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Transition behavior and phase structure of chitin/poly(2-hydroxyethyl methacrylate) composites synthesized by a solution coagulation/bulk polymerization method

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Chitin/poly(2-hydroxyethyl methacrylate) (PHEMA) composites were synthesized via photo-polymerization in a gel state of chitin swollen with HEMA monomer as reactive impregnant. The transition behavior and phase structure of the chitin/PHEMA composites were characterized by differential scanning calorimetry, dynamic viscoelastic analysis, and solid-state ^{13}C NMR spectroscopy. For compositions containing $\leq$ 20wt% chitin, it was reasonably assumed that an original network structure of chitin gels was sufficiently perpetuated into the cross-linked PHEMA matrix, resulting in the formation of an interpenetrating polymer network (IPN) type organization. Owing to this IPN effect, the lowering of the dynamic modulus E' of the composites in the glass transition temperature region was extremely suppressed, compared with the corresponding E'-drop observed for plain PHEMA samples. From measurements of the proton spin-lattice relaxation times $T_{1\rho}{}^{H}$ in the NMR study, the IPN-like composites were estimated to be homogeneous on a scale of less than ~2.4 nm. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

In recent years, many attractive systems of polymeric blends and composites have been investigated extensively. Among them, multicomponent systems containing a naturally occurring polysaccharide e.g., cellulose, as a component may be of particular significance, in view of the utilization and new functionalization development of inexhaustible natural products. Against the generally believed intractability of unmodified cellulose owing to the poor solubility in most organic solvents, considerable efforts have been devoted to preparing intimate blends of the polysaccharide with various synthetic polymers. In several combinations, highly miscible blends have been shown to be attainable, by using a suitable solvent and procedure for each individual case (Nishio *et al.*, 1987; Nishio and Manley, 1988; Nishio *et al.*, 1989; Masson and Manley, 1991a, b).

Attention should be paid to the design of "chitin"-based hybrid materials as well as cellulosic blends and composites. This carbohydrate polymer has also been re-evaluated as an attractive resource, possessing the potential to be newly developed for industrial and medical applications. There have already been a few examples of the study of chitin/synthetic polymer blends, usually prepared from mixed polymer solutions in a common solvent (Kim *et al.*, 1995; Miyashita *et al.*, 1995, 1996a).

Quite recently, the authors proposed a novel preparation technique to design unique microcomposites of cellulose/synthetic polymers having an interpenetrating network (IPN) type of architecture. *In situ* polymerization of a vinyl monomer as coagulant and/or impregnant used to form cellulose gels is an essential part of this method. As has already been

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reported, three series of IPN-type cellulosic composites, i.e., cellulose/poly(2-hydroxyethyl methacrylate) (CELL/PHEMA) (Nishio and Hirose, 1992), cellulose/poly(*N*-vinylpyrrolidone) (CELL/PVP) (Miyashita *et al.*, 1994), and cellulose/poly(*N*-vinylpyrrolidone-co-glycidyl methacrylate) [CELL/P(VP-co-GMA)] (Miyashita *et al.*, 1996b) were obtained successfully via bulk polymerization in a gel state of cellulose impregnated with the corresponding monomers. Appropriate modification of this method, termed a "solution coagulation/bulk polymerization" method, may enable us to accomplish the incorporation of chitin with synthetic polymers at a hyperfine structural level. Actually, an attempt was made in our previous work (Miyashita *et al.*, 1997) to synthesize chitin-based composites according to this method, and an IPN-like organization was realized in a chitin/poly(glycidyl methacrylate) (PGMA) system, not withstanding the fact that the polymer pair is thermodynamically immiscible.

In the present work, phase characterization is performed on the microcomposites of chitin with poly(2-hydroxyethyl methacrylate) (PHEMA) synthesized by a solution coagulation/bulk polymerization method. The thermal transition behavior and dynamic mechanical properties of chitin/PHEMA composites are examined mainly through differential scanning calorimetry and dynamic viscoelastic analysis. In addition, the scale of homogeneous mixing in the polymer composites with an IPN character is estimated by solid-state ^{13}C NMR spectroscopy.

