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Preparation, characterization and mechanical properties of the polylactide/perlite and the polylactide/montmorillonite composites

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Abstract In this study polylactide (PLA)/perlite and PLA/montmorillonite (MMT) composites were prepared by melt extrusion and solvent dissolution methods. The effects of organic/inorganic ratios and the kind of inorganic compounds on the characterization of the composite materials were investigated. The thermal stability of the organic–inorganic composite materials was evaluated by TGA and DSC, and the morphology of these composites was measured as SEM images. The modulus of elasticity was evaluated by Dynamic mechanical analysis (DMA). The PLA/inorganic composites exhibited remarkable improvement of mechanical and thermal properties when compared with those of the pure PLA.

Introduction

Polylactide (PLA) is a linear aliphatic thermoplastic polyester, produced by the ring-opening polymerization of lactides and lactic acid monomers, which are obtained from the fermentation of sugar feed stocks such as corn [1]. PLA is of increasing interests because PLA is biocompatible or biodegradable polyesters, which are benign to the environment [2–6].

PLA is currently used in a number of biomedical applications, such as sutures, dialysis media and drug delivery devices, however, it is also evaluated as a materials for tissue engineering. Being biodegradable it can also be employed in the preparation of bio-plastic for producing compost bags, food packaging and disposable tableware.

However, the strength and some other properties such as thermal stability, gas barrier, solvent resistance, and flame retardant nature are often not enough for end use.

Generally, to enhance the performance of the polymer, both chemical and physical methods can be applied. In chemical methods, the structure of the polymer is modified by adding functional groups to the backbone of the polymer, which improve the solubility or modify the band gap of the materials [7, 8]. Chemical techniques generally lead to good performance, however, the modification strongly depends on the step of the synthesis indicating the restriction for users. In physical methods, the properties such as stability of the materials can be improved by adding inorganic particles to the polymer [9].

On the other hand, PLA is not widely used because of its high cost compared to conventional plastics. To reduce the cost, it has been proposed to blend starch to PLA. However, the blends have rather poor mechanical properties due to the poor adhesion between starch and PLA [10–13]. Varying types of chemicals, such as citrate esters, have been added to plasticize PLA [14]. Although the cost can be reduced by such chemical methods, it is not easy to improve the quality of the polymer.

Therefore, physical methods is a popular method to enhance the performance of the polymer. For this decade, the field of polymer nanocomposites [15, 16] based on layered silicates, such as montmorillonite

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(MMT) [17, 18] or hectorite, has given rise to steadily increasing interests from scientists and industrials, as the nanoscale distribution of such high aspect ratio fillers produces some significant improvements in the polymer matrix in terms of the mechanical, fire retardant and optical properties [19].

On the other hand, perlite is a unique aluminosilicate volcanic mineral holding and retaining substantial amounts of water, which can be released as required. Expanded perlite is being used in many applications, particularly in the construction, horticulture and other various industrial fields. It is recommended as an efficient purifying agent and as a carrier for pesticides, feed concentrates, herbicides and other similar applications. It is also used as a solid support in solid-state fermentations [20].

There are few reports on the composite using perlite to enhance the properties of the polymer as organic–inorganic composite. Perlite has similar element compositions with that of the MMT. As shown in Table 1, the main constituent of perlite and MMT is SiO_2, so in this study PLA composites with MMT and perlite were prepared by melt extrusion method and solvent dissolution method and compared. The effects of the organic/inorganic ratios and the kinds of inorganic compounds on the characteristics of composite materials were investigated. The modulus of elasticity was evaluated by Dynamic mechanical analysis (DMA) and the thermal stability of the organic–inorganic composite materials was measured by TGA and DSC profiles. The morphology of these nanocomposites was investigated by SEM and XRD. The polymer composites mixed with the inorganic compounds exhibited a remarkable improvement in the mechanical and thermal properties when compared to the pure polymer.

