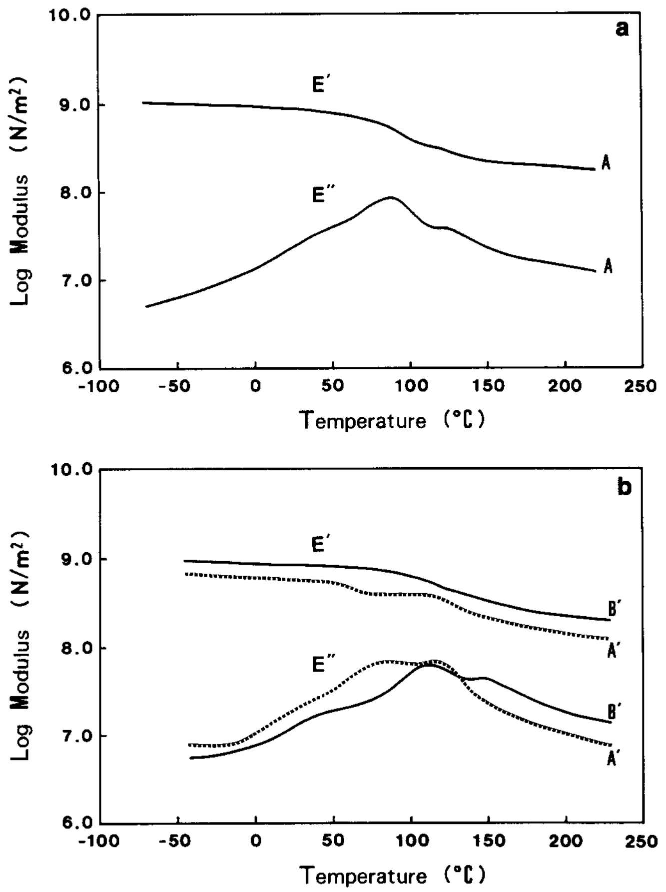

Figure 4 Temperature dependence of E' and E'' for CELL/PHEMA samples with intermediate compositions prepared by (a) photopolymerization and (b) thermal polymerization. PHEMA content: A, 71 wt%; A′, 68 wt%; B′, 54 wt%

homopolymers, and reveal the presence of two major dispersions above 50°C. For instance, we find the E'' of the 46/54 sample yielding two peaks at around 110 and 150°C in *Figure 4b*. Also, in *Figure 4a* there appears to be a clear shoulder at ~125°C as well as a peak centred at 86°C in the E'' curve of the 29/71 sample. Such a dual transition phenomenon was usually more prominent in the measurements for composites prepared by thermal polymerization (which required lengthy curing times to obtain solid films). From these observations, it follows that there coexist two amorphous phases in the CELL/PHEMA films that differ from each other largely in composition. One is a PHEMA-rich phase, giving rise to a transition in the lower temperature region, and the other is more rich in its cellulose constituent, which is responsible for the occurrence of another transition in the higher temperature region. It is unclear at present whether both phases are intermingled to assume discontinuous domain structures, or a steep composition gradient is generated in the direction normal to the planes of the film surface. Detailed elucidation of the morphology has not yet been undertaken. It is conceivable that each phase has an IPN character that results from the chemical blending procedure.

Figure 5 shows stress–strain curves obtained for film specimens of several CELL/PHEMA composites and the corresponding homopolymers. All the measurements were carried out at room temperature (25°C), and at ~60% humidity. Photopolymerized PHEMA and CELL/PHEMA samples were used for this tensile testing. For pure cellulose, two data are presented in the figure. One of them, denoted by solid circles, is of a cellulose sample prepared in the usual way by drying an 'as-coagulated' film with its ends free. This may serve as data to compare with those for the composites with PHEMA. The other cellulose data (denoted by open circles), which are shown for reference, refer to a sample obtained by drying an original gel film at fixed length. The apparently higher Young's modulus and tensile strength of this film can be ascribed to some degree of molecular orientation induced in the course of the drying. Individual values of Young's modulus, tensile strength, elongation at rupture, and yield stress (if a yield point is observable) for the samples investigated here are listed in *Table 1*. The following observations are worth noting on the result of the tensile measurements.

A cellulose-rich composite containing 8.5 wt% PHEMA shows tensile strength and elongation at rupture values that are somewhat smaller than those for the cellulose film dried with released ends; however, the modulus value

