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Phase structure of chitin/poly(glycidyl methacrylate) composites synthesized by a solution coagulation/bulk polymerization method

Yoshiharu Miyashita, Yasuhiro Yamada, Noritaka Kimura and Hidematsu Suzuki
Department of BioEngineering, Nagaoka University of Technology, Kamitomioka 1603-1, Nagaoka, Niigata 940–21, Japan

and Minoru Iwata
Department of Industrial Chemistry, Nagaoka College of Technology, Nishikatakai 888, Nagaoka, Niigata 940, Japan

and Yoshiyuki Nishio*
Department of Material Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan
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Chitin/poly(glycidyl methacrylate) (PGMA) composites were synthesized via bulk polymerization in a gel state of chitin impregnated with reactive GMA monomer. The thermal transition behaviour and phase structure of the chitin/PGMA composites were characterized by differential scanning calorimetry (d.s.c.), dynamic mechanical analysis (d.m.a.), and solid-state ^{13}C n.m.r. spectroscopy. For compositions rich in PGMA (chitin $\lesssim 20$ wt%), it was revealed by d.s.c. and d.m.a. that the polymerized samples gave a T_g value higher than that of PGMA homopolymer, and the magnitude of lowering of their modulus E' in the glass transition region became extremely small, compared with the corresponding E'-drop noted for PGMA alone. To interpret these observations, it was reasonably assumed that an original network structure of chitin gels was sufficiently perpetuated into the polymerized bulks, accompanied by the formation of an IPN-like organization. Through the measurements of proton spin-lattice relaxation times in the n.m.r. study, the scale of homogeneous mixing in the IPN type of polymer composites was evaluated. The result suggested that the chitin and PGMA components were mixed mutually on a scale of a few nanometres in those composites. © 1997 Elsevier Science Ltd

(Keywords: chitin; poly(glycidyl methacrylate); composites)

INTRODUCTION

Much attention has been paid to the design and fabrication of multicomponent polymer systems over the past years. Among the numerous blend studies, a limited number of works have been concerned with the microscopic incorporation of naturally occurring carbohydrate polymers, which may be represented by 'cellulose', the most abundant biomass and a renewable resource. Generally, such a fibrous natural polymer shows poor solubility in conventional organic solvents. Despite the intractability, however, considerable efforts have been devoted to the preparation of intimate blends or microcomposites of cellulose with several synthetic polymers by using a suitable solvent and procedure for each individual case[1–7].

In quite recent works[8–10] accomplished by the authors, a novel approach has been proposed to design unique microcomposites made up of cellulose/synthetic polymer networks. *In situ* polymerization of a vinyl solvent as coagulant and/or impregnant used to form cellulose gels is an essential part of the method. In fact, an interpenetrating network (IPN) type of organization was realized in a few binary polymer systems; e.g., cellulose/poly(2-hydroxyethyl methacrylate) (CELL/PHEMA)[8], cellulose/poly(N-vinyl pyrrolidone) (CELL/PVP)[9], and cellulose/poly(N-vinyl pyrrolidone-co-glycidyl methacrylate) [CELL/P(VP-co-GMA)][10], which were synthesized via bulk polymerization of cellulose gels impregnated with the corresponding monomer of the cellulose partners.

The above-mentioned method, termed a 'solution coagulation/bulk polymerization' method, would also be applicable to the hybridization of another inexhaustible polysaccharide 'chitin' with various synthetic polymers at a hyperfine structural level. This natural polymer, supplied mainly from marine crustaceans, has also been re-evaluated recently as a promising and

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* To whom correspondence should be addressed