Experimental

Materials

PLA was supplied by chemical company (M_n = 11,470, M_w = 13,160, I = 1.142). MMT, LDH and perlite were used as three inorganic compounds to prepare organic–inorganic composites in this study. MMT was provided by the Kunimine Co. Ltd. The unmodified MMT-Na has a cation exchange capacity of 119 meq/100 g at pH = 10. Perlite was supplied kindly by chemical company.

Preparation of composites

PLA/inorganic composites were prepared by two methods. One was the melt extrusion method and the other was solvent dissolution method.

Melt extrusion method

The composites were prepared via the melt-compounding of PLA with MMT or perlite at 240 °C in an intensive mixer that is counter-rotating mixer, Labo Plastomill, Model 30C150, Toyoseiki Co. Ltd. The rotor speed was set at 70 rpm and the total mixing time was 5 min. The total content of the inorganic compound was 10, 20, 40 or 50 wt%, respectively.

Solvent dissolution method

Two types of composites were prepared by solvent dissolution method. PLA in chloroform was mixed with the inorganic compound at room temperature for 24 h. The type 1 sample was obtained after the removal of chloroform by evaporation in air for 24 h. The type 2 sample was obtained by dropping methanol into the mixture, then filtered out the solvent and dried in the air for 24 h to remove chloroform.

Characterization

Thermal properties

The inorganic contents in the composites were determined by thermogravimetric analysis. The glass transition temperature (T_g), melting point (T_m) and cold crystallization temperature (T_c) as well as the melting enthalpy, ΔH, of PLA before and after the nanocomposite preparation were determined by differential scanning calorimetry (DSC) operating at the heating rate of 10 °C/min.

Table 1 The element contents of MMT and perlite

Elements (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	TiO_2	MnO
Montmorrilonite	57.96	21.87	1.92	0.54	2.98	3.44	0.14	Trace	Trace
Perlite	75.00	14.00	0.90	0.10	3.50		4.20		

X-ray diffraction (XRD)

The X-ray diffraction (XRD) measurements were performed for PLA and the composites using a RAD-RA diffractometer (RIGAKU Co. Ltd.). Ni-filtered CuKα radiation (λ = 0.154 nm) was utilized at 40 kV and 100 mA. The samples were scanned in the θ–2θ mode using a step-scanning method with a step-width of 0.05°and 4 s intervals in the range from 2θ = 2–50°.

Scanning electron microscope (SEM)

Morphology of the samples was investigated using a scanning electron microscope (JEOL JSM-6330F, SEM) equipped with EDS (JEOL Super Mini-cup, EDS). The images obtained were analyzed with a personal computer (JEOL JED-2140) with EDS-ZAF correction software.

Dynamic mechanical analysis (DMA)

The Dynamic mechanical analysis (DMA) measures the response of a given material to a cyclic deformation as a function of the warp and frequency. The DMA results are expressed by two main parameters: (a) the storage modulus (E') corresponding to the elastic response to the deformation; and (b) the loss modulus (E'') corresponding to the plastic response to the deformation.

Results and discussion

Morphological characterization

Morphological characterization of PLA/perlite and PLA/MMT composites obtained by melt extrusion method

The XRD patterns for PLA, MMT and the PLA/MMT composites were shown in Fig. 1. The contents of MMT in the PLA/MMT composites by melt extrusion method were 10, 20 and 50%. Peaks in the XRD patterns of the MMT and PLA/MMT composite were almost the same as 2θ = 7.5° nearby. It suggested no occurrence of intercalation reaction of PLA into MMT. The intercalation of PLA into the organic modified montmorillonite-Na was reported [19]. However, it is difficult to intercalate PLA into the unmodified MMT, because most of the polymers are hydrophobic. Furthermore, MMT layer was made up