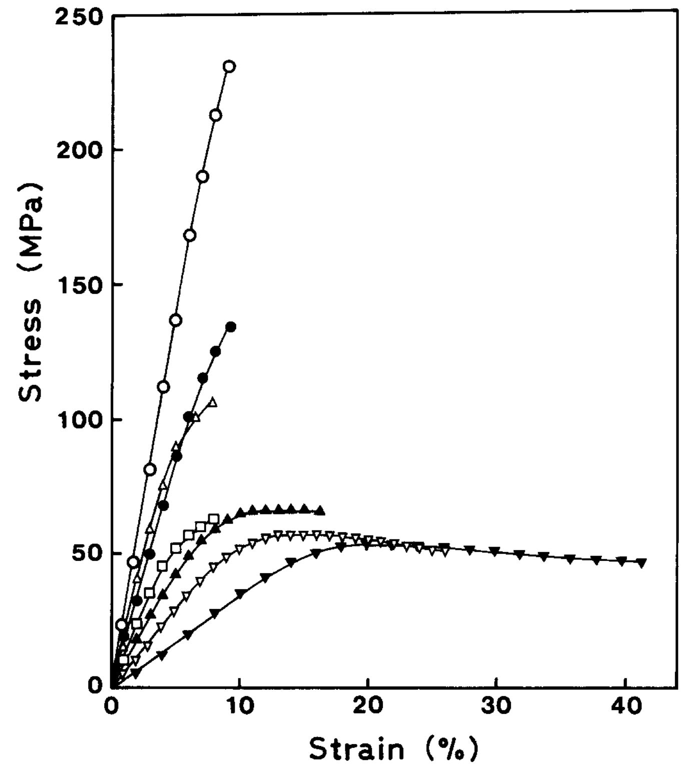

Figure 5 Stress–strain curves of CELL/PHEMA samples. PHEMA content: ○, 0 wt% (a cellulose film dried at fixed length after coagulation); ●, 0 wt% (a cellulose film dried with its ends free after coagulation); △, 8.5 wt%; □, 40 wt%; ▲, 84 wt%; ▽, 93 wt%; ▼, 100 wt%

Table 1 Tensile properties of CELL/PHEMA films

PHEMA content (wt%)	Young's modulus (GPa)	Yield stress (MPa)	Elongation at rupture (%)	Tensile strength (MPa)
0	1.72 (2.81)[a]	–	9.0 (8.8)[a]	132 (231)[a]
8.5	1.85	–	7.5	105
40	1.13	–	8.1	61.8
84	0.82	68	16.4	65.8
93	0.56	58	26.0	50.0
100	0.37	53	41.0	46.7

[a] For a cellulose sample dried at fixed length after coagulation followed by washing

for the composite is found to be slightly higher than that for the cellulose sample. At an intermediate composition of CELL/PHEMA = 60/40, the value of Young's modulus is about equal to that calculated using the law of simple additivity, and the tensile strength value is not overly large, considering the cellulose content. For the intermediate compositions of ~70/30–30/70, the dynamic mechanical analysis revealed a dual glass transition phenomenon resulting from the coexistence of two distinct amorphous mixtures in those samples. The relatively clear phase separation appears to result in a poor, synergistic improvement in the tensile properties of the present CELL/PHEMA system.

The most notable feature in the tensile behaviour of the CELL/PHEMA system can be observed in PHEMA-rich compositions containing >80 wt% PHEMA. In *Figure 5*, the stress–strain curve for a PHEMA homopolymer sample shows a yield point at an elongation of ~20%, followed by a strain softening region. It is likely that the network of cross-linked PHEMA molecules is not sufficiently tight, resulting in the occurrence of plastic deformation in uniaxial stretching of the homopolymer. When cellulose is incorporated into the PHEMA matrix at concentrations of <20 wt%, the rise of the stress–strain curves at the initial stage of elongation becomes very steep, indicating a marked increase in the Young's modulus. Furthermore, the strain-softening phenomenon becomes less prominent with the shift of a yield point to the upper and left side in the stress *versus* elongation plots. Accordingly, it can be said that 0–15 wt% cellulose constituent, introduced into the composites with appreciable retention of a gel structure, acts as an effective reinforcing agent to stiffen the polymer materials.

CONCLUSIONS

Cellulose/poly(2-hydroxyethyl methacrylate) (CELL/PHEMA) composites were prepared from solutions of cellulose in DMAc–LiCl by coagulation with a vinyl solvent HEMA and subsequent bulk polymerization of the resulting gelatinous films. Phase behaviour and thermal and mechanical properties were examined.

For CELL/PHEMA samples synthesized at compositions rich in PHEMA (PHEMA content > 80 wt%), it was reasonably assumed that an original structure of 'as-coagulated' cellulose gels was sufficiently preserved within the polymerized bulks to form semi-IPN organization with cross-linked PHEMA. As revealed by the dynamic mechanical measurements, the PHEMA-rich composites gave a T_g value higher than that of plain PHEMA, and the magnitude of an E'-drop in the glass transition region became very small with increasing cellulose content. It was also found from the tensile testing that the cellulose component acts as an effective reinforcing agent to make the polymer materials stiff. From another viewpoint, such composites would serve as good samples to elucidate the structure of cellulose gel itself, through detailed morphological studies using, for example, electron microscopy. Work along these lines is now in progress.

Cellulose-rich composites containing <30 wt% PHEMA exhibited a single, broad dispersion above 150°C in the viscoelastic measurements. The position of the principal dispersion shifted to higher temperatures with increasing cellulose content. The mechanical dispersions can be explained to be due to a molecular relaxation in the cellulose amorphous regions into which PHEMA molecules are incorporated intimately.

At other compositions with intermediate CELL/PHEMA ratios, the samples showed a double glass transition behaviour in the dynamic mechanical tests, originating from the coexistence of two amorphous phases having different polymer compositions. It is presumed, however, that some degree of interpenetration of the two different polymer molecules was realized in each phase by means of the chemical blending adopted.

In the present study, HEMA was used as an impregnating and polymerizing agent to prepare a new type of cellulosic composite. If another vinyl solvent, which has a chemical group capable of reacting with the hydroxyl groups in cellulose, is available as an impregnant, it is possible to obtained a 'joined-IPN' type of cellulose composite with synthetic polymers. This is a topic that is to be described in subsequent research.

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