EXPERIMENTAL

Materials

An original chitin sample isolated from crab shells (Fluka 22720 chitin, Lot No. 329999/1 993) was purified according to a method described by Hackman (1954). The degree of deacetylation of the purified chitin was approx. 15%, determined by infra-red spectroscopy (Sannan *et al.*, 1978). 2-Hydroxyethyl methacrylate (HEMA) monomer (Nacalai Tesque) was purified by distillation under reduced pressure (~62°C, 2 mmHg). 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 8 h in a vacuum oven. A radical initiator α,α'-azobisisobutyronitrile (AIBN), being guaranteed reagent-grade, was used without further purification.

Sample preparation

The purified chitin was first treated by a solvent exchange technique (Nishio *et al.*, 1987; Miyashita *et al.*, 1996a) successively with water, methanol, and DMAc. A solvent system DMAc–LiCl was used at a salt concentration of 5wt%. A viscous solution of chitin in DMAc–LiCl was prepared at a polymer concentration of ~0.5 wt%, in a similar manner to that described in a previous paper (Miyashita *et al.*, 1997).

A weighed amount of the chitin solution was poured into a glass tray, and kept for ~12 h in a container filled with ethanol vapor as coagulant. The resulting gelatinous film of chitin was washed with ethanol several times. Then the impregnant was exchanged for HEMA monomer, by soaking the chitin gel for ~6 h in HEMA containing a radical initiator AIBN at a concentration of 1 wt%.

The proportion of chitin/HEMA in the swollen gels thus obtained was controlled by removing an appropriate amount of the impregnating HEMA with filter papers. Following this, the gel samples were allowed to solidify via *in situ* polymerization of HEMA monomer. Photo-polymerization was carried out with a curing chamber equipped with a 15 watt ultraviolet (UV) lamp which gave an intensity maximum at 352 nm. UV-irradiation onto the chitin/HEMA gels was conducted at 30°C over a period of 60 min under a nitrogen atmosphere. The chitin/poly-HEMA (PHEMA) composites thus synthesized were washed with ethanol to extract monomer traces, and then dried at 50°C for 12 h *in vacuo*.

PHEMA homopolymer films were also prepared by photo-polymerization under the same conditions as described above. In this case, the monomer was charged between thin polyethylene sheets. Chitin homopolymer films were prepared from solutions in DMAc–LiCl by coagulation with ethanol, followed by drying.

Measurements

Differential scanning calorimetry (DSC) was conducted on ~6 mg samples with a Seiko DSC210/SSC5000 apparatus. The measurements were performed at a scanning rate of 20°C min^{-1} under a nitrogen atmosphere, after calibration of the temperature readings with indium standard. The samples were first heated up to 180°C and then immediately quenched to −30°C. The second heating scans were run from −30 to 210°C, to record stable thermograms.

Dynamic mechanical measurements were carried out with a Rheovibron model DDV-II-C viscoelastometer (Orientec), operated at an oscillatory frequency of 11 Hz. The temperature was raised at a rate of 1.5°C min^{-1} in the range −50–245°C. Film strips 4 mm×25 mm were employed, which were heat-treated at 140°C for 5 min prior to the measurement.

Solid-state ^{13}C NMR experiments were carried out with a JEOL JNM-GX-270 spectrometer operated at a ^{13}C frequency of 67.8 MHz. The cross-polarization (CP), magic-angle spinning (MAS), and high-power

spin decoupling techniques were used. A magic-angle spinning rate was usually about 6 kHz. ^{13}C CP/MAS NMR spectra were measured with a contact time of 1 ms, and a 90° pulse width of 4.4–5 μs was employed. In the measurements of proton spin-lattice relaxation times in the rotating frame ($T_{1\rho}{}^{H}$), a contact time of 0.1 ms was used and the proton spin-locking time τ ranged from 0.5 to 30 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 standard.

