Colloid Polym Sci (2007) 285:1019–1027
DOI 10.1007/s00396-007-1647-3

ORIGINAL CONTRIBUTION

Synthesis and characterization of poly(lactic acid) and glucosamine-formaldehyde/dodecylbenzenesulfonate composite films

**Yoshikazu Kondo · Yutaka Harima · Koji Hyakutake ·
Nobumitu Yamada · Masafumi Uota · Go Sakai ·
Tsuyoshi Kijima**

Received: 17 September 2006 / Accepted: 8 January 2007 / Published online: 31 March 2007

Abstract The composite films of poly(lactic acid) (PLA) doped with glucosamine(Gluc)-formaldehyde(FA) polymer/sodium dodecylbenzenesulfonate (SDBS) complexes at 1–5 wt% were synthesized to demonstrate striking improvement of their structural and mechanical properties. The polymer complexes were obtained by the hydrothermal polymerization of Gluc and FA at a molar ratio of 1:2 in the presence of SDBS. The atomic ratios of S in $-\mathrm{SO}_3^-$ to N in $-\mathrm{NH}_3^-$ (=S/N) in the polymer complexes limitedly range from 0.52 to 0.69, indicating that the complexation develops through the nonstoichiometric reaction between $-\mathrm{NH}_3^+$ groups of (Gluc-FA) polymer and $-\mathrm{SO}_3^-$ ones of SDBS and 31–48% of the $-\mathrm{NH}_3^+$ groups remain unbound. The PLA composite film doped with 1 wt% (Gluc-FA)/SDBS showed the elongation-at-break of as large as 194% compared with 37% for PLA film, together with an appreciable increase of the crystallites size (D_{200}) of PLA from 21.8 to 33.3 nm.

Keywords Glucosamine-formaldehyde polymer · Poly(lactic acid)(PLA) · Composite · Crystallite size · Mechanical property

Introduction

Increasing attention has been focused on the development of highly functional materials based on nanometer-sized building units such as nanowires, nanobelts, and nanotubes. Inorganic synthesis using surfactants as a templating agent has devoted to afford nanostructured materials such as mesoporous silica [1–3], alumina [4–6], zirconia [7], and rare earth oxides [8] and nanotublar vanadia [9], titania [10], and lantanid oxides [11].

The surfactant templating approach similar to those used for nanostructured inorganic materials was employed to prepare mesoporous organosilicates [12, 13], mesostructured complexes of phenol-formaldehyde polymer with surfactant [14], and nanotubular phenol-furfural polymers templated or detemplated with surfactant assemblies [15].

Naturally or artificially fabricated inorganic nanosized particles such as clay minerals and carbon nanotubes were applied as reinforcing materials for polymer composites in which the layered or tubular fillers are uniformly dispersed on a microscopic level in a matrix of high density polyethylene [16], nylon [17, 18], polystyrene [19], or other engineering polymers. This leads to a new family of engineering polymers characterized by their high strength, high modulus, high heat distortion temperature, and low gas permeability.

In recent years, biodegradable and naturally renewable polymers such as poly(lactic acid) (PLA) have attracted considerable interest, and the improvement of their physical properties such as strength and heat distortion temperature has been strongly desired for spreading practical use. Our recent study on PLA nanocomposites with hexagonal-structured nanoporous silica showed that the synthetic nanostructured fillers have a significant reinforcing-effect

---

Y. Kondo · Y. Harima · K. Hyakutake · N. Yamada · M. Uota ·
G. Sakai · T. Kijima (✉)
Department of Functional Materials Science, Materials Science
and Energy Engineering, Graduate School of Engineering,
Miyazaki University,
Miyazaki 889-2192, Japan
e-mail: t0g102u@cc.miyazaki-u.ac.jp

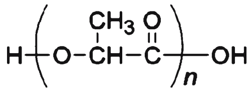
on the tensile strength, tensile modulus, and elongation [20]. Biodegradable organic nanotubular or nanosized materials, however, would be more desirable as a reinforcing material for biodegradable and naturally renewable polymer composites. For example, the self-assembled fibrous nanotubes of arylglicolipids derived from cardanol [21] may be useful as a reinforcing filler of polymers. Biodegradable polyectrolyte–surfactant complexes may be also applicable to the reinforcement of polymers, as suggested from a previous observation that the complex of polyacrylic acid and didodecyldimethylammonium counterions by itself shows a high elasticity and storage modulus [22, 23].

In this paper, we report the synthesis of glucosamine (Gluc)-formaldehyde(FA) copolymer/dodecylbenzenesulfonate (SDBS) complexes and PLA composite films doped with (Gluc-FA)/SDBS complexes. It is also demonstrated that the mechanical and structural properties of PLA are strikingly improved by doping of as little as 1 wt% (Gluc-FA)/SDBS complex.

Experimental

Materials

The reagent grade D-glucosamine hydrochloride (Gluc) and 8 wt% methanol–55 wt% water mixed solution of FA were purchased from Wako and sodium dodecylbezenesulfonate (SDBS) from Tokyo Kasei, and all were used without further purification. The commercial grade of PLA (from Shimadzu, Mw=123,000, Mw/Mn=1.8, Tm=171 °C, Tg=59.7 °C) was used as the matrix of polymer composites. The chemical structure of PLA is shown as the following formula.



$$H\left(-O-\overset{CH_3}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-\right)_n OH$$

Syntheses of (Gluc-FA)/SDBS complexes

In the typical reactions, Gluc (5.00 g), FA (1.395 g), SDBS (8.10×x g), and water (20.90 g) were homogeneously mixed at a molar ratio of 1:2:x:50 (x=0, 0.1, 0.5, 1.0) and then hydrothermally reacted in an autoclave with a built-in poly(tetrafluoroethylene) (PTFE) vessel at 120 °C for 24 h. In this reaction, the condensation reaction of Gluc and FA developed under the condition with or without ionic interaction between the $-NH_3^+$ groups in Gluc and the $-SO_3^-$ groups in SDBS. The resulting solids were separated by centrifugation, washed several times with distilled water, and then dried in a vacuum oven to obtain (Gluc-FA) polymer **1** and (Gluc-FA) polymer/SDBS complexes **2**.

