Synthesis and FTIR Spectroscopic Studies on Shear Induced Oriented Liquid Crystalline Chitin/Poly(acrylic acid) Composite

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ABSTRACT: Liquid crystalline chitin/poly(acrylic acid) composite, with its unique optical properties, was fabricated by the free-radical photopolymerization of acrylic acid in an aligned mesophase. Alignment of the mesophase was achieved by unidirectional shearing. The developed composites, coated on calcium fluoride (CaF_2) substrate, were transparent, and the alignment was retained depending on the mesophase composition of the ternary dispersion (chitin microfibrils, water, acrylic acid). According to studies from polarized FTIR spectroscopy, both the degree of orientation and the molecular interactions were strongly affected by respective mesophase behavior. The average molecular chains of chitin microfibrils were oriented along the shear direction. A high dichroic ratio value of about 25, observed in composites of chitin/poly(acrylic acid) with a w/w ratio of 55:45, opens an interesting avenue to prepare a new chitin-based optically anisotropic composite. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1932–1940, 2003

Key words: FTIR; liquid-crystalline polymers; shear; orientation; composites

INTRODUCTION

Composites of ordered polymeric materials with tailor-made optical, electrical, and mechanical properties are one of the modern trends of materials science. In this field, fabricating polymer composites using liquid crystalline materials is highly relevant because of the interesting optical properties of the composites. The structure and orientation of liquid crystal (LC) moieties can be stabilized by polymeric systems in such a way that free-radical photopolymerization of nonmesogenic vinyl monomers occurs in the mechanically oriented lyotropic mesophase. There have been several reports[1–5] on cellulose-based composites, one of the interesting groups of liquid crystal materials, synthesized with preserved mesomorphic structure using this method. However, there has been no significant study of liquid crystalline chitin-based composites with preserved liquid crystalline properties. With the increasing demand for the utilization of naturally occurring biopolymers, such as cellulose, chitin has drawn attention as a liquid crystalline material for developing such a composite.

Chitin occurs in nature in the form of microfibrils with diameters varying from 2.5 to 25 nm, and lengths of about 0.36 μm. These chitin microfibrils are embedded in a matrix of proteins, which are presumably linked covalently to the polysaccharide. The stiffness of the chitin fibers is 70–90 GPa, and that of the protein matrix is 120 MPa. The mechanical properties of biological structures are clearly correlated with the packing of chitin microfibrils to form smectic, nematic, or cholesteric mesophases.[6] Liquid crystal systems, including fibrillar cellulose and partially deacetylated chitin from acid hydrolysis, have been reported in several studies.[7–13] The acid-hydrolyzed chitin suspension spontaneously disperses into rodlike microfibrillar fragments and self-assembles to form a lower liquid crystalline phase (chiral nematic order) and an upper isotropic phase above a certain concentration. The stability of colloidal chitin suspensions has been attributed to the presence of positive charge (NH_3^+) at the surface of the crystallites arising from protonation of amino groups already present in the chitin sample, as well as those which may be formed by additional deacetylation during acid hydrolysis.[13]

We selected acrylic acid as a nonmesogenic vinyl monomer because acrylic acid is water miscible, and it can readily mix with aqueous chitin suspension. Studies on phase separation behavior upon mixing with acrylic acid over a range of concentrations[14] also show the liquid crystalline phase depending on the ternary

TABLE I
Ternary Components of Chitin, Water, Acrylic Acid (AA) Monomer, and Chitin/Poly(AA)
Ratio of Developed Composites (w/w%)

	Chitin (g)	For Given Amount of AA Monomer (g)				
		Sample A 2.00 g	Sample B 1.50 g	Sample C 1.00 g	Sample D 0.50 g	
Anisotropic	0.5993	9.83	10.70	10.70	10.70	chitin
		57.38	62.51	71.44	80.37	water
		32.79	26.79	17.86	8.93	acrylic acid
		23/77	29/71	37/63	55/45	chitin/poly(AA)
Aniso[a]/Biphase	0.4281	7.89	7.89	7.89	7.89	chitin
		55.27	64.48	73.69	82.90	water
		36.84	27.63	18.42	9.21	acrylic acid
		18/82	22/78	30/70	46/54	chitin/poly(AA)
Biphase[b]	0.3425	6.41	6.41	6.41	6.41	chitin
		56.15	65.51	74.87	84.23	water
		37.44	28.08	18.72	9.36	acrylic acid
		15/85	19/81	25/75	40/60	chitin/poly(AA)

[a] Anisotropic phase in A, B, and C.
[b] Stable flow-birefringence phase in A, B, and C.

composition (chitin, water, and acrylic acid monomer). In this study, alignment of LC chitin/AA mesophase was achieved by manual shearing. This article explores subsequent solidification of the aligned mesophase by photopolymerization of acrylic acid to afford a novel optically anisotropic composite material composed of natural chitin fibers in a synthetic poly-(acrylic acid) matrix, a model of naturally occurring biocomposites of chitin microfibrils embedded in protein matrices. The effect of mesophase concentration on the alignment of developed composites was investigated by polarized FTIR spectroscopy.