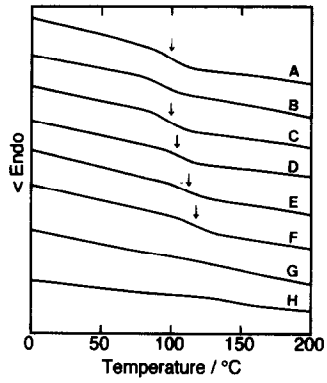

Fig. 1. DSC thermograms of chitin/PHEMA composites. Chitin content: (A) 0 wt%; (B) 2 wt%; (C) 10 wt%; (D) 20 wt%; (E) 50 wt%; (F) 70 wt%; (G) 80 wt%; (H) 100 wt%. Arrows indicate a T_g position taken as the midpoint of the discontinuity in heat flow.

RESULTS AND DISCUSSION

Transition behavior of chitin/PHEMA composites

Optically clear, hard films of chitin/poly(2-hydroxyethyl methacrylate) (PHEMA) composites were prepared successfully over a wide composition range by the specific method mentioned above. In the case of bulk polymerization of HEMA, the monomer tends to undergo a cross-linking reaction to form a network structure (Nishio and Hirose, 1992). Actually, PHEMA homopolymers synthesized in the present work were found to swell but did not dissolve in various organic solvents and water.

Figure 1 shows DSC thermograms for a series of chitin/PHEMA composites synthesized by the solution coagulation/bulk polymerization method, together with data obtained for film samples of PHEMA and chitin homopolymers. In the DSC data (curve A) of the plain PHEMA sample, a baseline gap reflecting the glass transition is clearly observed. From the midpoint of the discontinuity in heat flow, the glass transition temperature T_g of this PHEMA was evaluated to be ~100°C. Concerning the T_g of the other polymer chitin, it was predicted previously to be latent in a decomposition temperature range of >230°C (Miyashita *et al.*, 1997), as in the case of cellulose. In the thermogram of chitin (curve H) shown in Fig. 1, there appears to be a gradual change in slope of the DSC baseline in the neighbourhood of 125°C. This is probably ascribed to a certain subtransition of this amino polysaccharide, not due to the glass transition, as described below in the dynamic mechanical study. Looking over the DSC data (curves B~G) for the composites of the two polymers, we can see a general trend of the T_g elevation with an increase in chitin content, at least in the composition range of 2/98 to 70/30, the first numeral referring to the chitin concentration. This observation of a systematic, composition-dependent shift of T_g indicates that the two constituent polymers are coexistent in a fairly good state of compatibility in the composite materials. At compositions containing ≥80 wt% chitin, the DSC baseline gap in the respective thermograms was so obscure (e.g., see curve G) that the T_g values could not be determined precisely. Additional care should be taken in interpreting an unexpected result obtained for the 2/98 and 10/90 samples; i.e., their T_gs, evaluated as 94°C and 98°C, respectively, are somewhat lower than that (100°C) of the plain PHEMA sample prepared under the same condition as adopted for the composite synthesis. This T_g depression phenomenon may be attributable to a slight difference in the covalent cross-linking density between the PHEMA alone and the PHEMA component in the composites. It is plausible to assume that, in the latter system, the cross-linking reaction of HEMA occurring during the bulk polymerization is restricted to sa certain extent due to the presence of chitin gel networks.

In Fig. 2, the temperature dependence of the storage modulus E' and loss modulus E'' of two composites containing 2 and 10 wt% chitin is compared with the corresponding data for a PHEMA homopolymer film. The E'' vs temperature curve of the PHEMA homopolymer exhibits a dispersion peak centering at approx. 100°C, which may be associated with the glass transition. A prominent feature of the viscoelastic

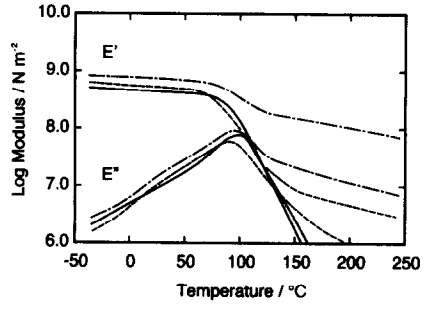

Fig. 2. Temperature dependence of the dynamic storage modulus E' and loss modulus E'' for chitin/PHEMA composites with PHEMA-rich compositions. Chitin content: (—); 0 wt%; (- - -), 2 wt%; (— - —), 10 wt%.

behavior of the homopolymer sample is the occurrence of a rapid and intense fall of the dynamic modulus E' in the glass transition region; after onset of the transition on heating, the micro-Brownian motions of PHEMA molecules appear to become more and more violent with increasing temperature, and above 160°C, both E' and E'' values were out of the measurement range.