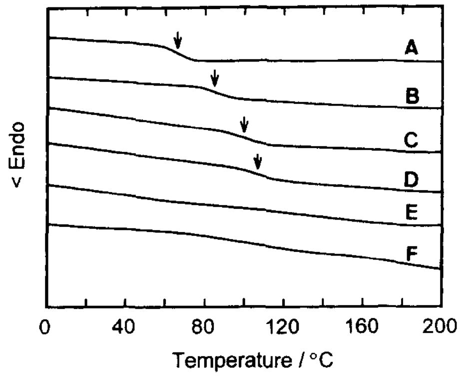

Figure 1 D.s.c thermograms of chitin/PGMA composites. Chitin content: A, 0 wt%; B, 8 wt%; C, 48 wt%; D, 70 wt%; E, 90 wt%; F, 100 wt%. Arrows indicate a T_g position taken as the midpoint of the discontinuity in heat flow

attracting resource, possessing a potential to be newly developed for industrial and medical applications in itself or in combination with other polymers. In contrast to the relatively progressed studies on the chemical modifications (including grafting) of chitin molecules, there have been only a few examples of the study of chitin-based polyblends[11-13], usually prepared from mixed polymer solutions in a common solvent.

In this present work, we made an attempt to synthesize an IPN type of microcomposites based on chitin, according to the solution coagulation/bulk polymerization method. Chitin/poly(glycidyl methacrylate) (PGMA) composites were successfully prepared in transparent film form from homogeneous chitin solutions in *N*,*N*-dimethylacetamide–lithium chloride by coagulation in a nonsolvent and subsequent bulk polymerization of the resulting gels swollen in GMA monomer. Thermal and dynamic mechanical properties and spectroscopic characterization of the composites thus obtained are described in connection with the phase construction.

EXPERIMENTAL

Original materials

The original material of chitin isolated from crab shells (Fluka 22720 Chitin, Lot no. 329999/1 993) was purified by treatment with aqueous hydrochloric acid and sodium hydroxide solution according to Hackman's method[14]. The degree of deacetylation of the purified chitin was usually several percent[13,15]. Glycidyl methacrylate monomer (Nacalai tesque, Inc., Kyoto, Japan) was 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 purified chitin sample was first treated by a solvent exchange technique[1,2,13] successively with water, methanol and DMAc. Then the DMAc-wet chitin was added to a solvent system DMAc-LiCl and stirred at room temperature for ~ 5 days. The solvent DMAc-LiCl was used at a salt concentration of 4 wt% with respect to DMAc. After continuous stirring, the resulting viscous solution was centrifuged to remove insoluble residue. The actual concentration of chitin in the clear supernatant was controlled to be *ca.* 0.5%, determined precisely by weighing the solid film regenerated from a portion of the solution.

A weighed amount of the chitin solution was poured into a glass tray, and kept for ~ 6 h in a container filled with ethanol vapour as coagulant, whereupon the original chitin solution was transformed into a gelatinous film. The resulting chitin gel was washed with ethanol several times, followed by exchange of the impregnant for GMA monomer containing the radical initiator AIBN at a concentration of 2.0 wt%. The chitin content in the swollen gels thus obtained was controlled by removing an appropriate amount of the impregnating GMA with filter papers. Following this, the chitin/GMA gel samples were allowed to solidify by bulk polymerization of GMA monomer at *ca.* 30°C for 120 min under irradiation of u.v. light. The photopolymerization was conducted under reduced pressure in a curing chamber equipped with a 15 W u.v. lamp which gave an intensity maximum at 352 nm. The chitin/PGMA samples thus synthesized were washed with methanol to extract residual monomer, then dried at 50°C for 24 h *in vacuo*. PGMA homopolymer films were also synthesized by photopolymerization under the same conditions as described above. In this case, the monomer fluid was charged between polyethylene thin sheets. Chitin homopolymer films were obtained from solutions in DMAc-LiCl by coagulation with ethanol, followed by drying.

For comparison, another series of chitin/PGMA samples (physical blends) were made from mixed polymer solutions in DMAc–LiCl in the ordinary way of coagulation[1,2,7]. For this purpose, PGMA homopolymer was synthesized by polymerization of GMA in $CHCl_3$ at 60°C with the aid of AIBN. A solution of PGMA and that of chitin were prepared at 1.5 wt% and 0.5 wt%, respectively, and mixed with each other in the desired proportions. After stirring for at least 1 day at room temperature, each blend solution was poured into a glass tray and coagulated with ethanol vapour. The gelatinous chitin/PGMA films thus obtained were washed with ethanol, and then dried at 50°C *in vacuo*.