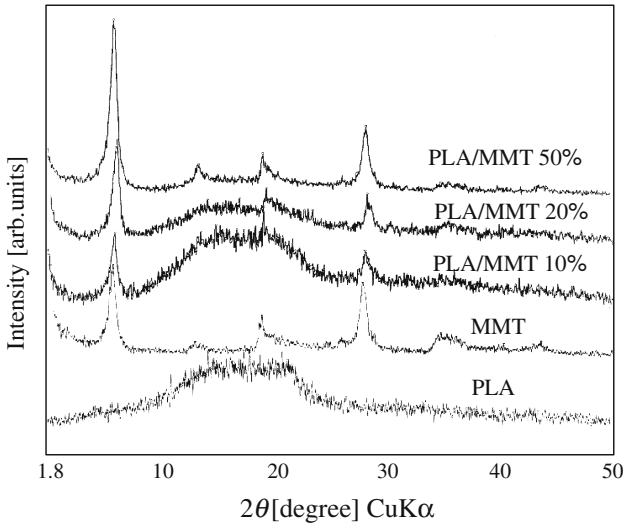

Fig. 1 XRD patterns of PLA, MMT and PLA/MMT composites with various contents of MMT prepared by melt extrusion method

of the stacking of alumina and silicate, which generate negative charge layers. So it is not easy to incorporate PLA into the interlayer space of MMT.

Contrary to the MMT, the Layered double hydroxide (LDH) hold the positive charge in the layers. LDH is well known inorganic layered compound that can intercalate anionic compounds [21–26]. In this study, PLA/LDH composite was also prepared to compare with the PLA/MMT and PLA/perlite composites. The interlayer distance of the LDH composite increased from 7.6 nm to 13.6–14.1 nm. The mechanism of the layer expansion has not been understood yet, however, the monomer and/or lower molecular weight polymer were intercalated into the interlayer space of the LDH.

The XRD patterns of PLA/MMT and PLA/perlite composites were compared with that of MMT. A new broad peak at around 2θ = 15° was observed in the PLA/MMT 10% and PLA/MMT 20%, which was assigned to the PLA. In the case of the PLA/perlite composites, the new broad peak was also observed as shown in Fig. 2.

The SEM images show that the surface of PLA/MMT was relatively flat as like as PLA, and the SEM image of the PLA/perlite by melt extrusion method show rugged surface as shown in Fig. 3. The fragments of perlite were dispersed in the PLA matrix.

Morphological characterization of PLA/perlite and PLA/MMT composite obtained by solvent dissolution method

In the XRD patterns of the PLA/perlite composites prepared by the solvent dissolution method, a new peak

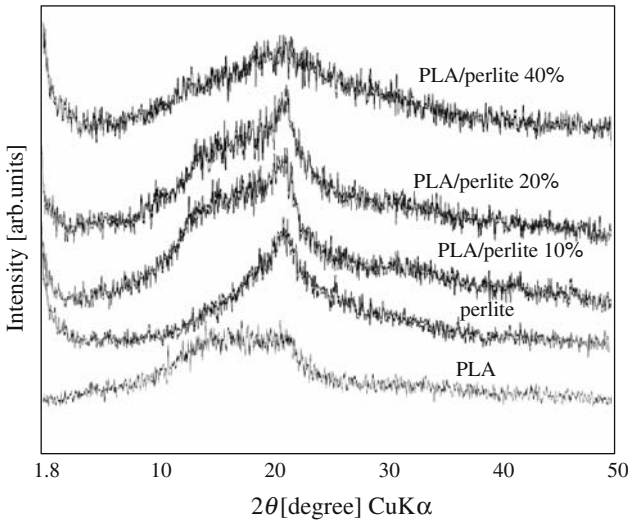

Fig. 2 XRD patterns of PLA, perlite and PLA/perlite composites with various contents of perlite prepared by melt extrusion method