For the two examples of PHEMA-rich compositions given in Fig. 2, the T_gs were estimated to be 89°C (2/98 sample) and 96°C (10/90 sample), from precise readings of a peak-maximum position in the respective E'' vs temperature curves. This observation relating to T_g location is consistent with the DSC result described already; i.e., the composite samples with ≤10 wt% chitin give a T_g value lower than that of plain PHEMA, but the increase in chitin content from 2 to 10 wt% is attended by a T_g elevation. Of great significance in the dynamic mechanical data is the following observation: in contrast to the viscoelastic behavior of PHEMA alone, the introduction of chitin into the PHEMA bulk leads not only to a drastic suppression of the E'-drop in the glass transition region, but also to a more gradual decrease of E'' with increasing temperature after onset of the transition. It should be emphasized that the chitin component incorporated at a concentration of only 2 wt% acts as an effective reinforcer for the PHEMA matrix. A similar effect due to the chemical blending was noted usually for composite samples prepared so that the chitin content was ≤ 20 wt%, with avoidance of intemperate compression of the as-coagulated gels before polymerization. These composites were all transparent and retained almost completely the starting gel form to the naked eye. Thus, for the PHEMA-rich compositions (chitin <20 wt%), it seems natural from the visual and dynamic mechanical observations to assume that an initial network structure of chitin gels was sufficiently fixed into the polymerized bulks to form an IPN type organization with partially cross-linked PHEMA.

The dynamic viscoelastic characterization was also made for other compositions richer in chitin content. Figure 3 illustrates the data of E' and E'' vs temperature for three selected chitin/PHEMA compositions of 50/50, 80/20, and 0/100. The regenerated chitin sample (0/100) exhibits only a small dispersion signal around 110°C in the E'' vs temperature curve. This dispersion may be interpreted as due to a local relaxation of the backbone chain of chitin (Ogura *et al.*, 1980; Pizzoli *et al.*, 1991). In our previous study (Miyashita *et al.*, 1996b), the activation energy (E_a) for this dispersion was estimated to be ca. 13 kcal mol^{-1}, which is comparable with an E_a value required for the so-called β-relaxation mode, usually

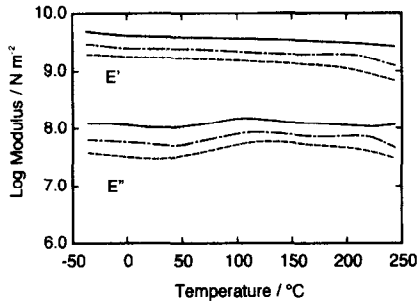

Fig. 3. Temperature dependence of E' and E'' for chitin/PHEMA composites containing ≥50 wt% chitin. Chitin content: (- - -), 50 wt%; (– – –), 80 wt%; (——), 100 wt%.

observed as a sub-transition for many polymer materials. The principal (α) dispersion signal of chitin, associated with the glass transition, could not be detected in the present measurement before the thermal degradation began to occur above ~240°C. The chitin T_g is, therefore, predicted to lie in a temperature range of ≤ 240°C.

In the E' and E'' data for the 80/20 composition given in Fig. 3, a small, but clear dispersion is perceptible around 210°C, in addition to the β dispersion of chitin centered at ca. 120°C. The location of the former dispersion signal was moved sensitively by changing the chitin content, i.e., it shifted towards higher temperature with increasing chitin content, which was ascertained by using other chitin/PHEMA compositions ranging from 75/25 to 90/10. When the chitin content exceeded 90 wt%, however, the signal intensity was vanishingly small and, eventually, only the β transition of chitin came into prominence in the E' curve. In the preparation of these chitin-rich samples, it was necessary to extract a large amount of HEMA monomers from the as-coagulated gels before polymerization. For this purpose, the original chitin/HEMA gels were sandwiched between filter papers and compressed into a considerably thinner film form, whereupon the chitin component might have cohered to form agglomerates in places within the films. It is therefore plausible that the resulting chitin-rich composites would have less IPN character. However, the observation of a primary dispersion around 200°C in the dynamic mechanical measurements allows us to assume that a quantity of molecules of the PHEMA component are incorporated intimately in the chitin amorphous regions, instead of making discrete domains.