Preparation of PLA-(Gluc-FA)/SDBS composites

A given amount of the (Gluc-FA)/SDBS complex (x=0.5) was sonically dissolved in dioxane and then mixed with PLA at 1, 2, and 5 wt% of (Gluc-FA)/SDBS, where the concentration of PLA in dioxane was adjusted to 10 wt%. The resulting viscous mixed solutions of PLA and (Gluc-FA)/SDBS in dioxane were spread on a glass plate by using a doctor knife and then dried in an air oven of 60 °C to obtain their composite films of 0.1-mm thick. The film of PLA alone was prepared in a similar procedure.

Characterization

The thermal and physical properties and the structure of the resulting composites films were characterized as follows. Transmission and scanning electron microscopic (TEM and SEM) images were taken by a Hitachi H-8000MU and a Hitachi H-4100M, respectively. Wide-angle X-ray diffraction (XRD) measurement was performed on a Shimadzu XD-D1 diffractometer with CuK_α radiation (λ=0.1541 nm) at a scanning rate of 2°/min. The crystallinity (χ_c) of PLA for the composite films was estimated in an usual manner [24]. The crystallite size along 200-axis (D_{200}) of PLA were calculated from the half value of peak width of 200 diffraction by the following Scherrer's formula (Eq. 1):

$$D_{200} = 0.9\lambda/(\beta\cos\theta_{200}) \tag{1}$$

where λ (nm), β (radian), and θ (degree) are the wavelength of X-ray used, half width, and Bragg's angle of 200 diffraction, respectively. Fourier transform infrared (FT-IR) spectra were measured by KBr pellet method using a Jasco FT-IR 300. Energy dispersion X-ray microanalysis (EDX) was carried out on a Horiba Emax-5700. Elemental analysis of C, H, N, and S was carried out on a Perkin Elmer 2400II. The tensile test of the composite film was carried out at 25 °C by using a Shimadzu EZ Test-20N.

Results

Synthesis of (Gluc-FA)/SDBS complexes

The hydrothermally synthesized products were morphologically feature-poor polymeric materials as shown for x=0.1 in Fig. 1a. Table 1 lists the elemental analysis data for the resulting products, **1** and **2**a–c, together with the calculated values. In the SDBS-free system, the observed composition of $C_{8.6}H_{15.7}N$ for the product **1** is in close agreement with the calculated one of $C_8H_{16}NO_6$ for the (Gluc-FA) copolymer ideally formed by the condensation reaction of Gluc and FA at the Gluc/FA molar ratio of 0.5, as shown in Fig. 2a.

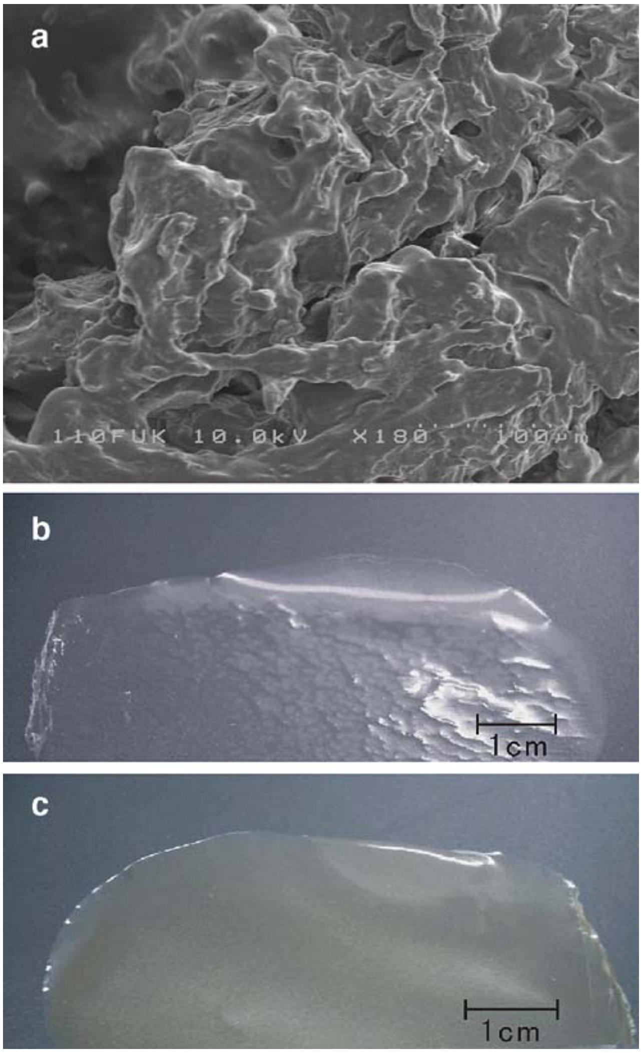


Fig. 1 **a** SEM image of (Gluc-FA)/SDBS complex (x=0.1), **b** optical photo (OP) image of PLA film, and **b** OP image of PLA-(Gluc-FA)/SDBS composite film. The scale bar in **a** shows 100 μm

The calculated compositions of **2**a–c in Table 1 were obtained by assuming that the reaction of Gluc-FA copolymer with SDBS process by Fig. 2b and that the atomic ratios of S in $-SO_3^-$ to N in NH_3^+ for the products are equal to the observed values. The close agreement between the calculated and the observed values of C and H for **2**a–c indicates that in Fig. 2b, **2** is validated for the complexation reaction. The resulting products in the SDBS-added system can thus be identified as the complexes of (Gluc-FA) and SDBS. It is also remarked that the S/N atomic ratios, i.e., the ratios of SDBS to the repeating unit of (Gluc-FA) polymer for **2**a–c, are in the narrow range of 0.52–0.69 independent of the SDBS amount added (x=0.1–1.0). This fact implies that these products are not mixtures of SDBS and (Gluc-FA) copolymer but of their complexed forms.