EXPERIMENTAL

Materials

Chitin powder (α-chitin from crab), acrylic acid monomer (AA), concentrated hydrochloric acid (HCl), poly-(ethylene glycol) (M_r, 20000), photoinitiator [2,2'-azo-bis-(2-amidinopropane) dihydrochloride] were purchased from Wako Pure Chemical Industries Ltd., Tokyo, Japan. Seamless cellulose tubing (UC-36-32-100) with a cutoff molecular weight of 14000, purchased from Sanko-Junyaku Co., Tokyo, Japan, was used for dialysis. CaF_2 (calcium fluoride crystal) windows (25.4 × 1 mm), purchased from Pier Optics Co., Ltd., Tatebayashi-shi, Japan, was used as a substrate for composite synthesis. All of the chemicals were used without further purification. Deionized water was used for all experiments.

Sample Preparation

A suspension of chitin crystallites was prepared by acid hydrolysis of α-chitin powder obtained from crab shells. A detailed description of the preparation of

chitin suspension is presented elsewhere.[14] The dialyzed tubes containing colloidal rodlike chitin suspensions of a concentration of about 0.5% (w/w) were immersed in an aqueous poly(ethylene glycol) solution to produce concentrated birefringent aqueous gels (14–15% by weight). The individual rodlike fragments ranged from ≈80 to 350 nm in length, and from ≈8 to 12 nm in width.[14] The starting liquid crystalline chitin concentration used for composite synthesis was 14.62% (w/w). After mixing with acrylic acid by ultrasonication (Nissei US-150 sonicator) for 2 min, photoinitiator was added. The vials were kept in a cold dark place overnight. UV photopolymerization was carried out in microscale for polarized FTIR measurement. Specimens were prepared by placing LC chitin/AA liquid mixture together with the photoinitiator, near the edge of one side of calcium fluoride substrate and rubbing unidirectionally towards the opposite side. The specimen was then irradiated by UV light (400 W UV lamp) from a 20 cm distance for 35 min followed by vacuum drying at 30°C for 48 h. The compositions of the three components with their respective mesophase behavior[14] are given in Table I.

From phase behavior studies of ternary dispersion, an apparent stable flow-birefringence glassy phase was observed at a 6.41% chitin concentration and an AA concentration of ≈9% to ≈37%. This phase will remain for more than a year if the system is not disturbed. The vial can be turned upside down without flow, but slight oscillation of the sample vial by hand causes it to flow. Up to ≈9% AA, with increasing chitin concentration, the system displayed a typical isotropic phase, a biphase (upper isotropic and lower anisotropic phase), and an anisotropic monophase. The lower anisotropic phase showed chiral nematic order, a fingerprint-like texture. Above ≈9% AA (from

≈9% to ≈37%), with increasing chitin concentration, the system developed an isotropic phase, a stable flow-birefringence glassy phase and an anisotropic monophase. No phase separation occurred. The optical textures of the birefringent glassy phase and the anisotropic phase displayed nematic order.[14] We selected the concentration range that showed nematic order and conducted orientation studies of the developed composite, which are reported in this article.

The oriented specimen of pure anisotropic phase LC chitin (14.62 w/w%) was prepared by the same procedure mentioned above and solidified by evaporation of water at room temperature.

Measurements

An Olympus polarizing optical microscope was used to obtain the polarized optical micrographs of the composite. FTIR Nicolet Model Magna IR 860 was used to collect the absorption spectra. The ZnSe wire grid polarizer (Spectra-Tech IR Polarizer, Thermo Nicolet, USA), including a rotary holder calibrated with 2° scale divisions, positioned adjacent to the sample was used to obtain polarized spectra of the oriented LC chitin film and oriented LC chitin/poly(AA) composite films coated on the CaF_2 substrates, in the region of 4000–1100 cm^{-1}. The beam passes first through the polarizer, and the resulting polarized IR radiation propagates through the sample coated CaF_2 substrate before reaching the detector. The position of the specimen was constant, with its shear direction vertical, throughout the measurement. When the polarizer is set in the 0° position, the wire grid will be in the horizontal plane and the electric field will be east-west. Rotation of the polarizer enables the absorption spectra to be recorded with the plane of polarization successively. A band is designated as a parallel band (‖ or P-0) where the electric field vector of the incident radiation is parallel to the shear direction and a perpendicular band (⊥ or p-90) where the electric field vector of the incident radiation is perpendicular to the shear direction. All of the polarized spectra were collected with a spectral resolution of 4 cm^{-1}, and 64 scans were carried out.