In the E'' data for the just intermediate composition (50/50), depicted by a dashed-line curve in Fig. 3, a very broad dispersion takes place with a peak maximum at 125°C and another weaker dispersion is also visible around 200°C. Such a dual transition behavior over a wide temperature range suggests the coexistence of multiple phases having different polymer

compositions in the bulk composite. Comparatively PHEMA-rich phases would give rise to the major dispersion signal in the lower temperature region, possibly with partial overlapping of the β transition of chitin *per se*. The temperature 125°C giving the E''-peak maximum is close to a value (117°C) of the T_g detected by the DSC analysis. The existence of other phases relatively rich in chitin would be responsible for the appearance of the additional transition signal as almost a shoulder on the E'' vs temperature curve. Taking account of the chemical blending procedure adopted for the sample preparation, there is as much probability that a certain degree of interpenetration of the two constituent polymer molecules is attained in each phase. A similar dual transition phenomenon was commonly observed for compositions containing 30–60 wt% chitin. With an increase in the chitin content in this composition range, the location of the major dispersion (at < 150°C) tended to shift to the higher temperature side, but by less than 20°C, and the secondary dispersion became more pronounced above ~180°C.

Homogeneity in IPN composites as estimated by NMR spectroscopy

Solid-state ^{13}C NMR spectroscopy is a useful tool for characterization of multicomponent polymer systems, by which one can quantify the scale of homogeneity in a polymer–polymer mixing state (Masson and Manley, 1991a, b; McBrietry and Douglass, 1981; Zhang *et al.*, 1992). For example, from measurements of the proton spin-lattice relaxation time $T_{1\rho}{}^{H}$, it is possible to determine an upper limit in heterogeneity on a scale of a few nanometers or less. Information about interactions at the molecular level (~1 nm) is also obtainable through analysis of ^{13}C CP/MAS NMR spectra. In the present study, these NMR techniques were employed for further characterization of chitin/PHEMA composites rich in PHEMA (chitin ≤ 20wt%), which were usually assumed to be endowed with IPN type organization.

^{13}C CP/MAS NMR spectra measured for film samples of regenerated chitin, PHEMA, and a chitin/PHEMA composite containing 8 wt% chitin are shown in Fig. 4. The peak assignments of the spectra were made based on literature data given for chitin (Takai *et al.*, 1989) and PHEMA (Kiremitci *et al.*, 1993). The chemical shifts of the assigned resonance signals are listed in Table 1. In the spectrum of the composite sample, the intensities of ^{13}C resonance peaks derived from the chitin component are considerably small due to the low concentration, and the signals of C1, C4, C5, and C3 carbons are only distinguishable in the range 75–105 ppm. In general, if there is a strong interaction on a molecular scale (less than 1 nm) between two components in a binary blend,