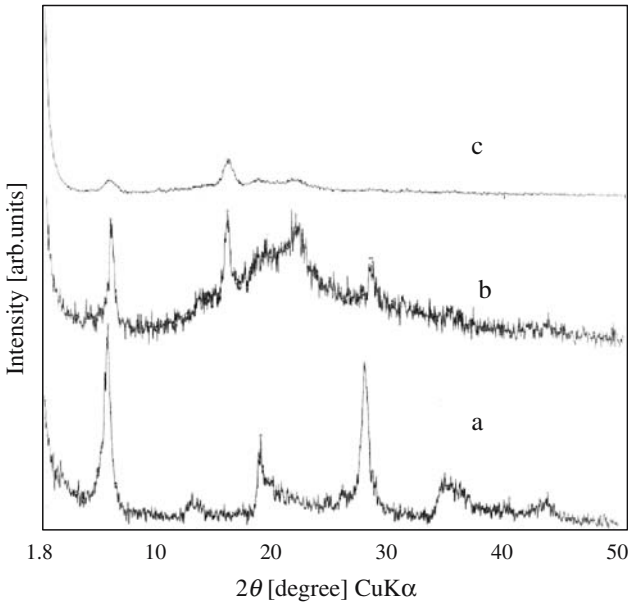

Fig. 4 XRD patterns of (**a**) MMT, (**b**) the type 1 of the PLA/MMT 10%, and (**c**) the type 2 of the PLA/MMT 10% prepared by solvent dissolution method

at around $2\theta = 16°$ was observed. The similar new peak was also observed in the PLA/MMT composite. XRD patterns of two types of samples were shown in Figs. 4 and 5. In type 2 sample, clear peaks were observed when compared with that of type 1 and inorganic compound. The SEM images of the PLA/MMT and PLA/perlite prepared by type 1 and type 2 of the solvent dissolution method were shown in Figs. 6 and 7, respectively. In Fig. 6(a) a relative flat surface was observed although the irregular porous surface was observed in Fig. 6(b). The SEM images of the type 2 of the PLA/perlite were the same with those of PLA/MMT composites. Figure 7(a) shows that the fragment of perlite was dispersed among the PLA matrix and rugged surface was observed. The irregular porous surface of PLA

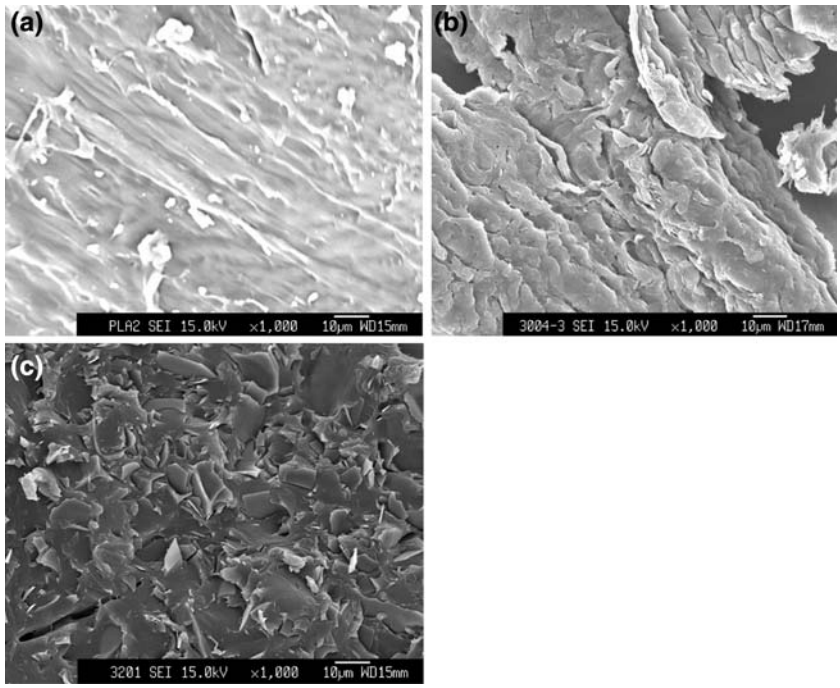

Fig. 3 SEM images of (**a**) PLA, (**b**) PLA/MMT and (**c**) PLA/perlite composites prepared by melt extrusion method

