
Biopolymers for Environmental Applications: Highly Functional Poly(lactic Acid) Composites Used for Durable Products

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Abstract

Highly functional biomass-based plastics (bioplastics) based on renewable plant resources, advanced poly(lactic acid) (PLA) composites, have been developed for use in durable products such as electronic instruments. The PLA composites exhibit high practicability including good heat resistance, strength, and flame retardancy while fully preserving high biomass-based component ratio and chemical safety. They also possess desirable new properties such as good shape memory and thermal diffusivity for use in upcoming instruments. Moreover, a self-assembling siloxane nano-sized particle (nanoparticle) was developed to increase the tenacity of the PLA composites. Adding natural kenaf fiber increased heat resistance and elastic modulus of PLA, and using a PLA-polyester copolymer improved the impact strength of the PLA composite. High flame retardancy and other important characteristics including strength and moldability were successfully achieved by adding heat-absorbing aluminum hydroxide and a phenol novolac-type charring agent in PLA. Combinations of the shape memory and recyclability (thermoplasticity) were performed by cross-linking PLA using a thermoreversible bond for the use in wearable devices, which are deformable and recyclable. Also, a high thermal diffusivity comparable to that of stainless steel was achieved by including carbon fibers cross-linked by natural amide compound as a binding agent in PLA to improve heat release issues caused by small and thin electronic devices. Furthermore, self-assembling siloxane nanoparticles with three phases (high-density siloxane phase, elastomeric silicone phase, and caprolactone oligomer phase) increase the tenacity of PLA to advance the application of the PLA composites for thin-sized equipments.

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1 Introduction

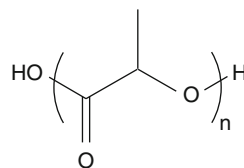
As an alternative to petroleum-based plastics, bioplastics using renewable plant resources such as starch and natural plant oil have distinct advantages, such as the ability to fix CO₂ gas that causes global warming and prevent depleting petroleum resources. Therefore, bioplastics are currently envisaged as a highly promising environment friendly material. Bioplastics can be classified into three basic types, according to how they are made: by chemical synthesis (polylactic acid, biomass-based polyamide and polyolefin, etc.), by microbial production (polyhydroxyalkanoate, etc.), and by natural processes (chemically modified starch and cellulose derivatives).

Polylactic acid (PLA) (Scheme 62.1) is a main bioplastic being massproduced by chemical synthesis using starch as raw material (Li et al. 2010). Due to the fact that it has a relatively high heat resistance, it is already being used for durable products such as electronic equipments and automobiles in addition to conventional products such as table ware, sealing, and fiber. However, before PLA can be used more widely in the durable products, material performance of PLA needs to be enhanced further. Thus, while fully preserving its environment friendly properties (high biomass-based component ratio and chemical safety), PLA's practicability has been improved, and also its values have been augmented by endowing it with desirable new properties. A highly heat-resistant PLA composite including natural kenaf fiber was developed. Flame retardancy of the composite was successfully achieved by using safe metal hydroxide to expand the use. New functional PLA composites were developed, offering new performance attributes including combination of shape memory and recyclability by thermoreversibly cross-linking PLA and high thermal diffusivity by containing cross-linked carbon fibers in PLA. Furthermore, high tenacity of PLA was achieved by using newly self-assembled siloxiane nano-sized particle with three functional layers as an advanced nanofiller.

The PLA composites consisting of PLA and these additives showing high functions are introduced as follows (Fig. 62.1).

2 Heat-Resistant PLA/Kenaf Composite

To enable PLA to be used for the housings of durable products including electronic equipments, it is necessary to significantly improve its heat resistance and strength characteristics. New PLA composite material, kenaf fiber-reinforced PLA



Scheme 62.1 Structure of polylactic acid (PLA)