Measurements

Differential scanning calorimetry (d.s.c.) was made on *ca.* 6 mg samples with Seiko DSC 210 apparatus equipped with a thermal analysis station SSC 5000. The temperature readings were calibrated with an indium standard. The measurements were performed at a scanning rate of 20°C min^{-1} under a nitrogen atmosphere. The samples were first heated up to 180°C and subsequently quenched to −30°C. The second heating scans were run from this temperature up to 210°C, to record stable thermograms.

Dynamic mechanical measurements were carried out with a Rheovibron model DDV-II-C viscoelastometer (Orientic Corp., Tokyo, Japan). The oscillatory frequency was 11 Hz, and the temperature was raised at a rate of 1.5°C min^{-1} in the range −60 to 240°C. Film strips 4 mm × 30 mm were employed, which were heated in an oven at 120°C for 5 min prior to the measurement, for removal of trace amounts of solvents and/or moisture and relaxation of possible stresses.

Solid-state n.m.r. experiments were carried out with a

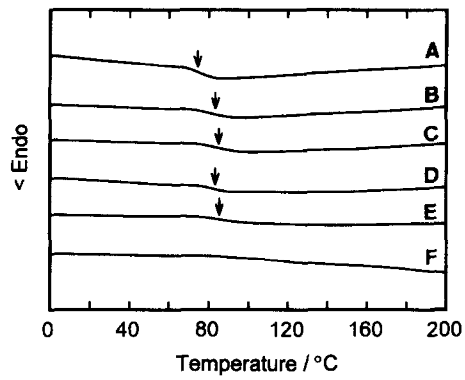

Figure 2 D.s.c thermograms of chitin/PGMA blends prepared from mixed polymer solutions by coagulation in a nonsolvent. Chitin content: A, 0 wt%; B, 36 wt%; C, 42 wt%; D, 60 wt%; E, 77 wt%; F, 100 wt%

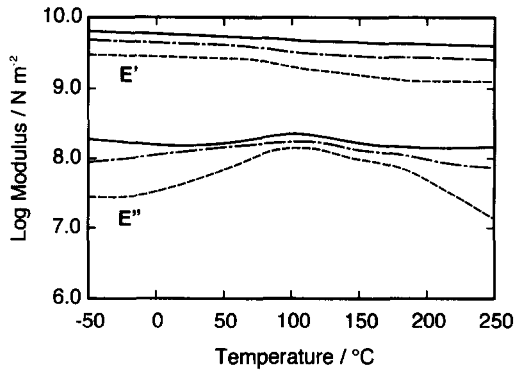

Figure 4 Temperature dependence of E' and E'' for chitin/PGMA composites containing more than 45 wt% chitin. Chitin content: (- - - -), 48 wt%; (— — —), 70 wt%; (——), 100 wt%

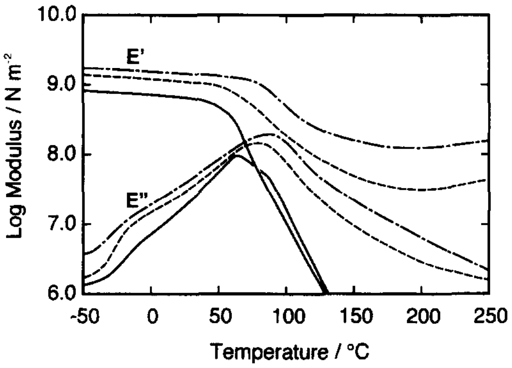

Figure 3 Temperature dependence of the dynamic storage modulus (E') and loss modulus (E'') for chitin/PGMA composites with PGMA-rich compositions. Chitin content: (——), 0 wt%; (- - - -), 8 wt%; (— — —), 19 wt%