Table 1 Elemental analysis of the resulting (Gluc-FA)/SDBS complexes

Sample	x^a	Composition							
		Observed/atomic ratio				Calculated/atomic ratio			
		C	H	N	S	C	H	N	S
1	0	8.6	15.7	1	0	8	16	1	0
2a	0.1	16.8	27.0	1	0.52	17.4	30.6	1	0.52
2b	0.5	20.6	36.3	1	0.69	20.4	35.7	1	0.69
2c	1.0	21.1	36.3	1	0.66	19.9	34.8	1	0.66

[a] x means the molar ratio of SDBS to Gluc in feed.

The complexation of Gluc-FA polymer and SDBS was confirmed by the infrared spectra of the resulting products indicating the $\nu_{C\text{–}H}$ band at 2,966 cm^{-1} due to the $–CH_3$ group of SDBS, the $\delta_{H\text{–}C\text{-}H}$ band at 1,396 cm^{-1} due to the $–CH_2–$ group of both SDBS and (Gluc-FA) copolymer, the $\nu_{C=C}$ band at 1,630 cm^{-1} due to the benzene group, and the $\nu_{S=O}$ band at 1,184 cm^{-1} due to the sulfate of anion groups of SDBS, as shown in Fig. 3.

No definite XRD peaks were observed for 1, whereas the XRD patterns of **2**a–c showed a major diffraction peak around 2θ=2.8° (d=2.7–2.9 nm) and a hallo band around at 2θ=20°, as shown in Fig. 4. This XRD observation indicates that the resulting complexes **2**a–c consist of (Gluc-FA) copolymer/SDBS micelle complexed sheets of 2.7–2.9 nm thick. It is clear that the complexed structures are formed through the ionic interaction between $-NH_3^+$ groups of Gluc-FA copolymer and $-SO_3^-$ groups of SDBS.

Preparation and characterization of the composite films of PLA and (Gluc-FA)/SDBS as nanofillers

PLA and PLA composite films were prepared by casting from a solution of PLA in dioxane or mixed solution of PLA and the (Gluc-FA)/SDBS complex (x=0.5) in the same solvent. Upon drying the film of PLA alone shrunk and caused wrinkles to exhibit a rough surface, the PLA-(Gluc-FA)/SDBS composites yielded very smooth and uniform films, as shown in Fig. 1b and c. This is because the PLA molecules in the additive-free system easily move to aggregate inhomogeneously during drying, finally resulting in a film with a rough surface. In contrast, the PLA molecules in the PLA-(Gluc-FA)/SDBS mixed systems cannot move freely due to the strong interaction between PLA and (Gluc-FA)/SDBS, as explained later, leading to smooth and uniform films.

Figure 5 shows the XRD patterns of the obtained films from which the crystallinity (χ_c) and the crystallite size (D_{200}) of PLA in the films were evaluated in a manner as described above. The χ_c value for the PLA composite film doped with 1 wt% (Gluc-FA)/SDBS increased up to 75.1% relative to 71.1% for the PLA film, but those for 2 and 5 wt% Gluc-FA/SDBS-doped films exhibited almost the same values as the latter film (Fig. 6). Gupta et al. [25] proposed that the PLA molecules would fold and crystallize in the 200 direction and estimated the crystallite size D_{200} as 22.3 nm. The D_{200} value