Because the dichroic ratio gives information about the mean orientation of the transition moments of the corresponding vibrational modes, the optical anisotropy of oriented LC chitin/poly(AA) composites can be determined by using the glycosidic linkage (C_1—O—C_4, bridge oxygen stretching mode) at 1157 cm^{-1} as a measure of orientation. The glycosidic linkage is approximately co-aligned with the molecular long axis or fiber axis[15–18] as in the case of cellulose.[19–21] All of the polarized infrared spectra were normalized with a corresponding absorption band of CH_3 deformation mode at 1378 cm^{-1}.
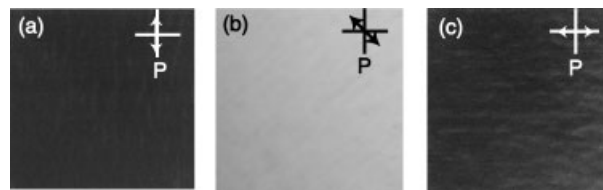
Figure 1 Polarized optical micrographs of oriented LC chitin/poly(AA) composite D prepared from anisotropic phase with different angles between shear (rubbing) direction (↔) and polarization plane of the polarizer (P): (a) 0°, (b) 45°, (c) 90°.

The dichroic ratio R is defined as $R = A_{\|}/A_{\perp}$, where $A_{\|}$ and $A_{\perp}$ are the absorbances measured with parallel and perpendicular polarization, respectively.[22,23]

RESULTS AND DISCUSSION

Polarized Optical Microscopy

It is known that under the crossed polarizing light, the transmission of polarized light is strongest when the orientation direction of molecular chains (shearing direction in this specimen) is at an angle of 45° to the polarization plane of the polarizer and weakest when the shearing direction is parallel to either the polarizer or the analyzer axis.[24] The polarized optical micrograph of oriented LC chitin/poly(AA) composite D [chitin/poly(AA) = 55:45 (w/w%)], shown in Figure 1, displays brightness (at 45°) and darkness (at 0° and 90°) with changes in the angle between the shearing direction and the polarization plane of the polarizer, as mentioned above. The alignment or the optical anisotropy of the initial LC chitin/AA monomer liquid mixture was preserved after the transition of mesophase to the solid state upon UV photopolymerization of acrylic acid monomer. However, bulk anisotropic orientation was not observed in the composite without alignment. The orientation direction of the molecular long axes was determined by polarized FTIR study.

Polarized FTIR Study of Oriented LC Chitin Film

The absorption of infrared radiation occurs to a maximum degree when the direction of the electric vector of the radiation is parallel to the direction of the dipole moment changes (transition-moment) involved in the various vibrational modes of the absorbing molecule. If the direction of the electric vector lies at an angle to the direction of the dipole moment change, the component of the former resolved along the latter direction is involved in the absorption process, which thus occurs less strongly. This is the directional property that makes infrared spectroscopy useful for orientation studies.[22,23]
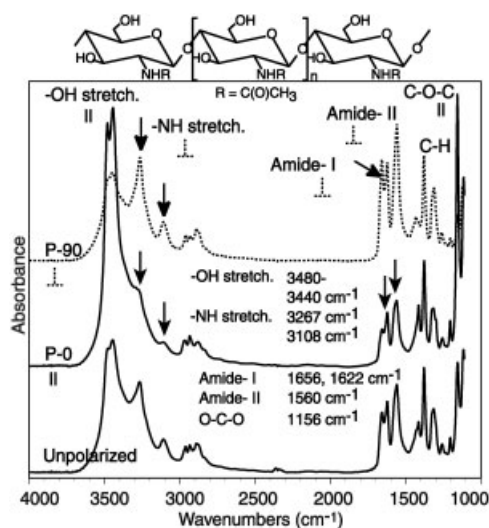
Figure 2 Polarized FTIR spectra of oriented LC chitin film (chitin 14.62%, anisotropic phase) coated on CaF$_2$ substrate. IR spectra were recorded with incident IR beam polarized parallel (P-0) and polarized perpendicular (P-90) to shear (rubbing) direction.

Polarized FTIR spectra of the oriented LC chitin film (14.62% w/w) coated on CaF$_2$ substrate are shown in Figure 2. The spectra absorption frequency, polarization properties and band assignment of LC chitin, based on literature data from X-ray and infrared studies,[15–18] in the region from 3480 cm^{-1} to 1110 cm^{-1} are described in Table II. The active group that is especially important in the infrared spectrum of chitin is C=O...N—H in common with a hydroxyl group because the N-acetyl amino group is the characteristic feature of chitin.