JEOL JNM-GX270 spectrometer. Samples cut in *ca.* 1 mm × 1 mm strips were packed in zirconia rotors. Magic angle spinning rates were generally about 6 kHz. ^{13}C CP/MAS spectra were measured with contact time of 1 ms. A 90° pulse width of 4.5–5 μs was employed with 1000–2000 FID signal accumulations. In the measurements of proton spin-lattice relaxation times ($T_{1\rho}^{H}$), a contact time of 0.1 ms was used and proton spin-locking time τ ranged from 0.5 to 20 ms. Chemical shifts of ^{13}C spectra, represented in ppm, were referred to tetramethylsilane by using the methine carbon resonance of adamantane (29.5 ppm) as an external reference standard.

RESULTS AND DISCUSSION

Transition behaviour of chitin/PGMA composites

Figure 1 displays d.s.c. curves for a series of chitin/PGMA composites prepared by the solution coagulation/bulk polymerization method. The plain PGMA sample exhibits a clear base-line gap reflecting the glass transition in the thermogram. From the midpoint of the discontinuity in heat flow, the glass transition temperature T_g of the PGMA sample was estimated to be 65°C. Concerning the glass transition of the other polymer chitin, we could not detect it explicitly before the polymer began to undergo thermal degradation above *ca.* 240°C. For the composites of the two polymers, the compiled d.s.c. data indicate that the T_g of PGMA shifts systematically to the higher temperature side along with the increase in the chitin content up to 70 wt%. From this composition-dependent T_g elevation phenomenon, it is reasonable to judge that a state of good miscibility prevailed in the present binary system. At compositions containing ≥ 80 wt% chitin, however, the change in slope of the d.s.c. base-line became so broad that it was no longer possible to estimate their T_g precisely.

A control d.s.c. experiment was carried out for chitin/PGMA blends prepared via a process of mixed-solution coagulation followed by just drying. Selected thermograms obtained for this series are collected in *Figure 2.* Here we can readily see a sign of poor miscibility of the blends, evidenced from the less-significant shift in the T_g of PGMA depending on the composition. PGMA is a rather hydrophobic polymer and, essentially, may be immiscible thermodynamically with most hydrophilic polymers including chitin. In contrast to this d.s.c. result for the blends solution-coagulated as usual, the other series of chitin/PGMA samples arranged chemically exhibited a more marked T_g elevation, as has already been demonstrated. Thus the present method, based on the combined use of solution coagulation and bulk polymerization processes, may be proposed as a successful route leading to the microscopically intimate mixtures of chitin/synthetic polymers, even though the relevant polymer pair is thermodynamically immiscible.

The bulk polymerization of chitin/GMA gels with avoidance of intemperate pretreatment, e.g. compression into an extremely thin film, gave rise to the formation of clear, hard films of PGMA-rich composites, usually containing $\lesssim 20$ wt% chitin. Visual inspection of the resulting chitin/PGMA films indicated complete retention of the starting gel form. In *Figure 3*, the temperature dependence of the storage modulus E' and loss modulus E'' for two composite samples whose chitin/PGMA compositions are 8/92 and 19/81 is compared with that for a PGMA homopolymer film synthesized under the same conditions as adopted for the composite preparation. THe PGMA homopolymer exhibits a dispersion peak with a maximum value at *ca.* 60°C in the E'' vs. temperature curve. This dispersion can be associated with the glass transition of the PGMA sample. In the case of PGMA homopolymers, it is of importance to observe a rapid and intense decrease of the dynamic modulus E' in the glass transition region, as exemplified in the figure. After onset of the glass transition on heating, the micro-Brownian motions of PGMA chains appears to become more and more conspicuous with increasing temperature, and above 130°C the values of E' and E'' were actually out of the measurement range.