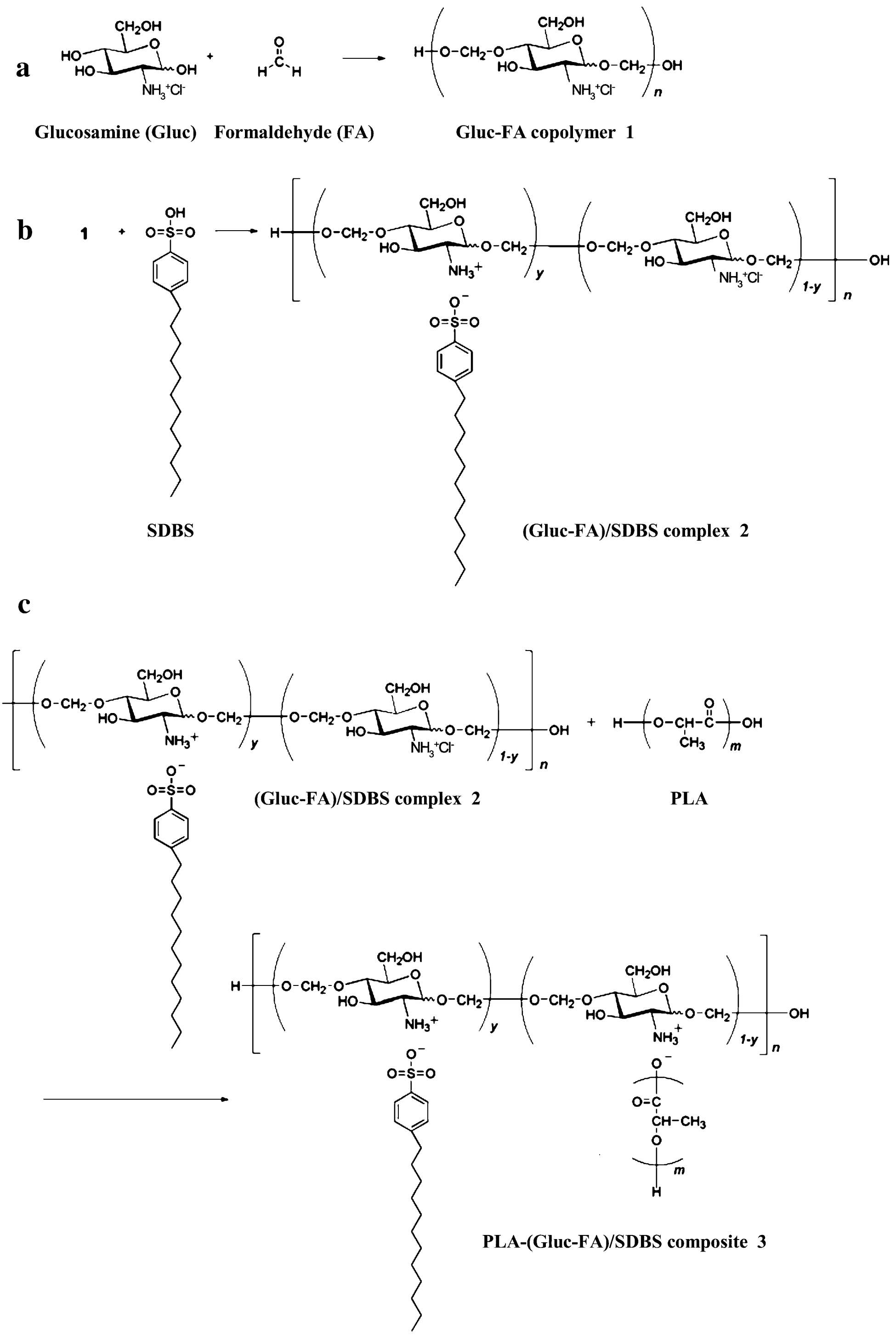


Fig. 2 **a** Formation of (Gluc-FA) copolymer **1** through the polymerization of glucosamine and formaldehyde, **b** formation of (Gluc-FA)/SDBS complexes **2**a–c through the polymerization of glucosamine and formaldehyde in the presence of SDBS, and **c** preparation of PLA-(Gluc-FA)/SDBS composite **3**. The parameters *n*, *y*, and *m* mean the degree of polymerization of (Gluc-FA) copolymer, the mole fraction of the NH_3^+ groups bound to SDBS in the repeating unit and the degree of polymerization of PLA, respectively

of 21.8 nm for the present PLA film is in close agreement with the reported value, whereas those for the composite films doped with 1, 2, and 5 wt% (Gluc-FA)/SDBS showed a marked increase to 33.3, 34.8, and 33.9 nm, respectively (Fig. 6). The significant increase of χ_c and/or D_{200} for the PLA-(Gluc-FA)/SDBS composite films relative to those for PLA film would be arisen from the ionic binding between the –COOH groups of PLA and the $-NH_3^+$ groups of (Gluc-FA)/SDBS and the crystal growth of PLA from the binding sites. The XRD pattern for PLA-5 wt% (Gluc-FA)/SDBS composite film also showed a weak shoulder band around d=3 nm, indicating that the SDBS micellar structures in the (Gluc-FA)/SDBS complex are essentially maintained after the casting treatment (Fig. 5, inset).

Figure 7 shows the stress–strain (SS) curves obtained by a tensile elongation test. It is of quite interest that the

Fig. 3 FTIR spectra of (**a**) Gluc, (**b**) SDBS, and (**c**–**e**) (Gluc-FA)/SDBS complexes obtained at the molar ratios (x) of SDBS to Gluc; (**c**) x=0.1, (**d**) x=0.5, and (**e**) x=1.0

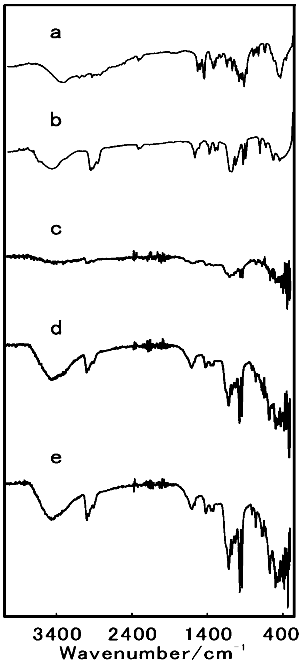
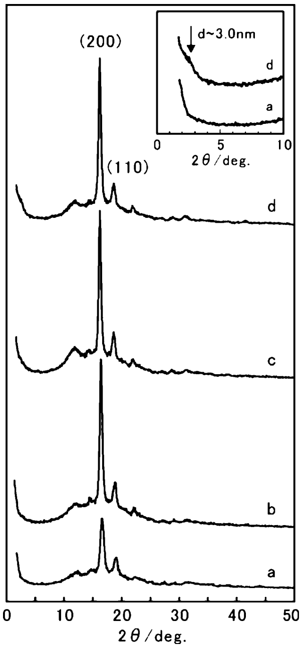