The parallel dichroism of the OH stretching absorption band shows as doublet at 3480 cm^{-1} and 3440 cm^{-1}. The band at 3440 cm^{-1} is assigned to the intramolecular hydrogen bond between the O(3')H and the ring oxygen in the next glucose ring [C(3')OH...O(5)], since a strong parallel band is found in this position in cellulose II.[25,26] The band at 3480 cm^{-1} may be assigned as a 50/50 statistical mixture of inter- and intramolecular hydrogen bonds formed from CH$_2$OH groups, according to X-ray data of crystal structures reported by Minke and Blackwell.[18] The CH$_2$OH groups form O(6)H...O(6') intermolecular hydrogen bonds to the CH$_2$OH groups on the adjacent chain along the *ab* diagonal as well as O(6')H...O(7) intramolecular hydrogen bonds to the carbonyl oxygen on the next residue.

All N—H absorption bands are perpendicular to the shear direction (average molecular long axes). The splitting of the amide I band at 1656 cm^{-1} and 1622 cm^{-1} accounts for a different hydrogen bonding environment. A singly hydrogen bonded amide I band (1656 cm^{-1}) is due to intermolecular hydrogen bonds C(2$_1$)NH...O(7$_3$), which are approximately parallel to

the *a* axis of the unit cell. In addition, there are also intramolecular hydrogen bonds with hydroxyl groups on C(6) [O(6')H...O(7)]. As a result, a doubly hydrogen bonded amide I band (1622 cm^{-1}) due to both inter- and intramolecular hydrogen bonds is observed in the spectrum of α-chitin. Because of the different hydrogen bonding environments, these two absorption bands showed different dichroic ratio values, 0.37 and 0.55 ($\approx$1.48-times) for singly and doubly hydrogen bonded bands, respectively. Iwamoto and co-workers reported ratios of 0.18 and 0.26 ($\approx$1.44-times) for these bonds.[27] The perpendicular dichroism of the amide II absorption band, arising from deformation of the N—H bond in the plane of the CO.NH group,[15–17] further confirmed that the plane of the CO.NH group as well as CO and NH bonds themselves are perpendicular to the chain axis.

A polar plot of absorbance against polarizer rotation angle is shown in Figure 3 in order to describe the whole polarization profile clearly. If chitin microfibrils were randomly distributed throughout the specimen, the absorbance would be the same for all polarization angles, resulting in a circular curve on the polar plot. Conversely, if the absorbance changed with polarization angle, then some degree of directional orientation would be present. A good orientation of the chitin microfibrils is proven by the strong dichroism of the specimen. The strong parallel dichroism observed in the bridge oxygen stretching region (C$_1$—O—C$_4$) indicates that the glycosidic linkage (which is co-aligned with the molecular long axis) is parallel to the shear (rubbing) direction.

TABLE II
Assignment of FTIR Absorption Bands for Oriented LC Chitin Film

| Absorption Frequency (cm^{-1})	Polarization	Assignment
3480, 3440	∥	O—H stretching
3267	⊥	N—H stretching (asymmetric)
3108	⊥	N—H stretching (symmetric)
2961	⊥	Asym. C—H$_3$ stretching
2933	∥	Sym. C—H$_3$ stretch. and asym. C—H$_2$ stretch.
2890	⊥	C—H stretching
1656	⊥	Amide I (singly H-bonded)
1622	⊥	Amide I (doubly H-bonded)
1560	⊥	Amide II
1431	⊥	CH$_3$ deformation and CH$_2$ bending
1414	∥	
1378	⊥?	Sym. CH$_3$ deformation (?- not significant)
1317	⊥	Amide III, CH$_2$ wagging
1156	∥	Asym. bridge oxygen stretch. (glycosidic link)
1117	∥	Asym. in-phase ring stretching
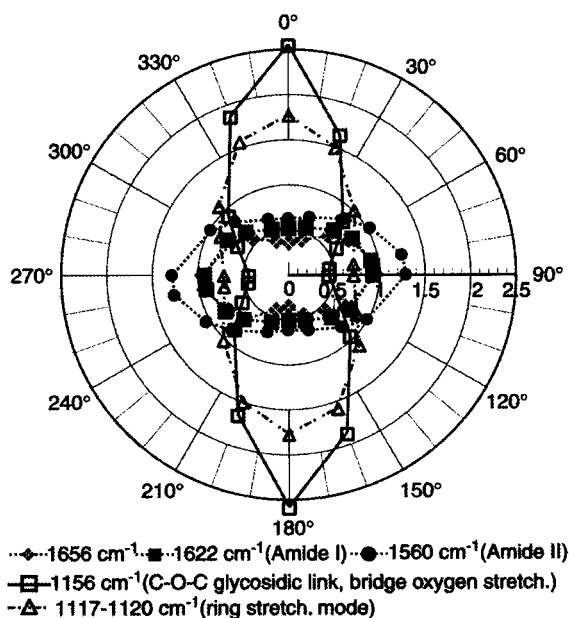
Figure 3   Polar plot of IR absorbance vs. polarizer rotation angle with respect to rubbing direction for shear induced LC chitin film (chitin 14.62%, anisotropic phase).