On introducing chitin into the PGMA polymerized bulks, there occurred a clear shift in an E''-peak of PGMA to the higher temperature side. For the two examples of PGMA-rich composites shown in *Figure 3*, the T_g values were estimated to be 77°C (8/92 composition) and 88°C (19/81 composition), from readings of the temperature position of the E'' peak maximum. These elevations of the T_g of PGMA due to addition of chitin are consistent with the d.s.c. result shown previously. Another observation to be noted for the dynamic mechanical data is as follows: the magnitude of an E'-drop after onset of the glass transition becomes extremely small with an increase in chitin content. Also, above T_g the loss modulus E'' of the composites does not fall so strikingly as in the case of plain PGMA. It follows that the chitin component acts as an effective reinforcer for the polymer matrix. A similar effect of hybridization was found in our previous studies for cellulosic composites synthesized by the solution coagulation/bulk polymerization method[8-10]; i.e. in those systems, the presence of even a few percent of cellulose gave rise to a marked suppression of the lowering of E' and E'' in the glass transition region. From these observations, it is reasonably assumed for the PGMA-rich composites that an initial network structure of chitin gels was successfully fixed into the polymerized bulks, resulting in the formation of an IPN-like organization.

The dynamic viscoelasticity was also examined for other compositions more rich in chitin concentration. *Figure 4* illustrates the data of E' and E'' vs. temperature for two selected chitin/PGMA samples, one having an intermediate composition (48/52) and the other a chitin-rich composition (70/30), and they are compared with the corresponding data for a chitin homopolymer film prepared by solution coagulation and drying. As can be seen from the E' and E'' curves depicted by solid lines, the pure chitin gave only a small dispersion signal in the neighbourhood of 100°C. This dispersion may be ascribed to a local relaxation of the backbone chain of chitin[13,16,17], not to the principal relaxation (α) corresponding to the glass transition of the polysaccharide. In a previous study[13], we estimated the activation energy (E_a) for the dispersion and obtained a value of *ca.* 13 kcal mol^{-1}; this is comparable to an E_a value for the so-called β relaxation, commonly observed as a subtransition for many polymer materials. With regard to the glass transition of chitin, Lee *et al.*[18] have reported recently a T_g value of $\sim$ 235°C with a chitin sample cast from solution in formic acid; possibly, however, the chitin is partly esterified by formic acid in the dissolution process[13]. Anyhow, no clear amorphous relaxation signal reflecting the glass transition of chitin could be detected in the present dynamic mechanical analysis, before the thermal degradation began to manifest itself above *ca.* 240°C. It is therefore predicted that the chitin T_g lies latently in a temperature range above 240°C.

From the data depicted by dashed-line curves in *Figure 4*, we find the 48/52 sample yield apparently two broad dispersions. A major peak is centered at 105°C and a secondary peak is located around 170°C in the E'' vs. temperature curve. The appearance of such a dual transition was most familiar at compositions containing 40–60 wt% chitin. In interpretation of this observation, it seems natural to assume that there coexist at least two phases in those composites that differ from each other in polymer composition: One is a comparatively PGMA-rich phase, giving rise to a transition in the lower temperature region, with partial overlapping of the β transition of chitin *per se*. The other is richer in the chitin constituent, which is responsible for the occurrence of another transition in the higher temperature region. At present, it is uncertain whether the two (or more) phases are inter-mingled to assume discontinuous domain structures, or a steep gradient of composition is generated in the direction normal to the surface planes of the film specimens. In any case, it is presumable that some degree of interpenetration of the two component molecules is realized in each phase, taking into consideration the chemical blending procedure adopted.

In the E'' data of the 70/30 sample shown in *Figure 4*, we can still find a feeble dispersion around 190°C in addition to a somewhat more perceptible dispersion centred at $\sim$ 120°C. When the chitin content was increased further, the feature of dual transition vanished, or rather, the β transition of chitin came into prominence in relative intensity. To prepare these chitin-rich ($\gtrsim$ 70 wt%) samples, it was necessary to extract a large amount of GMA monomers from the as-coagulated chitin gels before polymerization, by compressing them into a considerably thinner film form. In this process, part of the chitin constituent might have cohered rather exclusively, to form agglomerates within the thin films. Therefore, the resulting chitin-rich composites would have less IPN character, although the possibility of the presence of the chitin amorphous regions incorporated with a limited amount of PGMA molecules is admitted.