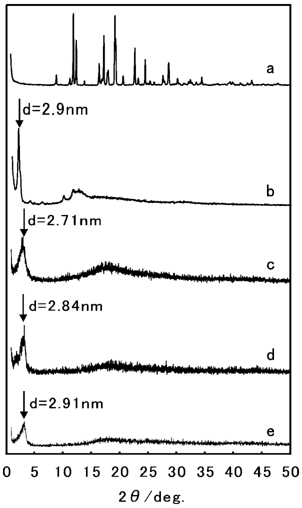
Fig. 5 XRD patterns of (**a**) PLA and (**b**–**d**) PLA-(Gluc-FA)/SDBS composite films: (Gluc-FA)/SDBS content; (**b**) 1 wt% (**c**) 2 wt% and (**d**) 5 wt%. The detail diffraction patterns at lower 2θ angles for (**a**) and (**d**) are shown in *inset*



elongation at break for the PLA-(Gluc-FA)/SDBS composite films doped with 1 and 2 wt% (Gluc-FA)/SDBS markedly increased to 194 and 54.9%, respectively, relative to 37.4% for the PLA film. Particularly, it is remarked that the use of as little as 1 wt% (Gluc-FA)/SDBS complex is highly effective, in marked contrast to a slight or negative effect observed for the composites with 2 wt% or more complexes. The energy required to break the film is estimated by the product of the stress (S) and the elongation (E). The fracture energy for the PLA-1 wt% (Gluc-FA)/SDBS composite film was evaluated to be 87.1 kJ/m^2, being 4.9 times larger than 17.9 kJ/m^2 for the PLA film.

It was thus first revealed that PLA can be considerably reinforced by forming the composite of PLA-(Gluc-FA)/SDBS, with an accompanying significant increase of χ_c and D_{200} of PLA crystallite, leading to improvement of the mechanical properties of PLA.

Fig. 4 XRD patterns of (**a**) Gluc-HCl, (**b**) SDBS, and (**c**–**e**) the (Gluc-FA)/SDBS complexes obtained at the molar ratios (x) of SDBS to Gluc; (**c**) x=0.1, (**d**) x=0.5, and (**e**) x=1.0



Discussion

Formation mechanism of (Gluc-FA)/SDBS complexes

Shirahama et al. [26] and another research group [27] proposed a cooperative binding mechanism of sodium decyl

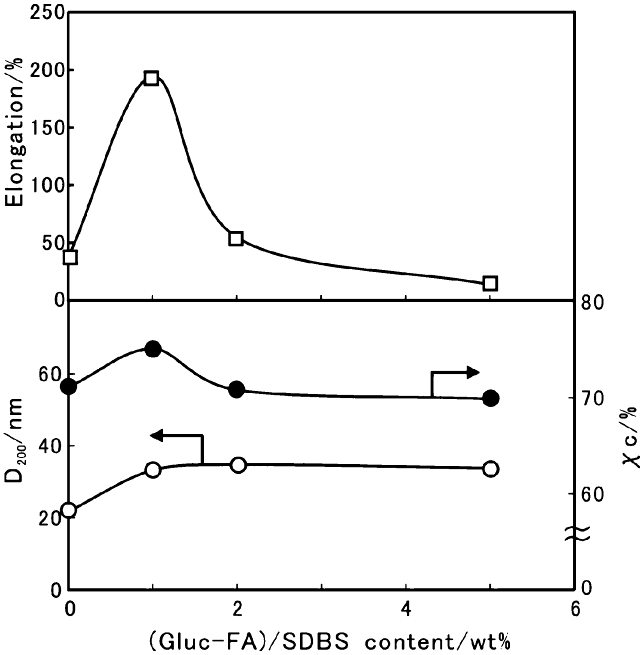


Fig. 6 Variation of the crystallite size along 200-axis, D_{200} (*open circle*), crystallinity, χ_c (*filled circle*), and elongation (*open square*) as a function of (Gluc-FA)/SDBS content for the PLA-(Gluc-FA)/SDBS composite films

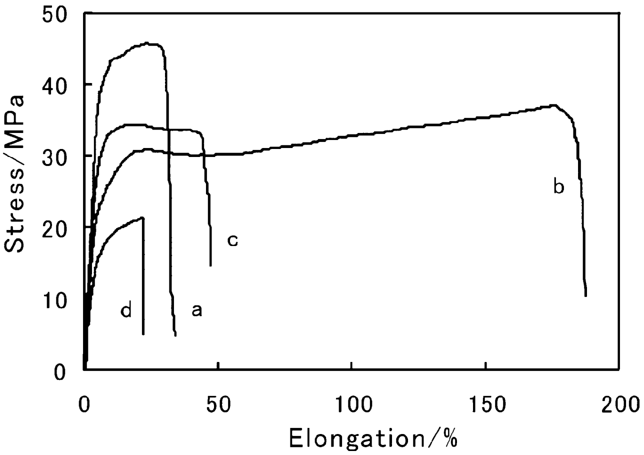


Fig. 7 Stress–strain curves of (**a**) PLA and (**b**–**d**) PLA-(Gluc-FA)/SDBS composite films. (Gluc-FA)/SDBS content, (**b**) 1 wt%, **c**) 2 wt%, and (**d**) 5 wt%

sulfonate onto a cationic poly(dimetyl-diallylammonium chloride). Similarly, the hydrothermal polycondensation reaction of Gluc and FA in the presence of the surfactant SDBS would proceed cooperatively with the ionic binding of the $-SO_3^-$ groups of SDBS to the $-NH_3^+$ groups of Gluc and the self-assembling micelle formation of SDBS molecules. It is also well known that the micelle formation of surfactants such as SDBS is promoted by the organization with the counter cations [28]. A similar effect would work for the formation of (Gluc-FA) copolymer/SDBS micelle complexes. Although the size of micellar blocks thus formed cannot be determined, the observed S/N atomic ratios (Table 1) indicate that 52–69% of the $-NH_3^+$ groups on the molecular chain of the (Gluc-FA) copolymer are bound to the $-SO_3^-$ groups of SDBS. In other words, the SDBS micellar blocks would be formed along more than half of the total length of the (Gluc-FA) polymer chain, as shown in Fig. 8a.