Polarized FTIR Study of Oriented LC Chitin/Poly(AA) Composites

The absorption spectra of LC chitin/poly(AA) composite showed sharp IR bands across the whole region from 4000 to 1100 cm^{-1}. The intense absorption and directional property of chitin crystallites compared to poly(AA) caused the polarized spectra to be dominated by the absorption bands of chitin crystallites.

The typical polarized (polarized parallel and polarized perpendicular) FTIR spectra and polar plot of oriented LC chitin/poly(AA) composite D are shown in Figures 4 and 5, respectively, in order to be compared to those of pure LC chitin film (Figs. 2 and 3). The strong parallel dichroism is visible at the OH stretching region (3440–3480 cm^{-1}), at the C—O—C bridge oxygen stretching region (1157 cm^{-1}), and at the ring stretching region ($\approx$1115 cm^{-1}); the perpendicular dichroism visible at the NH stretching region and the amide region is similar to the spectral profile of pure LC chitin film. The glycosidic linkage (C—O—C bridge oxygen stretching mode) was parallel to the shear direction, similar to that observed in the LC chitin film.

The polarized FTIR spectra and polarized optical micrographs clearly show that the aligned LC chitin, immobilized by matrix polymerization of acrylic acid and liquid crystallinity in the initial mesophase, was maintained in the final composite, like in composites of cellulose derivatives.[1–5] The molecular long axis of LC chitin in the developed composite was oriented along the shear direction. However, the degree of orientation in each composite depends on the compo-
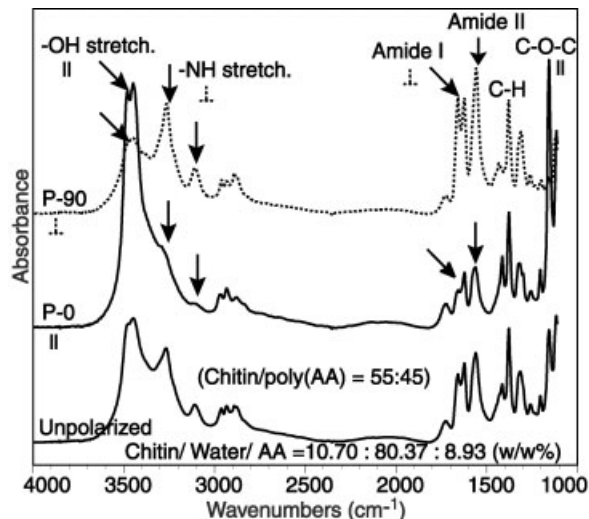

Figure 4   Polarized FTIR spectra of oriented LC chitin/poly(AA) composite D (chitin –10.70%, anisotropic phase). IR spectra were recorded with incident IR beam polarized parallel (P-0) and polarized perpendicular (P-90) to shear (rubbing) direction.

nent concentration (chitin microfibrils, water, and acrylic acid) of the ternary dispersion.

Effect of Acrylic Acid Concentration

The perpendicular polarized infrared spectra of LC chitin/poly(AA) composites over a range of AA concentrations with constant chitin concentration are shown in Figure 6. If the molecular chain of the LC
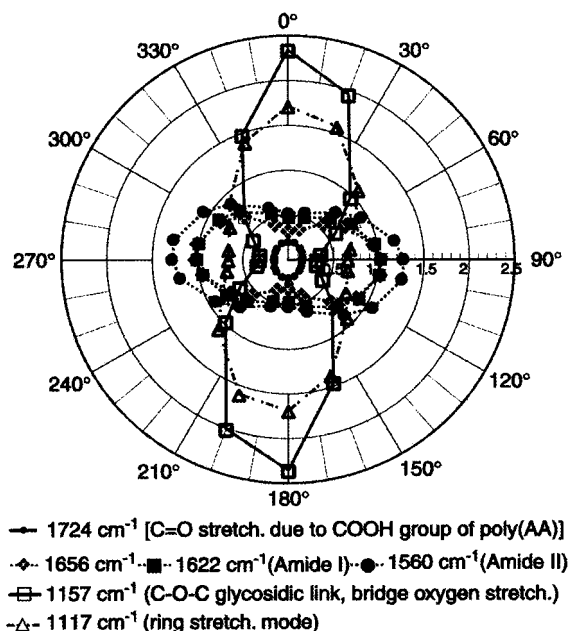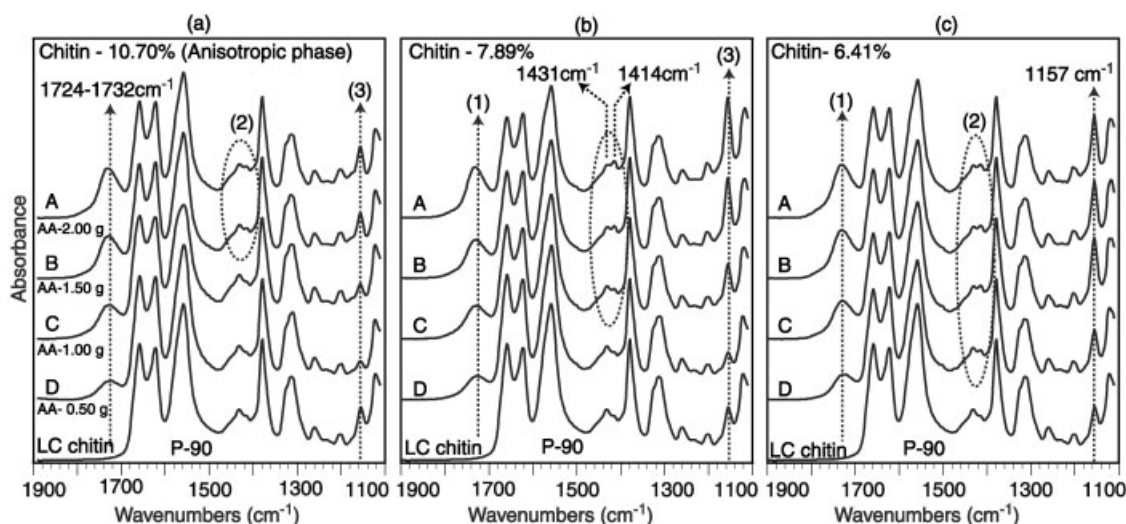