Solid-state n.m.r. spectroscopy

In the phase study of multicomponent polymer systems, it is of significance to give an insight into the scale of homogeneity that is produced on mixing polymers. Solid-state n.m.r. spectroscopy is a powerful tool for this purpose[5-7,19-21]. For instance, the quantification of the proton spin-lattice relaxation time $T_{1\rho}^{H}$ reveals an upper limit in heterogeneity on a scale of a few nanometres or less[5,6,19,20]. The analysis of ^{13}C CP/MAS spectra provides information about interactions at the molecular level between the constituent polymers[5,6,21]. In the present study, these n.m.r. techniques were employed for further characterization of chitin/PGMA composites (chitin $\lesssim$20 wt%) in which an IPN organization was embedded successfully.

Figure 5 shows ^{13}C CP/MAS n.m.r. spectra for three different samples: regenerated chitin; PGMA homopolymer; and their composite in which a chitin gel was immobilized at a concentration of 10 wt%. The peak assignments are based on literature data given previously for chitin[22,23] and PGMA[24,25]. In the spectrum of the 10/90 composite, the intensities of ^{13}C resonance peaks coming from the chitin component are relatively small due to the low concentration, and the signals of C1, C4, C5, and C3 carbons are only discernible in the range of 75–105 ppm. Generally, if two different polymers interact mutually on a molecular scale in the binary blend, there should be some noticeable changes in chemical shift and/or line shape of the resonance peaks in a spectrum of the blend, in comparison to those of their respective homopolymers. The CP/MAS spectrum of the