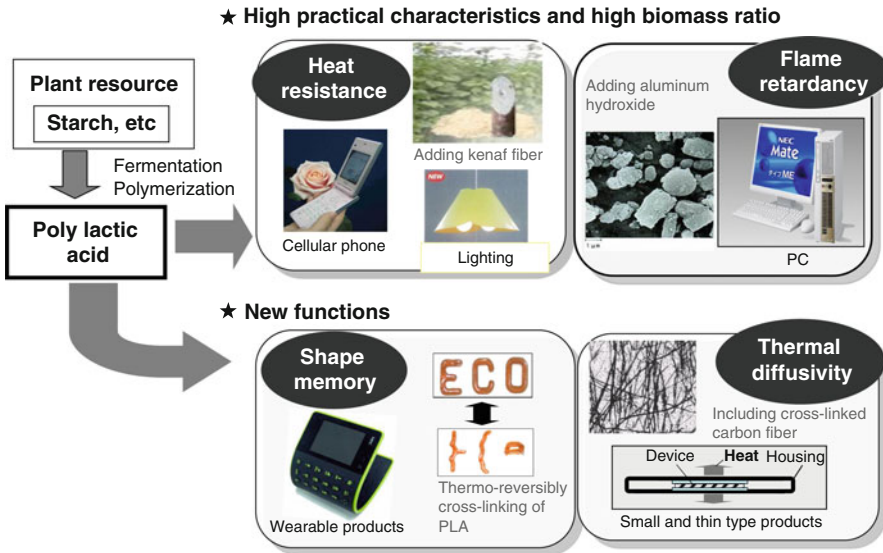


Fig. 62.1 Highly functionalized polylactic acid composites



Fig. 62.2 Kenaf, kenaf fiber, and molded PLA/kenaf composite

(PLA/kenaf composite), was developed to improve these characteristics (Fig. 62.2) (Serizawa et al. 2006). This material boasts extremely high biomass-based content (90% of resin content, excluding inorganic components) compared with current bioplastics for electronic equipments.

Kenaf is a plant originally grown in Africa, with one of the highest rates of CO₂ absorption of any plants (Lam et al. 2003). Its photosynthesis rate is three to nine times higher than ordinary plants, and it is capable of absorbing approximately 1.4 tons of CO₂ per ton of kenaf. It is thus a very effective plant in terms of global warming prevention. Kenaf is now being cultivated in Southeast Asia and many

Table 62.1 Characteristics of PLA/kenaf fiber composites

	PLA	PLA+ crushed kenaf			PLA+ cut kenaf	PLA+ flexibilizer	cut kenaf + flexibilizer	ABS resin
Fiber (wt%)	0	10	15	20	20	0	20	0
Flexibilizer (wt%)	0	0	0	0	0	20	20	0
HDT ^a (°C)	66	72	107	120	109	66	104	86
Flexural modulus (GPa)	4.5	5.4	6.3	7.6	7.1	4.0	6.8	2.1
Flexural strength (MPa)	132	111	110	93	115	106	72	70
Izod impact strength (kJ/m ²)	4.4	3.8	3.2	3.1	5.5	9.1	7.8	19

^aHeat distortion temperature (load: 1.8 MPa)

other countries around the world, mainly as a substitute for the existing materials for uses such as paper fiber and livestock feed.

The results of the tests conducted by kneading kenaf fiber (crushed kenaf, under 5 mm long) with PLA to enhance stiffness show that addition of 15% or more of the fiber results in better heat resistance (deformation temperature under load) and elastic modulus than that of the petroleum-based ABS resin (Table 62.1). This was not only from the fact that kenaf fiber inhibits the deformation of PLA but also by its ability to promote crystallization of PLA. Also, removal of kenaf particles (use of cut kenaf: 5 mm long) and addition of a biomass-based flexible agent (a PLA/polyester copolymer) to promote ductility resulted in the improved impact strength (see Table 62.1). The kenaf-PLA composite has been used in the housings of some electronic equipments such as cell phone and lighting devices.

3 Flame-Retardant PLA Composite

Plastics used for the housings of medium-sized and larger electronic equipments such as personal computers require a high degree of flame retardancy to prevent fire. Since PLA is quite easily flammable, its flame retardancy needs to be improved before it can be used for such applications. Conventional flame retardants such as halogen compounds are environmentally unsafe, and then, a flame-retardant PLA composite without using these substances was developed (Yanagisawa et al. 2009).