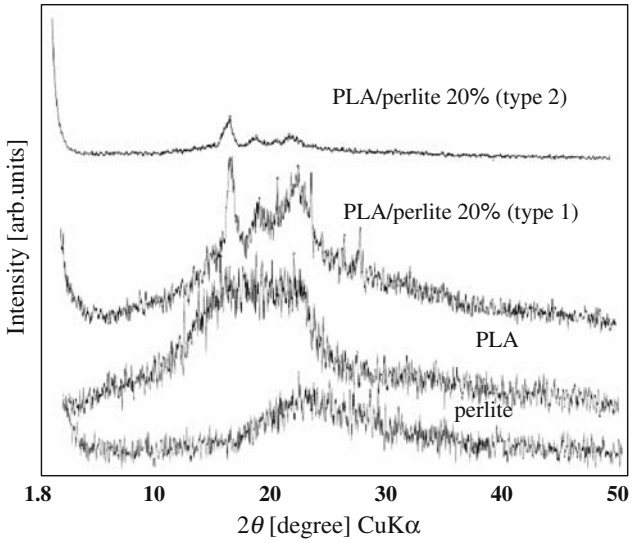

Fig. 5 XRD patterns of PLA, perlite and PLA/perlite composites with type 1 and type 2 prepared by the solvent dissolution method

which was stuck on the fragment of perlite was observed in Fig. 7(b). The difference between the type 1 and type 2 composites is considered that the PLA was separated

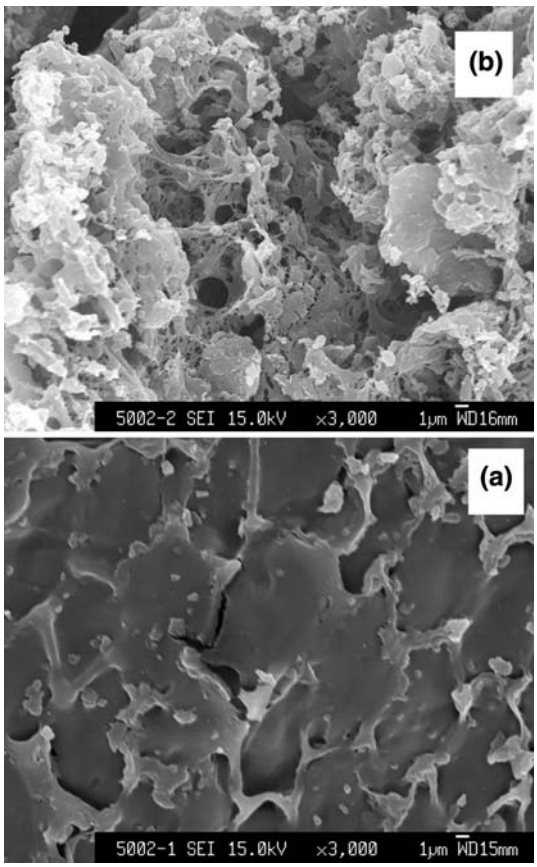

Fig. 6 SEM images of the PLA/MMT composites of (**a**) type 1 and (**b**) type 2 prepared by the solvent dissolution method