Figure 5   Polar plot of IR absorbance vs. polarizer rotation angle with respect to rubbing direction for shear induced LC chitin/poly(AA) composite D (chitin – 10.70%, anisotropic phase).

Figure 6 Polarized (perpendicular – P90) FTIR spectra of LC chitin/poly(AA) composites with constant chitin concentration and different AA concentrations: (a) 10.70%, (b) 7.89%, and (c) 6.41%. Changes in relative intense peak height and peak shape of (1) carbonyl absorption (C=O) at 1724–1732 cm^{-1}, (2) CH$_3$ deformation and CH$_2$ bending at 1431 cm^{-1} and 1414 cm^{-1}, and (3) C—O—C glycosidic link, bridge oxygen stretching mode, at 1157 cm^{-1} with increasing AA content.

chitin is not well oriented, one can determine the major parallel band by its rather large intensity even in the spectra of perpendicular dichroism. Generally, at a constant chitin concentration, the LC chitin/poly(AA) composite became less oriented with increasing AA concentration, as can be seen in all figures by tracing the absorption intensity of a strong parallel dichroism of (C$_1$—O—C$_4$) absorption band at about 1157 cm^{-1}. In Figure 6(a), the relative intensity of composites A and B was much higher than that of composites C and D. These composites were prepared from an anisotropic phase with a chitin concentration of 10.70%. While composites prepared from 7.89% chitin, the relative increased peak intensity was found in A, B, and C rather than D [Fig. 6(b)]. It was noticeable that all the composites prepared from 6.41% chitin concentration [Fig. 6(c)] show relative increased peak intensity at 1157 cm^{-1} regardless of acrylic acid concentration.
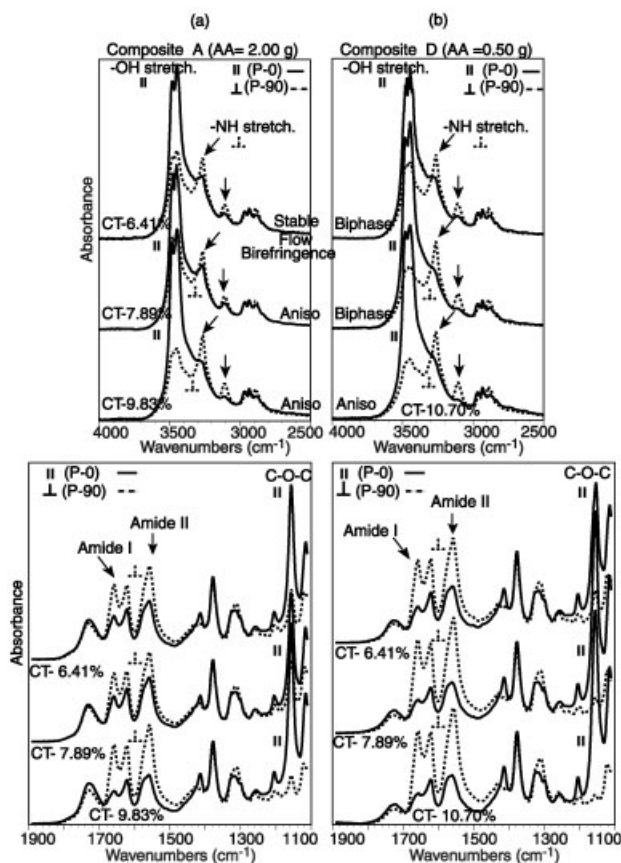
In addition, the parallel band at 1414 cm^{-1} for CH$_2$ bending mode, somewhat sensitive to backbone conformation, showed a slight change in peak height with increased AA concentration. Usually this peak is not distinct in instances of perpendicular dichroism and is observed with the CH$_3$ deformation mode at the same level with a polarization of 50° relative to the shearing direction in pure LC chitin (Fig. 7). Observation of this peak with the CH$_3$ deformation mode at the same level in composites A and B in Figure 6(a), in composites A, B, and C in Figure 6(b), and in all composites in Figure 6(c) also reveals that the degree of orientation decreases with increasing AA concentration and decreasing chitin concentration. This imperfect orientation can be explained by the phase behavior of LC chitin/AA mixture of respective composite when affected by increased AA concentration.[14]