After investigating a variety of safe materials to enhance the flame-retarding ability of PLA, a formula that displays a high degree of flame retardancy (UL standard: 94 V-0/1.0mm) as well as other important and useful properties was successfully developed by the combination of specific metal hydroxide: aluminum

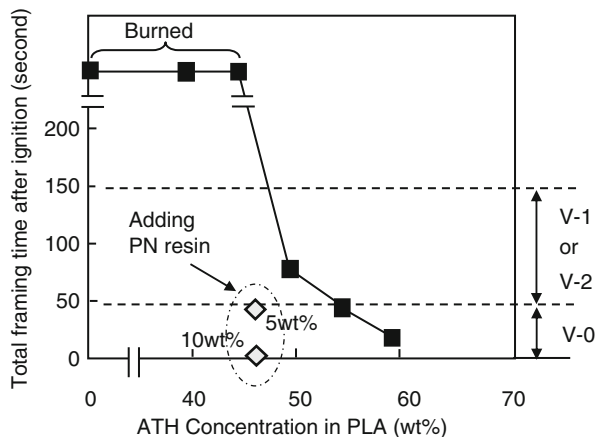


Fig. 62.3 Flame retardancy of PLA composites with aluminum trihydrate (*ATH*) and phenol novolac resin (*PN*) as charring agent

hydroxide, which is a soil component that acts as a heat-absorbing agent, and safe additives including a charring agent. A high level of flame-retarding ability was achieved by optimizing the composition of the formula by eliminating any substances that promote decomposition of PLA from the metal hydroxide and then combining a charring agent: phenol novolac resin (*PN*) that promotes carbonization of PLA (Fig. 62.3). Furthermore, combining other additives such as the above-mentioned flexible agent (PLA/polyester copolymer) greatly improved a variety of other important properties such as impacting strength and moldability (resin's fluidity in molding). Currently, the PLA composite has been used in the electronic equipments such as personal computers and projectors.

4 Recyclable Shape Memory PLA Composite

Shape memory plastics are plastics with the following ability. If they are deformed using heat and external force, then cooled and hardened, when they are heated again, they return to their original shape. Generally, this characteristic is seen in plastics having a cross-linked structure (mesh structure). Unfortunately though, due to their cross-linked structure, such plastics do not melt, even at high temperatures, so recycling them (remolding them in differently shaped metal molds) is difficult.

Needing to solve this problem, a technology to achieve thermoreversible cross-linking based on the Diels-Alder reaction (Engle and Wagner 1993; Chuijo et al. 1990) in the structure of PLA was developed, resulting in materials displaying a combination of shape memory and recyclability (Fig. 62.4) (Inoue et al. 2008, 2009). Thanks to this cross-linked structure, the material can be deformed and restored to its original shape by heating at a temperature of a hair dryer (approximately 60 °C),