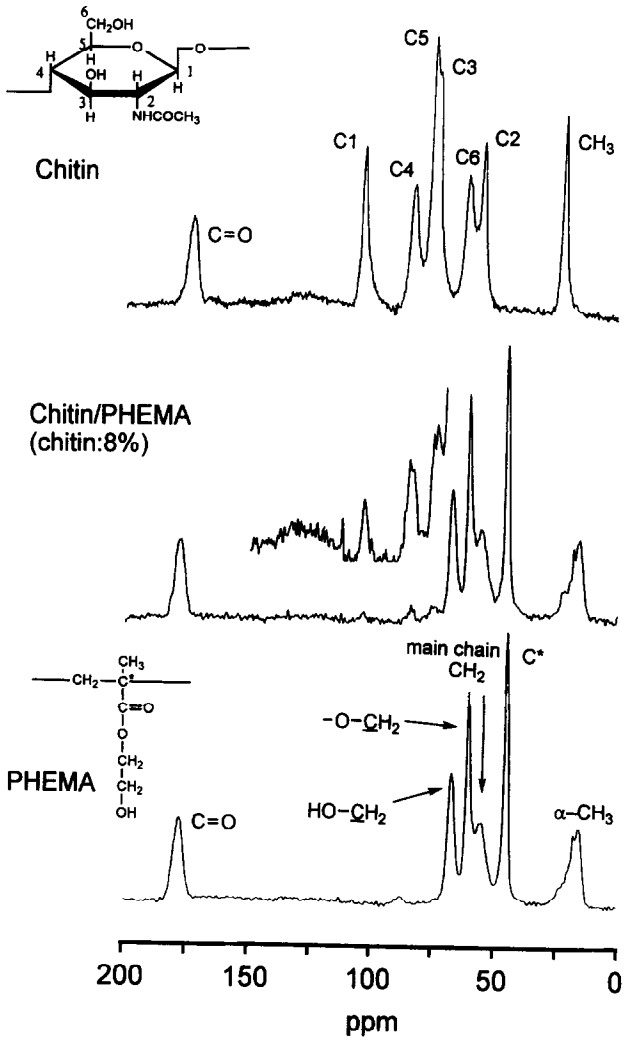

Fig. 4. Solid-state ^{13}C CP/MAS NMR spectra of chitin, PHEMA, and a chitin/PHEMA (8/92) composite.

the electron density around the carbons bearing the interacting groups is to be perturbed, so that some significant changes in chemical shift and/or line shape should be observed in a ^{13}C NMR spectrum of the blend, when compared with those of their respective homopolymers (Masson and Manley, 1991b; Zhang *et al.*, 1992). In the present NMR study, however, we could find none of these changes; i.e., the ^{13}C CP/MAS NMR spectra of PHEMA-rich composites were made up of simple superposition of the spectra of both homopolymers, with the apportioned peak intensities. From this observation, it is concluded that no specific intermolecular interaction such as hydrogen bonding takes place in the composites.

As is well established, $T_{1\rho}{}^{H}$ measurements conducted by an interrupted CP/MAS NMR technique provide information about the domain size in polymer blends on a scale of a few nanometers (Masson and Manley, 1991b, McBrietry and Douglass, 1981). Values of the

Table 1. ^{13}C chemical shifts of chitin, PHEMA, and a chitin/PHEMA (8/92) composite

	^{13}C Chemical shifts/ppm												
	$\underline{C}OCH_3$	C1	C4	C5	C3	C6	C2	$CO\underline{C}H_3$	OC=O	HO-$\underline{C}H_2$	-O-$\underline{C}H_2$	$\underline{C}H_2$-C*[a]	C*[a]	CH_3
Chitin	173.8	104.2	83.7	75.7	73.5	61.4	55.6	23.3	—	—	—	—	—	—
Chitin/PHEMA	ND	104.8	84.0	76.0	73.8	ND	ND	ND	177.8	67.2	60.3	55.7	45.3	16.1
PHEMA	—	—	—	—	—	—	—	—	178.0	67.1	60.3	55.0	45.1	16.5

[a]C*, asymmetric carbon in the main chain of PHEMA.
ND, not discernible.

relaxation times can be obtained practically by fitting the decaying carbon resonance intensity to the following single-exponential equation:

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

where $M(\tau)$ is the magnetization intensity observed as a function of the spin-locking time τ. Generally, if two different polymers are in a highly miscible state in the binary blend, the $T_{1\rho}{}^{H}$ values for different protons belonging to the respective components may be equalized to each other by spin diffusion. Figure 5 illustrates the decay behavior of ^{13}C resonance intensities for chitin, PGMA, and their 8/92 composite, depicted by monitoring the ^{13}C peak intensity of an asymmetric carbon (C*) in the main chain of PHEMA and that of C4 carbon in the pyranose ring of chitin. From the slope of each plot, a $T_{1\rho}{}^{H}$ value is obtained as the time constant of the relaxation process. The result of the estimations of $T_{1\rho}{}^{H}$ for the three samples is summarized in Table 2. The relaxation times evaluated for chitin and PHEMA are 8.0 and 12.3 ms in their respective pure states. In the composite sample, the $T_{1\rho}{}^{H}$ values for both components, i.e., 9.5 ms (for chitin) and 9.8 ms (for PHEMA) are almost identical with each other within the experimental error. This indicates that the two constituent polymers are coexistent in a range where the mutual 1H-spin diffusion is permitted over a period of approx. 9.7 ms. An effective distance (L) over which spin diffusion can proceed in a time $T_{1\rho}{}^{H}$