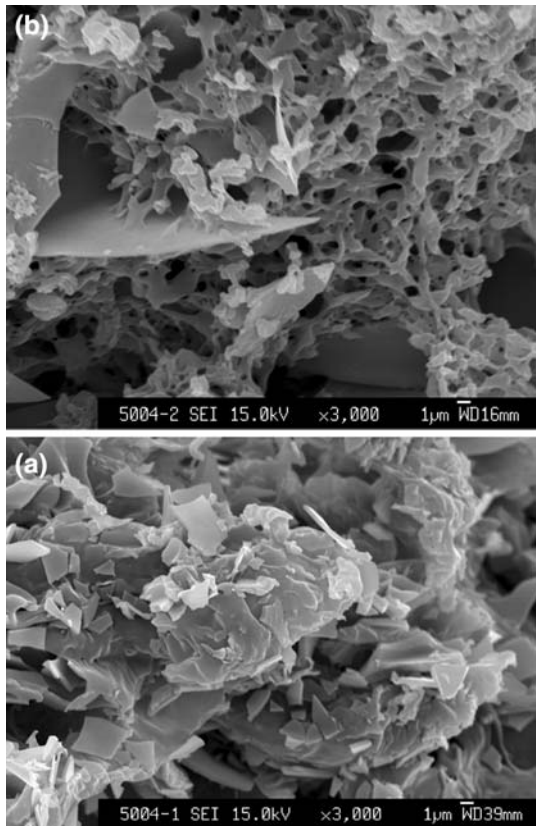

Fig. 7 SEM images of the PLA/perlite composites prepared by the solvent dissolution method (**a**) type 1 and (**b**) type 2

from the chloroform solution because the polarity of the solution changed by adding the methanol into the solution.

Thermogravimetric characterization

The DSC thermograms of the composites of the PLA with different inorganic compounds and different inorganic contents prepared by the melt extrusion and the solvent dissolution methods were measured. The melting enthalpy, ΔH, and the glass transition temperature (T_g) were calculated from the diagram of the DSC.

The ΔH of the composites prepared by two methods decreased with an increase in inorganic contents as shown in Fig. 8, and the DSC analysis show the ΔH of the PLA/MMT and PLA/perlite prepared by the melt extrusion method were obviously higher than those obtained by solvent dissolution method. It was considered that the binding force between the PLA and inorganic compound of the composite prepared by melt extrusion method was higher than that prepared by solvent dissolution method.

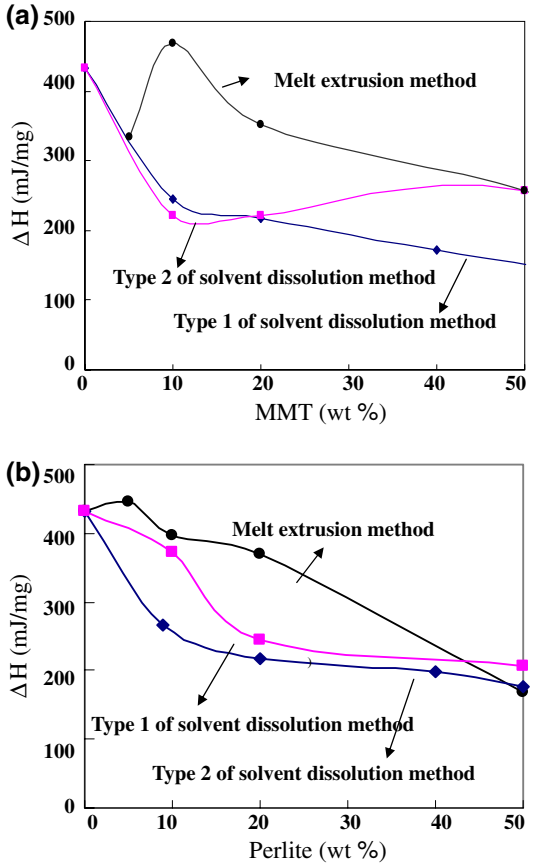

Fig. 8 The melting enthalpy, ΔH, of the (**a**) PLA/MMT and (**b**) PLA/perlite composites prepared by the melt extrusion and solvent dissolution methods

The effects of the inorganic contents and kinds of the inorganic compound on ΔH were shown in Fig. 9. In the composite prepared by solvent dissolution method, there were no difference between the PLA/MMT and PLA/perlite.