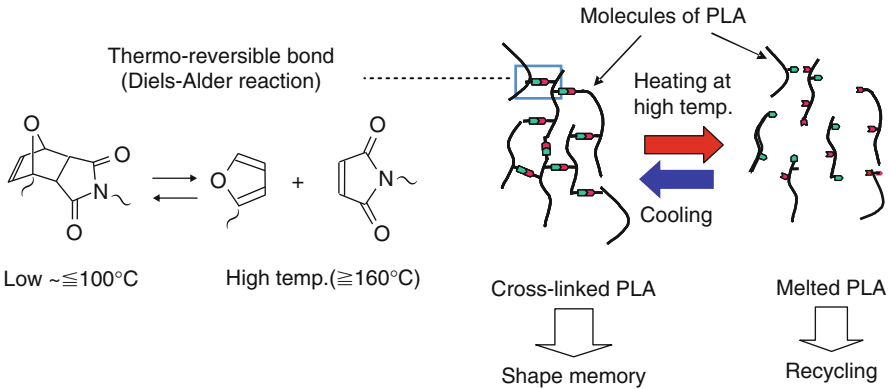


Fig. 62.4 Thermoreversibly cross-linked PLA composite

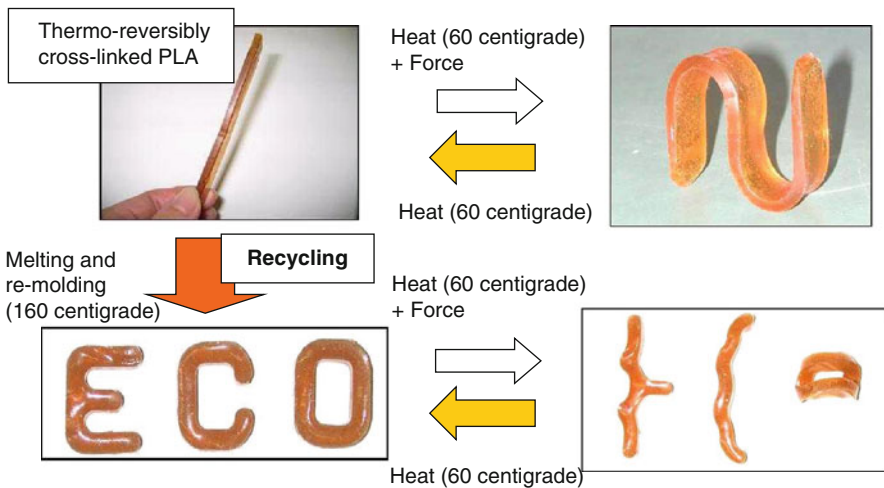


Fig. 62.5 Shape memory and recycling performed with thermoreversible cross-linked PLA composite

but if heated to a typical molding temperature (160°C), the cross-linked structure dissociates, causing the material to melt, thereby enabling easy recyclability (Fig. 62.5).

This recyclable shape memory PLA composite allows users to freely deform the material into any shape they like, making possible all kinds of new products and applications, like futuristic wearable electronic equipments for example Fig. 62.6.



Fig. 62.6 Wearable mobile equipments in future using shape memory PLA composite

5 Highly Thermal Diffusion PLA Composite

The rapid reduction of the size of electronic products is increasing the difficulty of dissipating the heat they produce. Because small and slim products such as the latest mobile phones and personal computers cannot easily be equipped with conventional cooling devices like fans and coolers, many of the plastic parts used in these products need to be able to conduct heat away from the electric parts. While adding conductive fillers such as metals oxides and carbon fibers to plastics increases their thermal diffusivity and thermal conductivity (Bigg 1995; Hill and Supancic 2002; Goyanes et al. 2001; Kumlutaş et al. 2003; Ishida and Rimdusit 1998), adding sufficiently large amounts of these fillers also increases the density of the plastics and reduces their mechanical strength and moldability.

A PLA composite which realizes thermal diffusivity higher than that of stainless steel was developed by including cross-linked carbon fibers in PLA (Nakamura and Iji 2009; Iji et al. 2011a, b). The material is expected to make electronic equipments more environmentally sound while improving conventional heat release issues. Creation of a cross-linked structure of carbon fibers (several millimeters long) through the use of a unique biomass-based binder, a natural amide compound (N,N' -ethylene bis-stearamide), in PLA achieves high heat diffusion (with carbon fiber of 10% and 30%, the heat diffusion ability of the PLA composite is comparable to and double that of stainless steel respectively) (Figs. 62.7 and 62.8). The gravities of the composites with carbon fibers are between 1.3 and 1.5, which are less than half the values comparing with the previous heat-conductive plastic composites containing high contents of heat-conductive fillers to perform the same heat diffusions.