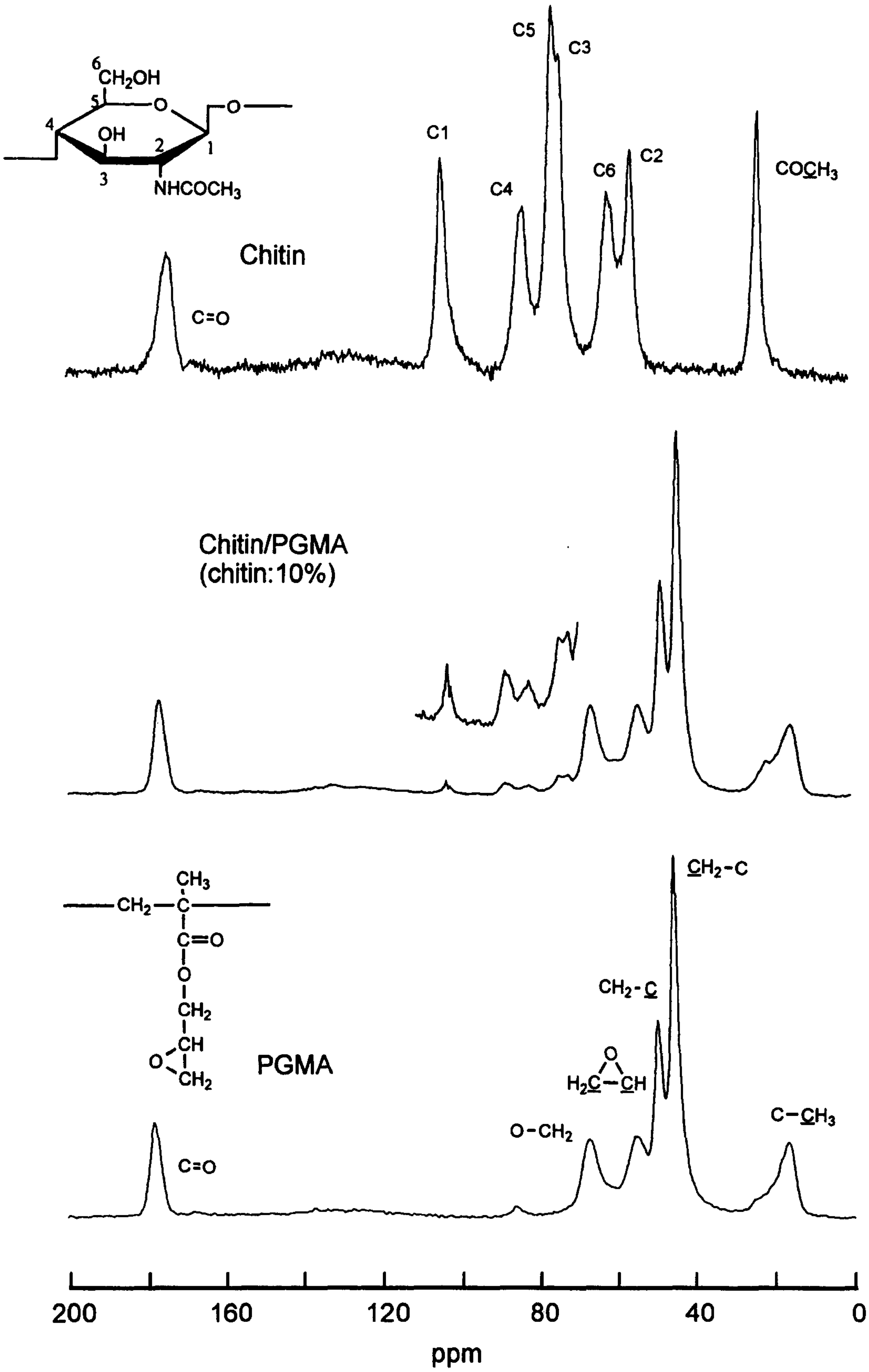

Figure 5 Solid-state ^{13}C CP/MAS spectra of chitin, PGMA and a chitin/PGMA (10/90) composite

chitin/PGMA sample was, however, confirmed to be made up by almost the superposition of the spectra of both homopolymers, with the prorated peak intensities. From this observation, it is concluded that no specific intermolecular interaction, e.g. through hydrogen bonding between proton-donating and accepting functionalities takes place in the composite. The result may be consistent with the essential absence of the thermodynamic miscibility of the present polymer pair.

As is established well[6,19,20], $T_{1\rho}^{H}$ values can be obtained in an interrupted CP/MAS experiment, through measurements of the decaying carbon resonance intensity that fits to the single-exponential equation

$$M(\tau) = M(0)\exp(-\tau/T_{1\rho}^{\mathrm{H}}) \qquad (1)$$

where $M(\tau)$ is the magnetization intensity observed as a function of the spin-locking time τ. *Figure 6* displays the decay behaviour for chitin and PGMA in their pure states and in the composite with a 10/90 composition. The resonance peak of CH_2 in the main chain of PGMA and that of C4 in the pyranose ring of chitin were monitored in this experiment. The slope of each semilogarithmic plot of the relative intensity vs. delay time (τ) yields a $T_{1\rho}^{\mathrm{H}}$ value as the time constant of the relaxation process. The result of the evaluations of $T_{1\rho}^{\mathrm{H}}$ for the three samples is summarized in *Table 1*. The relaxation times for chitin and PGMA are 9.0 and 18.9 ms in their respective pure states. In the composite, the $T_{1\rho}^{\mathrm{H}}$ values of both components do not perfectly coincide with each other, whereas being different appreciably from the values of the homopolymers; the $T_{1\rho}^{\mathrm{H}}$ of chitin rises up to 12.8 ms and that of PGMA diminishes to 15.6 ms, both allowed to become fairly close to each other between the respective original values. This result indicates that the spin diffusion of protons belonging to one component is much affected by that of protons belonging to the other component in the composite.