Effect of Chitin Concentration

Because of the contribution of chitin microfibrils to the formation of a liquid crystalline system, the concentration of chitin highly influences the optical anisotropy of the developed composites. Polarized spectra
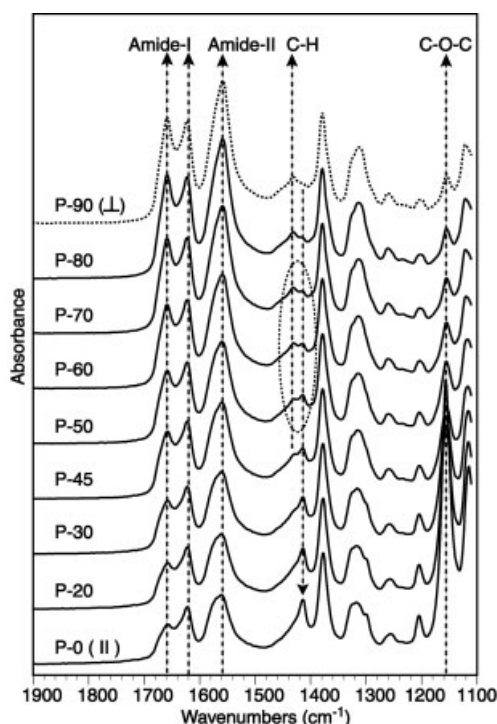
Figure 7 Polarized FTIR spectra of oriented LC chitin film (chitin – 14.62%, anisotropic phase) coated on CaF$_2$ substrate by induced shearing. Polarizer rotation angle with respect to shear direction (molecular long axis) was varied from 0 to 90°.
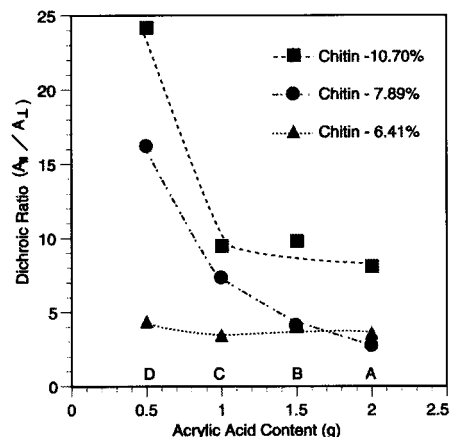
Figure 8 Polarized FTIR spectra of LC chitin/poly(AA) composites: (a) composite A and (b) composite D at different chitin:poly(AA) ratios (w/w%): (bottom line) 23:77 (composite A), 55:45 (composite D); (middle line) 18:82 (A), 46:54 (D); and (top line) 15:85 (A), 40:60 (D).

chroism and from 1186 cm^{-1} to 1140 cm^{-1} for perpendicular dichroism. The variations of the dichroic ratios with chitin concentration and AA concentration are shown in Figure 9. The orientation property is strongly influenced by the phase behavior of the respective mesomorphic state. Because chitin 10.70% is a completely anisotropic phase, all of the composites prepared from that phase had higher orientation than the other phases in general, but it decreased sharply and leveled off with increasing acrylic acid concentration. A chitin concentration of 6.41% in three components with AA 18.72% (1.00 g), 28.08% (1.50 g) and 37.44% (2.00 g) showed stable flow-birefringence phase,[14] and hence composites developed from this phase showed no significant difference in their degree of orientation. Because the chitin crystallites in the birefringent flow tend to be frozen in their preferred orientation after mixing with AA, the shearing does not greatly affect the crystallites' orientation. There was an apparent difference in the orientation property of composites prepared from chitin 7.89%, which originated from biphase behavior in sample D and the anisotropic phase in samples A, B and C in their mesomorphic states. The degree of orientation gradually decreased with increasing AA concentration. The increased AA concentration contributed to the increased viscosity of the mesophase system by means of the electrolyte effect, which in turn affected the orientation of chitin crystallites, even though there was a high enough concentration of chitin crystallites to form an anisotropic phase. Although the shearing condition has not been optimized and manually induced shear cannot be controlled to achieve exact uniformity in all samples, the high dichroic ratio of about 25 in composite of chitin/poly(AA) (55:45) indicates that the chitin microfibrils in this composite are highly oriented.

of composites A and D developed from different chitin concentrations are shown in Figure 8 in order to compare the effect of AA concentration and chitin concentration simultaneously. Both composites become less oriented with decreasing chitin concentration in general, as determined by tracing changes in the relative intensity of the NH absorption band. The perpendicular dichroism of the NH stretching band was observed, with a relatively intense band in parallel polarized spectra when chitin concentration was low compared to a higher one in each composite. They are more pronounced in composite A of higher acrylic acid concentration than in the lower acrylic acid concentration of composite D [Fig. 8(a)]. The same tendency was observed in carbonyl stretching (amide I) and amide II regions, as shown in Figure 8(b).