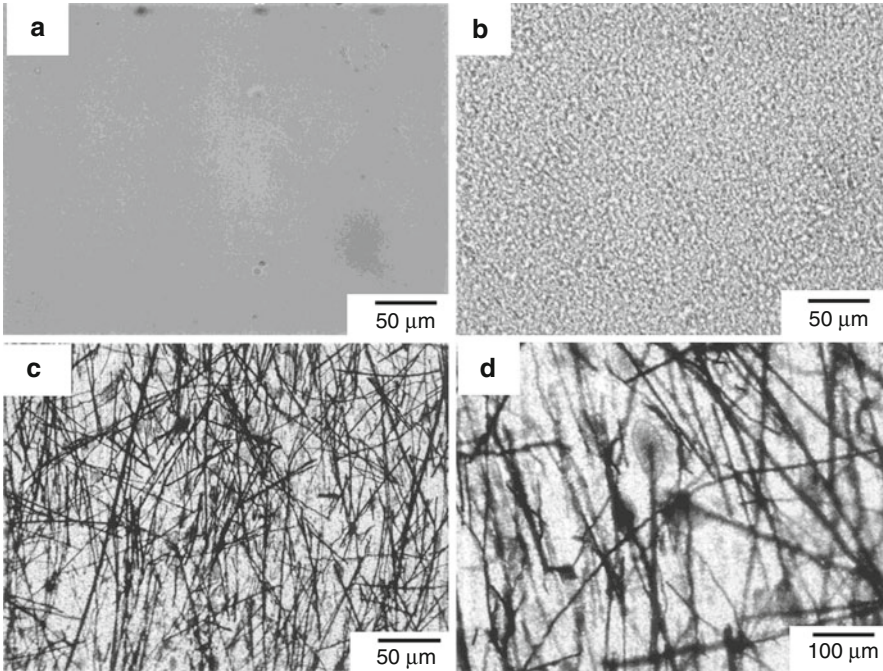


Fig. 62.7 Micrographs of PLA composites: (a) PLA, (b) PLA with 5 wt% of amide binder, (c,d) PLA with 10 wt% of carbon fiber (6 mm long) and 5 wt% of amide binder

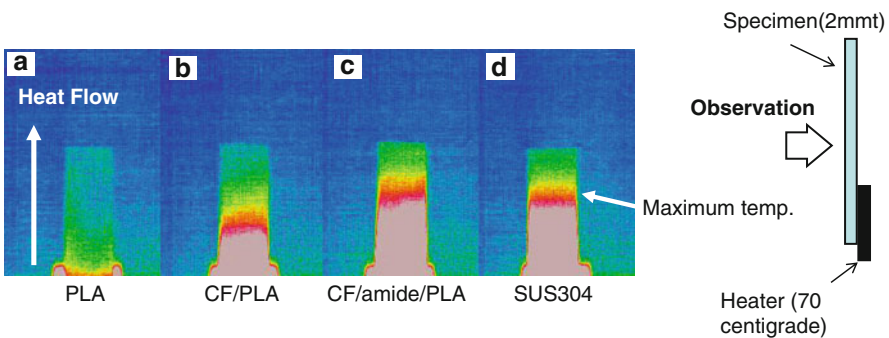


Fig. 62.8 Infrared thermography of PLA composite plates and stainless plate ($2.0 \times 7.0 \times 0.2$ cm): (a) PLA, (b) PLA with 10 wt% of carbon fiber (CF:6 mm long), (c) PLA with 10 wt% of CF and 5 wt% of amide binder, and (d) stainless steel

6 Self-assembling Nanoparticle Filler with Three Layers to Improve Tenacity of PLA

Inorganic nanometer-sized particles (nanoparticles) are attracting attention as reinforcing fillers for use in polymer-nanoparticle composites (procompromises) because they improve key characteristics of these composites at a relatively low content (Hussain et al. 2006; Jordan et al. 2005; Usuki et al. 2005; Rosso et al. 2006). However, currently available nanoparticles insufficiently improve the tenacity (elongation at breaking point while keeping maximum strength) of PLA, which is important if PLA is used in durable products. This is mainly because these nanoparticles lack rubberize elasticity and affinity for PLA matrix (Fig. 62.10: an example of silica nanoparticle).

A self-assembling siloxane nanoparticle (about 10 nm size) with three phases that improve the tenacity of PLA was developed. The particles consist of a high-density siloxane phase (plural cores), an elastomeric silicone phase (middle phase), and a caprolactone oligomer phase (outside phase) (Iji et al. 2011a). Self-assembly by aggregation and condensation of an organosiloxane with three units forms each phase in a solvent. The PLA nanocomposite with the particle was formed by mixing the particle and PLA in the solvent and removing the solvent (Fig. 62.9). Testing showed that the use of these nanoparticles greatly increases PLA's tenacity (Fig. 62.10). The mechanism of the improved tenacity due to the use of the three-phased nanoparticles is as follows. The nanoparticles maximize the strength because of their core rigidity and create the high breaking strain due to the rubberlike elasticity of the middle elastomeric phase and the plasticity of the outside phase with a high affinity with PLA.

The use of the nanoparticle will expand the use of PLA in durable product applications, especially thin-sized equipments and other new applications by increasing the toughness.