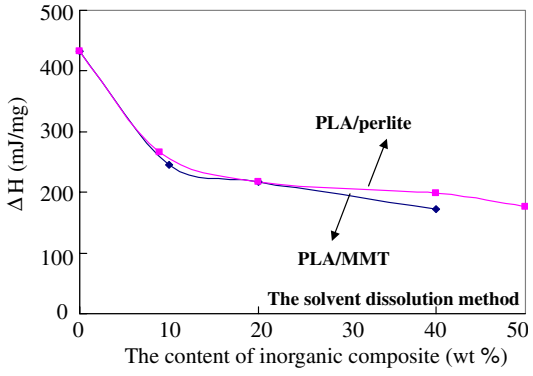

Fig. 9 The melting enthalpy, ΔH, of the PLA/MMT and PLA/perlite composites prepared by solvent dissolution method

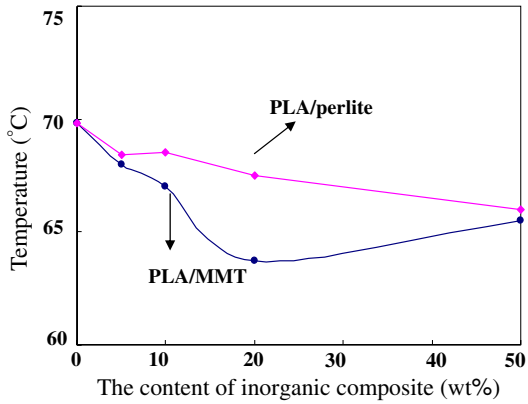

Fig. 10 The glass transition temperature (T_g) of the PLA/MMT and PLA/perlite composites prepared by the melt extrusion method

However, the glass transition temperature (T_g) of the PLA/MMT and PLA/perlite prepared by melt extrusion method decreased with an increase in inorganic content as shown in the Fig. 10. The T_g value of the PLA/perlite composite was higher than that of PLA/MMT composite.

Therefore, it was concluded that the mixed method, the inorganic contents and the kinds of inorganic compounds have the effects on the thermodynamics properties of the composites.

Dynamic mechanical characterization

Young's modulus, E^*, is expressed as $E' + i\,E''$. The real number section, $E' = E^* \times \cos$ delta, is called as storage modulus of elasticity, which indicates the hardness of the sample. The imaginary number section, $E'' = E^* \times \sin$ delta, is called as loss modulus of elasticity, which indicates the flexibility of the sample.

The effects of inorganic compound contents on storage modulus (E') and loss modulus (E'') were measured for neat PLA, PLA/MMT and PLA/perlite composites. They were prepared by melt extrusion method. The measurement conditions were $f = 100$, $r = 1.98$ μm and $f = 1$, $r = 100$ μm. The results are shown in Figs. 11 and 12. The E' and E'' increased with an increase in inorganic compound content. The E' and E'' of PLA/MMT and the PLA/perlite composites were higher than those of pure PLA. Therefore, it is considered that the modulus of the elasticity can be enhanced by adding the inorganic compounds. Compared to the PLA/MMT composite, the storage modulus of elasticity of the PLA/perlite was higher and the loss modulus of elasticity was lower than it.

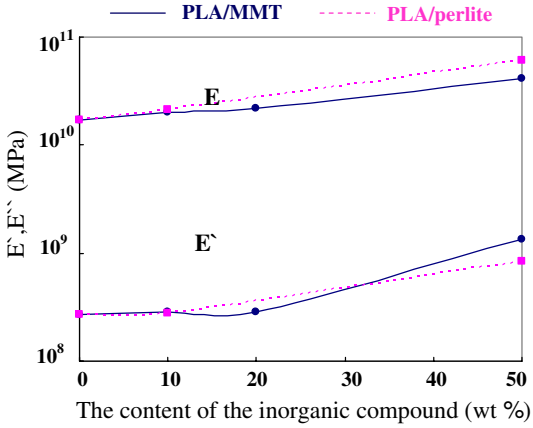

Fig. 11 The effects of inorganic contents on storage modulus (E') and loss modulus (E'') for neat PLA, MMT/PLA and perlite/PLA when frequency $f = 100$, $r = 1.98$ μm