Finally, the glycosidic (C—O—C) linkage at 1157 cm^{-1}, which is approximately co-aligned with the molecular long axis, was used as a quantitative measure of the degree of anisotropic orientation of the molecules in the sheared-film. The dichroic ratio of this absorption band was determined using a baseline drawn from 1187 cm^{-1} to 1130 cm^{-1} for parallel di-

Figure 9 Dichroic ratio of bridge oxygen stretching mode (glycosidic link) at 1157 cm^{-1} as measure of orientation of LC chitin in sheared films of LC chitin/poly(AA) composites.
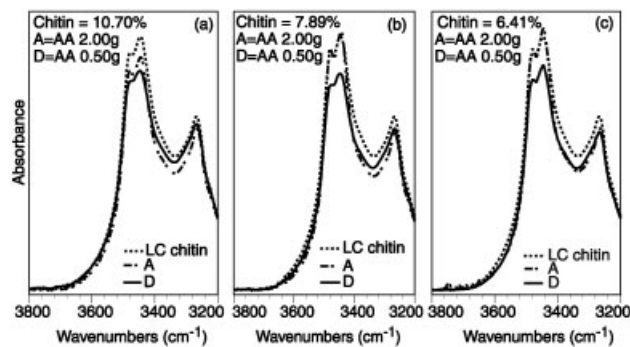
Figure 10 Unpolarized FTIR spectra of LC chitin/poly(AA) composite A and composite D for OH stretching region at given chitin concentrations: (a) 10.70%, (b)7.89%, (c) 6.41%.

Molecular Interaction

Because interactions between chitin and poly(AA) macromolecules can also affect the formation and properties of the composites, spectral changes in the OH stretching region and carbonyl absorption region were also investigated. These interactions were analyzed from unpolarized spectra. Figure 10 shows the unpolarized infrared spectra of the OH stretching region of composite A and D at different chitin concentrations. It can be seen that the OH stretching absorption band broadens to a lower frequency in composite D of lower AA concentration compared to composite A of higher AA concentration [Fig. 10(a)], resulting from interaction with the growing poly(AA) chains by hydrogen bondings. The extent of broadness decreased with decreasing chitin concentration [Fig. 10(b)], and no significant change was observed in composites of lower chitin concentration (6.41%) in Figure 10(c). This indicates that a lower AA concentration and higher chitin concentration favor the formation of intermolecular hydrogen bonds between the carbonyl groups of poly(AA) and the hydroxyl/amide groups of chitin.

Generally, the carbonyl absorption intensities increase and shift to a higher frequency (from 1724 cm^{-1} to 1732 cm^{-1}) with increased AA concentration at a given chitin concentration in the composite (Fig. 6). Composites prepared with a chitin concentration of 10.70% (anisotropic phase) have a strong tendency to participate in intermolecular associations because of their high chitin concentration and propensity to align as an ordered phase. Therefore, a relative parallel dichroism of the carbonyl absorption band was observed at both AA concentrations of composites developed from anisotropic phase (Fig. 8). However, composites prepared with 6.41% chitin showed no significant change in dichroism in this region because the viscous birefringent dispersion hindered interactions between two functional groups. From Figures 8

and 10, it can be concluded that the extent of molecular interaction of the developed composites was also reflected by the phase behavior of the corresponding mesophase of the ternary system.

CONCLUSIONS

Shear-oriented LC chitin/poly(acrylic acid) composites with preserved unique optical properties were prepared by photoinitiated free-radical polymerization, and orientation study was carried out by FTIR spectroscopy. Polarized FTIR spectra displayed the relative orientation of specific bonds with reference to the axis of the specimen (shear direction), which is consistent with the reported crystal structure of α-chitin. The dichroic ratio of the glycosidic link at about 1157 cm^{-1} gave valuable information on the degree of orientation of the molecular chains, which decreases with increasing AA concentration as well with decreasing LC chitin concentration. The composite showed highly oriented optical properties with a chitin/poly(AA) ratio of 55:45 (composite D), evidenced from both polarized optical micrographs and polarized FTIR studies. The composite prepared in this study is endowed with anisotropic organization, reflecting the liquid crystalline phase to a considerable extent.

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