7 Summary

As detailed above, highly functional PLA composites have been developed as advanced bioplastics that offer high performance while keeping environmental friendliness for use in durable products including electronic equipments. PLA's practical properties including heat resistance and strength were improved by using biomass-based additives such as natural kenaf fiber, and its flame retardancy was increased by using a safe soil component: aluminum hydroxide. Furthermore, PLA's new functions, recyclable shape memory producing wearable electronic equipments and high thermal diffusivity, which solve the heat-release issues caused by the latest mobile electronic equipments, were achieved. Also, a self-assembling siloxane nanoparticle with three phases was developed, which increases the tenacity of PLA to advance the application in the thin-sized equipments. These technologies will contribute to expand the use of PLA to durable products.

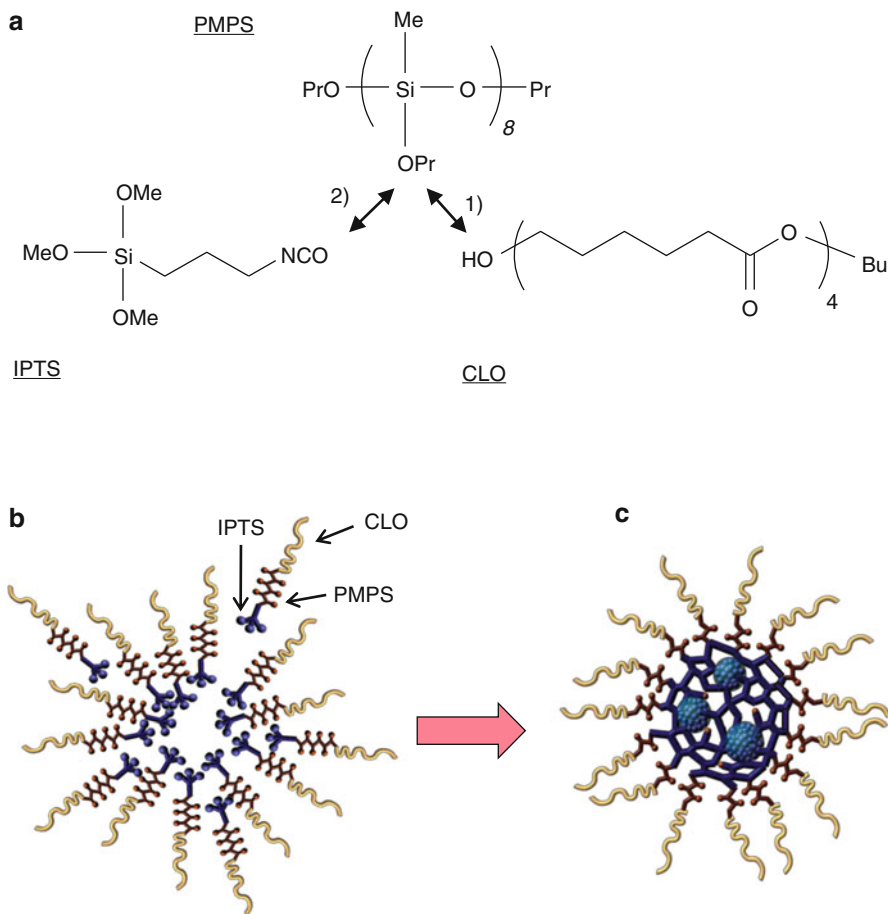


Fig. 62.9 Preparation of organosiloxane with three units (a) and self-assembly of three-phased nanoparticles through aggregation (b) and condensation (c) of organosiloxane. (*IPTS*: isocyanatepropyltrimethoxysilane, *PMPS*: polymethylpropyloxysiloxane, *CLO*: caprolactone oligomer)

The next subject of bioplastics is changing the resource from edible plant ingredients to inedible ones. PLA and current other major bioplastics use starch as the main resource, and starch is produced from plants that are generally edible. However, fears for future food shortages are driving an effort to use plant resources that are not edible. As inedible plant resources with stable supply, cellulose is the most likely candidate because it is the main component of most plants and the largest amount of nonfood plant resources produced in the ground. Cellulose is a polysaccharide like starch, but because of hydrogen bonding within and between its molecules, it forms a rigid crystalline structure, which is not suited to consumption as food and thus can be used as biomass resources. Therefore, research and development to convert cellulose to current bioplastics including PLA and new bioplastics are