It is also noted that the $-SO_3^-$ groups of SDBS would react nonstoichiometrically with the $-NH_3^+$ ones of Gluc units, and the 31–48% of $-NH_3^+$ groups in Gluc-FA copolymer remain unbound to the $-SO_3^-$ groups of SDBS (Figs. 2b and 8a). This is probably because the reaction proceeds depending on the equilibrium between the reactants and their complexed products [26, 27] and/or the steric filling relation between the interdistance of $-NH_3^+$ groups in (Gluc-FA) polymer chain and the molecular size of SDBS [29].

Formation mechanism of PLA-(Gluc-FA)/SDBS composites

The (Gluc-FA)/SDBS complexes used as fillers in the present study have about one third of the $-NH_3^+$ groups remaining unbound, as described above, while the individual PLA molecule has one –COOH group as the end group. Previous studies reported that PLA molecules are bound to the $-NH_3^+$ groups in Chitosan or modified glucose [30–33]. In the present system, it is reasonable to assume that the –COOH groups of PLA are first attracted ionically to the $-NH_3^+$ groups in (Gluc-FA)/SDBS to form the PLA-filler primary structure at the stage of precrystallization, which would accelerate the crystallization of PLA molecules under the effect of the hydrophobic intermolecular interaction, as schematically shown in Fig. 8b. Furthermore, the SDBS micellar blocks in (Gluc-FA)/SDBS complex would serve to stabilize the PLA-filler primary structure, which is also expected to contribute to the crystallization of PLA molecules. However, the crystallization behavior of PLA in the composites is not so simple because the (Gluc-FA)/SDBS content dependence of χ_c is not the same as that of D_{200}, as described above.

Therefore, we examined the quantitative relationship between the –COOH and the remaining $-NH_3^+$ groups on the fillers. Since the number average molecular weight of the PLA used is 6.83×10^4, the content of –COOH end group, [–COOH], is given by $1/(6.83 \times 10^4)$ or 1.46×10^{-5} mol per gram of PLA. From the elemental analysis data for the (Gluc-FA)/SDBS complex (x=0.5) **2**b used as the filler, the molar weight of the repeating unit of the complex is 468.3, and the fraction of $-NH_3^+$ groups remaining unbound to SDBS in the repeating unit is 0.31. Hence, the content of $-NH_3^+$ group, $\left[-NH_3^+\right]$, amounts to 0.31/468.3 or 6.62×10^{-4} mol per gram of (Gluc-FA)/SDBS complex. Accordingly, if the weight fraction of (Gluc-FA)/SDBS in the PLA composite is taken as w_f, the contents [–COOH] and $\left[-NH_3^+\right]$ in the composites can be calculated in the unit of mol/g composite from Eqs. 2 and 3, respectively.

$$[-COOH] = 1.46 \times 10^{-5} \times (1 - w_f) \tag{2}$$

$$\left[-NH_3^+\right] = 6.62 \times 10^{-4} \times w_f \tag{3}$$

Based on the combination of Eqs. 2 and 3, $\left[-NH_3^+\right]/[-COOH]$ ratios for the w_f=1, 2 and 5 wt% composites were evaluated to be 0.46, 0.93, and 2.4, respectively. Considering the crystallization behavior of PLA in the composites, this calculated data mean that the doping of 1 wt% (Gluc-FA)/SDBS results in the binding of about one half of COOH groups of PLA matrix to the remaining $\left[-NH_3^+\right]$ groups in the (Gluc-FA)/SDBS complexes as the filler, which is favorable for the enhancement in crystallinity of PLA rather than that of all the COOH groups of PLA to them. In the w_f=2 and 5 wt% systems, the PLA-filler primary structure densely linked to the matrix polymer molecules would decrease the number of PLA crystallites or PLA crystallinity but make them grow to their ultimate size.