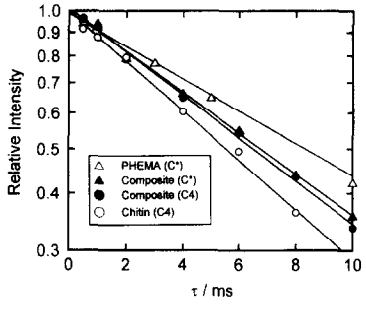

Fig. 5. Semi-logarithmic plots of the decay of ^{13}C resonance intensities as a function of spin-locking time τ, for film samples of chitin, PHEMA, and their composite (chitin/PHEMA = 8/92).

Table 2. $T_{1\rho}{}^{H}$ values for PHEMA, chitin, and a chitin/PHEMA (8/92) composite, determined from the decay plots given in Fig. 5

	$T_{1\rho}{}^{H}$/ms	
	C*	C4
Chitin	12.3	
Chitin/PHEMA	9.8	9.5
PHEMA		8.0

is represented in the following form (McBrietry and Douglass, 1981):

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

where D is the diffusion coefficient, usually taken to be $\sim 10^{-12}$ cm^2 s^{-1} in polymer systems. With an average $T_{1\rho}{}^{H}$ value of 9.65 ms for the chitin/PHEMA sample, the diffusion path length can be calculated as $L = 2.4$ nm, which gives an upper limit of the heterogeneous domain size in this composite. It is therefore inferable that the IPN-like composite is homogeneous on a scale between 1 and 2.4 nm, based on the combined estimation by both CP/MAS spectra and $T_{1\rho}{}^{H}$ measurements.

CONCLUSIONS

Chitin/poly(2-hydroxyethyl methacrylate) (PHEMA) composites were synthesized successfully via photopolymerization in a gel state of chitin impregnated with HEMA monomer.

For chitin/PHEMA compositions rich in PHEMA (chitin $\leq$ 20 wt%), it was reasonably assumed from observations of the visual appearance and thermal transition behavior that an initial network structure of chitin gels was sufficiently fixed into the cross-linked PHEMA matrix, resulting in the formation of a well-developed "IPN" type organization. As revealed by DSC and dynamic mechanical analysis, these composites exhibited a systematic shift of T_g with an increase in the chitin content, and the lowering of their modulus E' in the glass transition region was extremely suppressed in contrast to the corresponding E'-drop observed for PHEMA homopolymer. Solid-state ^{13}C NMR experiments were also carried out to evaluate the scale of homogeneous mixing in the PHEMA-rich samples. From measurements of the proton spin-lattice relaxation times ($T_{1\rho}{}^{H}$), the size of heterogeneity in the IPN-like composites was estimated to be less than 2.4 nm.

For chitin-rich compositions (chitin $\leq$ 70 wt%), polymerized samples were usually taken as poor in IPN architecture. However, it was possible to assume that some amount of PHEMA molecules were incorporated intimately in the chitin amorphous regions, instead of making discrete polymer domains, as supported by the dynamic viscoelastic data: for the chitin-rich composites, a primary transition signal was observed above 200°C with an E''-peak shifted depending on the chitin content, in addition to the appearance of the β transition of chitin *per se* at approx. 115°C. For intermediate chitin/PHEMA compositions containing 30–60 wt% chitin, samples showed a dual transition behavior over a wide temperature range, suggesting the coexistence of multiple phases having different polymer compositions in the bulk composites. In the respective phases, a certain degree of molecular interpenetration may be attained between the chemically blended polymer pair.

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