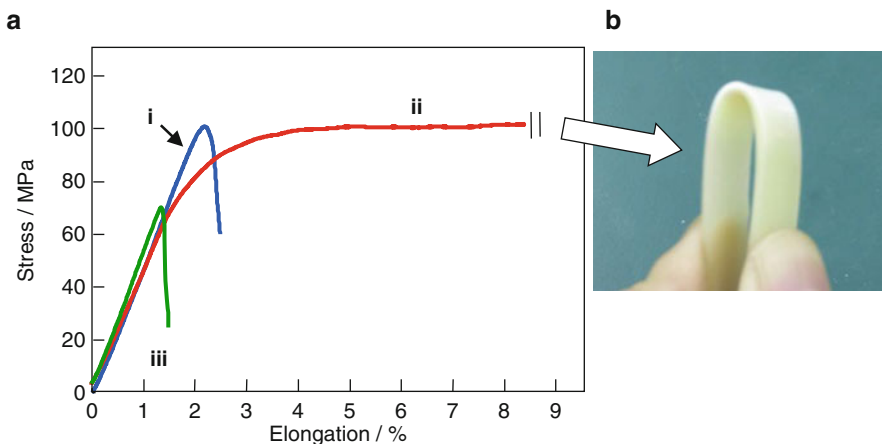


Fig. 62.10 (a) Flexural test of PLA nanocomposites containing nanoparticles (5 wt%): (i) PLA, (ii) PLA nanocomposite containing three-phased nanoparticle, (iii) PLA nanocomposite containing silica nanoparticle. (b) Test piece of PLA nanocomposite with three-phased nanoparticle after flexural test

required. For example, a new advanced cellulose-based resin has been studied, which is produced by bonding cellulose and a nonfood plant oil: cardanol derived from cashew nuts shell, an agricultural by-product (Iji et al. 2011b).

References

- D.M. Bigg, *Adv. Polym. Sci.* **119**, 1 (1995)
 Y. Chujyo, K. Sada, T. Saegusa, *Macromolecules* **23**, 2636 (1990)
 L.P. Engle, K.B. Wagner, *J.M.S.-Rev. Macromol. Chem. Phys.* **33**(3), 239 (1993)
 S.N. Goyanes, J.D. Marconi, P.G. König et al., *J. Polym.* **42**, 5267 (2001)
 R.F. Hill, P.H. Supancic, *J. Am. Ceram. Soc.* **85**, 851 (2002)
 F. Hussain, M. Hojjati, M. Okamoto et al., *J. Compos. Mater.* **40**, 1511 (2006)
 M. Iji, N. Morishita, H. Kai, *Polym. J.* **43**, 101 (2011a)
 M. Iji, S. Moon, S. Tanaka, *Polym. J.* **43**, 738 (2011b)
 K. Inoue, M. Yamashiro, M. Iji, *Polym. J.* **40**, 657 (2008)
 K. Inoue, M. Yamashiro, M. Iji, *J. Appl. Polym. Sci.* **112**(2), 876 (2009)
 H. Ishida, S. Rimdusit, *Thermochim. Acta* **320**, 177 (1998)
 J. Jordan, K.I. Jacob, R. Tannenbaum et al., *Mater. Sci. Eng. A* **393**, 1 (2005)
 D. Kumlutaş, İ.H. Tavman, M.T. Çoban, *Compos. Sci. Technol.* **63**, 113 (2003)
 T. Lam, K. Hori, K. Iiyama, *J. Wood Sci.* **49**, 255 (2003)
 S. Li, W. Ernst, P. Martin, *Biofuels Bioprod. Biorefining* **4**(1), 25 (2010)
 A. Nakamura, M. Iji, *J. Mater. Sci.* **44**, 4572 (2009)
 A. Nakamura, M. Iji, *J. Mater. Sci.* **46**, 747 (2011a)
 A. Nakamura, M. Iji, *J. Mater. Sci.* **46**, 1439 (2011b)
 P. Rosso, L. Ye, K. Friedrich et al., *J. Appl. Polym. Sci.* **100**, 1849 (2006)
 S. Serizawa, K. Inoue, M. Iji, *Appl. Polym. Sci.* **100**(1), 618 (2006)
 A. Usuki, N. Hasegawa, M. Kato, *Adv. Polym. Sci.* **179**, 135 (2005)
 T. Yanagisawa, Y. Kiuchi, M. Iji, *Koubunshi Ronbunshu* **66**(7), 49 (2009)