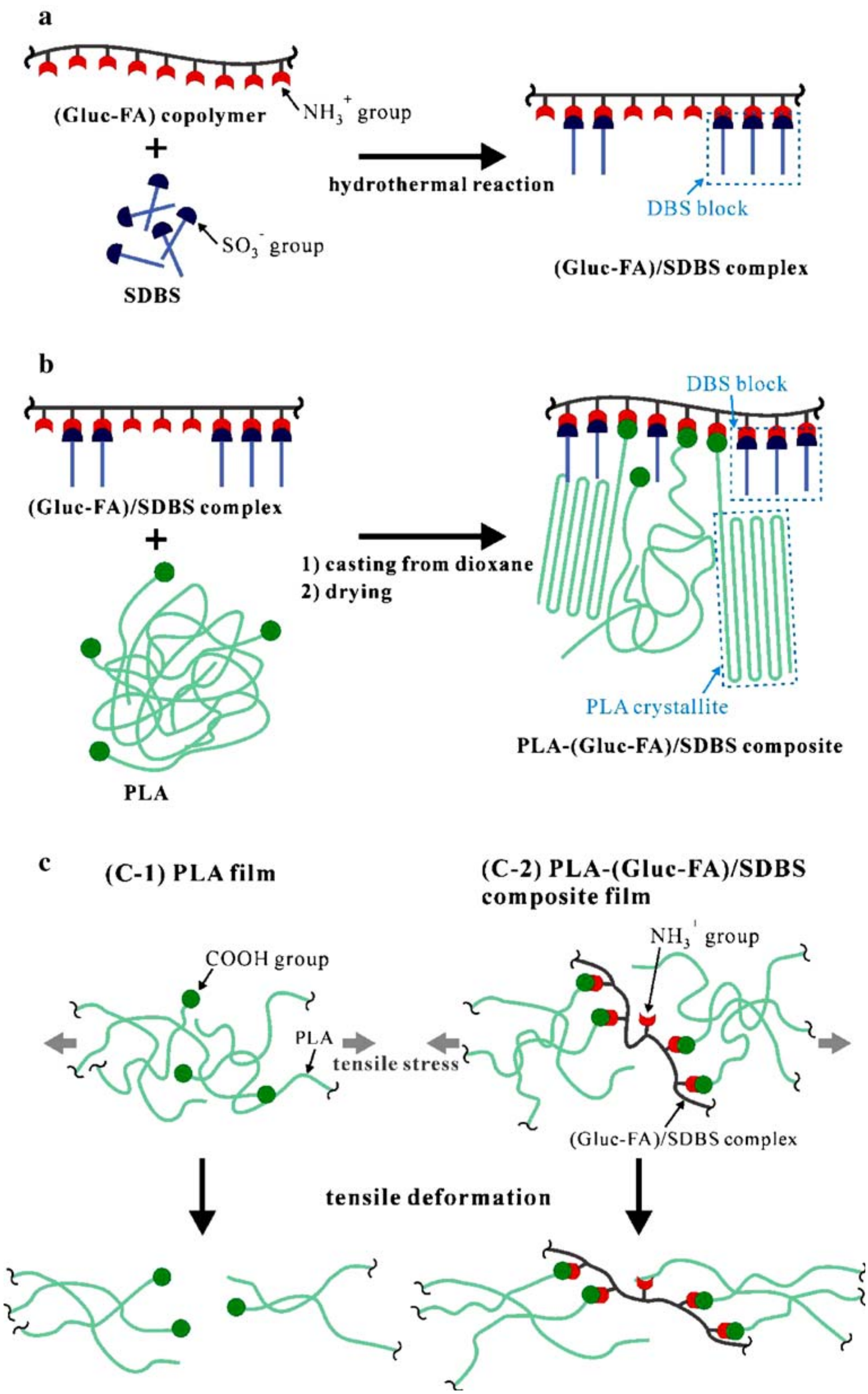


Fig. 8 Proposed formation mechanism of **a** (Gluc-FA)/SDBS and **b** PLA-(Gluc-FA)/SDBS composite and **c** deformation behavior of PLA molecules against tensile stress for PLA (C-1) and PLA-(Gluc-FA)/SDBS composite films (C-2). DBS block and PLA crystallite in **a** and/or **b** mean the DBS micellar block bound to the NH$_3^+$ groups and the PLA crystallite domain in the PLA-(Gluc-FA)/SDBS composite, respectively. The SDBS micellar blocks as well as PLA crystallites are omitted from the models in (C-2) to explain clearly the molecular behavior

Mechanical properties and deformation mechanism of PLA- (Gluc-FA)/SDBS composites

Chen et al. [34] reported that the stereo-complexation of the D- and L-isomers of PLA leads to the elongation at break of as large as 60.8%. On the other hand, the present PLA composite film doped with as little as 1 wt% (Gluc-FA)/SDBS showed a much larger elongation at break of 194%, in marked contrast to a slight or negative effect observed for the composites with 2 wt% or more fillers.

Moreover, the matrix crystallinity (χ_c) and elongation at break of the PLA composites exhibited quite similar behaviors depending on the filler content, including that their maximum values occur at the characteristic filler content of 1 wt% (Fig. 6). This finding suggests that the mechanical properties of the composite films might be improved by similar effects to those concerned with the matrix crystallinity.

In the PLA film subjected to tensile stress, the fracture of the film develops through the separation of PLA molecular chain ends, as usually observed for polymers [Fig. 8c (c-1)]. In the 1wt% (Gluc-FA)/SDBS-doped composite film, about one half of COOH groups of PLA matrix are bound to the remaining $\left[-\mathrm{NH}_3^+\right]$ groups in the fillers, as discussed above. The resulting PLA-filler primary structure can act as the cross-linking sites of PLA molecules, which would hamper the separation of PLA molecular chains and make them more easily unfolded and extended against the tensile stress, leading to the extremely high elongation of 194%, as schematically shown in Fig. 8c (c-2). In contrast to the bulk fillers such as silica nanoparticles, the (Gluc-FA)/SDBS complexes as molecular fillers can be easily deformed to additionally contribute to the film elongation. On further doping of the filler up to 2 wt%, almost all of COOH groups of PLA matrix are bound to the remaining $\left[-\mathrm{NH}_3^+\right]$ groups in the (Gluc-FA)/SDBS complexes. Consequently, the PLA molecules that can freely move or change their conformations would be greatly reduced in content, which suppress the deformation of the composite film, leading to the marked drop in elongation at break. The much lower elongation at break for the 5-wt% doping of the filler would be because the excess amount of the (Gluc-FA)/SDBS complexes added serves as structural defects to prohibit the entanglement of PLA molecular chains. It should thus be remarked that the (Gluc-FA)/SDBS complexes used as a novel nanofiller in the present study is quite different in their reinforcing mechanism for PLA from the conventional nanofillers such as $\mathrm{SiO_2}$ nanoparticles.