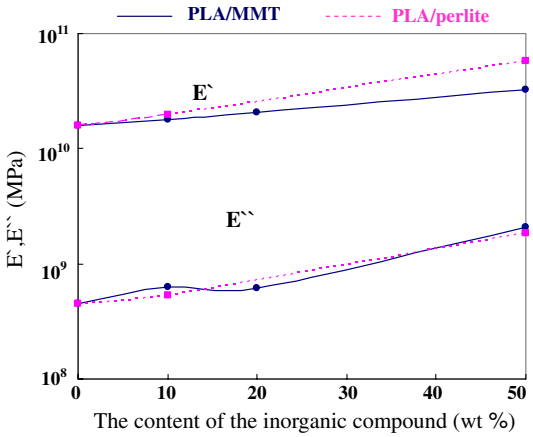

Fig. 12 The inorganic contents dependence of storage modulus (E') and loss modulus (E'') for neat PLA, MMT/PLA and perlite/PLA when warp $r = 100$ μm, $f = 1$

Conclusions

In this study, the PLA/MMT and PLA/perlite composites were prepared by the melt extrusion and the solvent dissolution methods. The morphological, thermogravimetric and Dynamic mechanical characterizations of the composites were measured. There was the clear effect of the mixing method on the morphology. The mixed method, the contents and kinds of inorganic compounds have the effect on the thermodynamics properties. The modulus of the elasticity can be enhanced by adding the inorganic compounds. The effect of perlite on E' and E'' was similar to the montmorillonite.

References

1. Lunt J (1998) Polymer Degrad Stabil 59:145
2. Grijpma DW, Pennings AJ (1994) Macromol Chem Phys 195:1649
3. Perego G, Cella GD, Bastioli C (1996) J Appl Polym Sci 59:37
4. Sinclair RG (1996) J Macromol Sci Pure Appl Chem A33:585
5. Tsuji H, Ikada Y (1998). J Appl Polym Sci 67:405
6. Martin O, Averous L (2001) Polymer 42:6209
7. Chung SJ, Kwon KY, Lee SW, Jin JI, Lee CH, Lee CE, Park Y (1998) Adv Mater 10:1112
8. Li AK, Yang SS, Jean WY, Hsu CS, Hsieh BR (2000) Chem Mater 12:2741
9. Neugebauer H, Brabec C, Hummenen JC, Sariciftci NS (2000) Solar Energy Mater Solar Cells 61:35
10. Mohanty AK, Misra M, Hinrichsen G (2000) Biofibres Macromol Mater Eng 276/277:1
11. Gerngross T, Slater SC (2006) Sci Am (August):24
12. Bogaert JC, Coszach P (2000) Macromol Symp 153:287
13. Eichhorn SJ, Baillie CA, Zafeiropoulos N, Mwaikambo LY, Ansell MP, Dufresne A (2001) J Mater Sci 36:2107
14. Herrmann AS, Nickel J, Riedel U (1998) Polymer Degrad Stabil 59:251
15. Giannelis EP, Krishnamoorti R, Manias E (1999) Adv Polym Sci 118:108
16. Alexandre M, Dubois P (2000) Mater Sci Eng 28(1/2):1
17. Ray SS, Maiti P, Okamoto M, Yamada K, Ueda K (2002) Macromolecules 35:3104
18. Pluta M, Galeski A, Alexandre M, Paul MA, Dubois P (2002) Appl Polym Sci 86:1497
19. Paul M, Alexandre M, Degée P, Henrist C, Rulmont A, Dubois P (2003) Polymer 44:443
20. Kerem Z, Hadar Y (1993) Appl Environ Microbiol 59:4115
21. Saber O, Tagaya H (2003) J Inclusion Phenom 45:109
22. Saber O, Tagaya H (2003) J Porous Mater 10:83
23. Saber O, Tagaya H (2005) J Inclusion Phenom 51:17
24. Tagaya H, Sato S, Morioka H, Kadokawa J, Karasu M, Chiba K (1993) Chem Mater 5:1431
25. Tagaya H, Sato S, Kuwahara T, Kadokawa J, Karasu M, Chiba K (1994) J Mater Chem 4:1907
26. Tagaya H, Ogata A, Kuwahara T, Ogata S, Karasu M, Kadokawa J, Chiba K (1996) Microporous Mater 7:151