An effective distance over which spin diffusion can proceed in a time $T_{1\rho}^{\mathrm{H}}$ is represented in the form[19]

$$L \cong (6DT_{1\rho}^{\mathrm{H}})^{1/2} \qquad (2)$$

where D is the diffusion coefficient, usually taken to be $\sim 10^{-12}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ in polymer systems. With the $T_{1\rho}^{\mathrm{H}}$ data obtained for the chitin/PGMA composite, i.e. 12.8 ms (chitin component) and 15.6 ms (PGMA component), the diffusion path length is calculated as $L = 2.8$ nm and 3.1 nm, respectively. Accordingly, a domain size permitting the efficient spin diffusion across the different constituents can be estimated to be approximately 3 nm.

Thus the scale of heterogeneity in the IPN-like composite is substantially small, in spite of the original character of the polymer pair showing poor miscibility. Again here, it should be stressed that the present method for hybridization of polysaccharide/synthetic polymer is quite useful for enhancement of the mixing level.

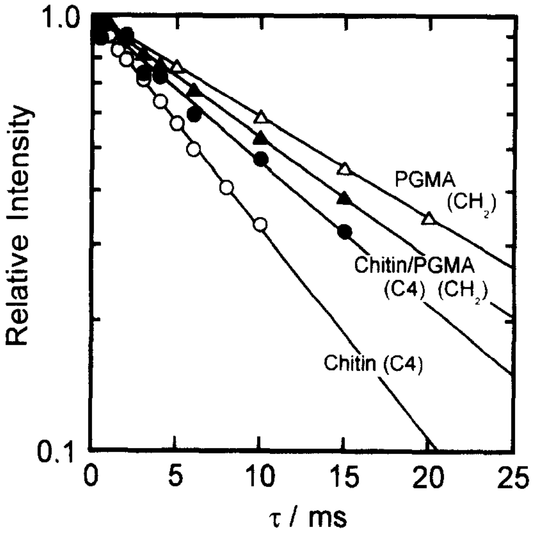

Figure 6 Semilogarithmic plots of the decay of ^{13}C resonance intensities as a function of spin-locking time τ, for film samples of chitin, PGMA and their composite (chitin/PGMA = 10/90)

Table 1 $T_{1\rho}^{H}$ values for PGMA, chitin, and a chitin/PGMA (10/90) composite, determined from the decay plots given in *Figure 6*

	$T_{1\rho}^{H}$/ms	
	CH_2 (main chain)	C4
PGMA	18.9	
Chitin/PGMA	15.6	12.8
Chitin		9.0

CONCLUSIONS

Chitin/poly(glycidyl methacrylate) (PGMA) composites were synthesized via photo-initiated polymerization in a gel state of chitin swollen with GMA monomer as reactive impregnant.

For chitin/PGMA compositions rich in PGMA (chitin $\lesssim 20$ wt%), it was reasonably assumed by visual inspection, d.s.c. and d.m.a. that a well-developed 'IPN' type organization was realized in the composites, as a consequence of successful perpetuation of an original gel structure of chitin into the polymerized bulks. These PGMA-rich composites gave a T_g value higher than that of plain PGMA, and the extent of lowering of their modulus E' in the glass transition region was extremely suppressed in comparison with the corresponding E'-drop observed for PGMA homopolymer. As a supplementary study, the scale of homogeneous mixing was evaluated for the composites endowed with IPN character by solid-state ^{13}C n.m.r. spectroscopy. It was inferred from measurements of the proton spin-lattice relaxation times ($T_{1\rho}^{\mathrm{H}}$) that the size of heterogeneity of the composites was fairly small (~ 3 nm) to permit effective spin diffusion across the different constituents.

For intermediate chitin/PGMA compositions containing approximately 40–60 wt% chitin, samples showed a dual transition signal in the dynamic mechanical test; possibly, this behaviour originates from the coexistence of two or more phases having different polymer compositions, but each phase retaining some degree of interpenetration of the two components. Other samples with chitin-rich compositions (chitin $\gtrsim 70$ wt%), were usually taken as poor in IPN architecture, even though the formation of the chitin amorphous regions incorporated with a limited amount of PGMA molecules may be admitted.

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