Conclusions

We demonstrated a new molecular-filler reinforcing approach to greatly improve the mechanical and structural properties of PLA film by only 1-wt% doping of (Gluc-FA)/SDBS complexes synthesized by the hydrothermal polymerization of Gluc and FA in the presence of SDBS. In PLA film, the chain end –COOH groups of PLA molecules act as a structural defect to initiate the breaking of film, and hence, to decrease the number of PLA molecular end groups would lead to the mechanical improvement. In the present approach, the use of as little as 1 wt% (Gluc-FA)/SDBS complex resulted in the remarkable mechanical improvement of PLA film. The outstanding reinforcing effect of this molecular filler is based on the linking of about one half of PLA molecules to the (Gluc-FA)/SDBS complexes through the ionic bonding between PLA chain end –COOH groups and the remaining $\left[-\mathrm{NH}_3^+\right]$ groups of Gluc units. In brief, the chain-end linking of not too much PLA molecules to the fillers caused a substantial decrease of the structural defects in the film and enabled the chain-end-linked PLA molecules in the amorphous domain to be more easily unfolded and extended against the tensile stress. The present concept could be also extended to the fabrication of filler-reinforced composite systems using various ionic polymers such as poly(butylene succinate), poly(hydroxy butylate), and other polyesters.

References

1. Kresge CT, Leonowiez ME, Roth WJ (1992) Nature 359:710
2. Yanagisawa T, Shimizu T, Kuroda K, Kato C (1990) Bull Chem Soc Jpn 63:988
3. Huo Q, Margolese DI, Ciesia U, Demuth DG, Freg P, Gier TE, Sieger P, Firouzi A, Chmelka BF, Schuth F, Stucky GD (1991) Nature 368:317
4. Yada M, Machida M, Kijima T (1996) Chem Commun 769
5. Yada M, Hiyoshi H, Ohe K, Machida M, Kijima T (1997) Inorg Chem 36:5565
6. Bagshaw SA, Pinnavaia TJ (1998) Angew Chem Int Ed 35:1102
7. Terns P, Hudson MJ, Denoyel R (1998) J Mater Chem 8:2147
8. Yada M, Ichinose A, Kitamura H, Machida M, Kijima T (1995) Angew Chem Int Ed 38:3506
9. Spahr ME, Bitterli P, Nesper R, Muller M, Krumeich F, Nissen HU (1998) Angew Chem Int Ed 37:1263
10. Harada M, Adachi M (2000) Adv Mater 12:839
11. Yada M, Mihara M, Mouri S, Kuroki M, Kijima T (2002) Adv Mater 14:309
12. Inagaki S, Guan S, Fukushima Y, Ohsuna T, Terasaki O (1999) J Am Chem Soc 121:9611
13. Inagaki S, Guan S, Fukushima Y, Ohsuna T, Terasaki O (2002) Nature 416:304
14. Moriguchi I, Ozono A, Mikuriya K, Teraoka Y, Kagawa S, Kodama M (1999) Chem Lett 1171
15. Uota N, Fujikawa D, Mohri S, Kuroki M, Kaikake K, Yada M, Machida M, Kijima T (2003) MRS Symp Proc 775:153
16. Kubat J, Rigdahl M, Welander M (1988) Colloid Polym Sci 266:509
17. Usuki A, Kojima Y, Okada A, Kurauchi T, Fukushima Y, Kamigaito O (1993) J Mater Res 8:1179
18. Park TW, Mark JE (2000) Colloid Polym Sci 278:655
19. Kondo Y, Someya K, Yamada N, Kijima T (2005) Nihon Reoroji Gakkaishi 33:273
20. Kijima T, Kondo Y, Yada M, Mihara M, Yamada N (2001) Proc 18th Intern Japan–Korea Semin on Ceramics 664
21. John G, Masuda M, Okada Y, Yase K, Shimizu T (2001) Adv Mater 13:715
22. Antonietti M, Neese M (1996) Langmuir 12:4436
23. Antonietti M, Goltner C (1997) Angew Chem Int Ed 36:910
24. Alexander LE (1973) Translated by Sakurada I, Hamada F, Kaji K (eds) Kobunsi no X-sen Kaisetsu, Kagaku Dojin, Tokyo
25. Gupta B, Revagade N, Anjum N, Atthoff B, Hilborn J (2006) J Appl Polym Sci 100:1239

26. Shirahama K, Yuasa H, Sugimoto S (1981) Bull Chem Soc Jpn 54:375
27. Rama-Rao GV, Konishi T, Ise N (2001) Polymer 42:6817
28. Hayakawa K, Shinohara S, Sasawaki S, Satake I, Kmak JCT (1995) Bull Chem Soc Jpn 68:2179
29. Chen Li, Yu S, Kagami Y, Gong J, Osada Y (1998) Macromolecules 31:787
30. Fujioka M, Nagashima A, Kenjo H, Sakurai K, Nishiyama S, Noguchi H, Ishii S, Yoshida Y (2005) Sen'i Gakkaishi 61:282
31. Nozaki T, Ishikawa A, Fujimoto I, Ohya Y (1997) J Polym Sci A Polym Chem 35:377
32. Ouchi T, Miyazaki H, Arimura H, Tasaka F, Hamada A, Ohya Y (2002) J Polym Sci A Polym Chem 40:1218
33. Ouchi T, Miyazaki H, Arimura H, Tasaka F, Hamada A, Ohya Y (2002) J Polym Sci A Polym Chem 40:1426
34. Chen CC, Chech JY, Tseng H, Hoang HM (2003) Biomaterials 24:1173