

# Effect of modified calcium carbonate on the thermal and mechanical properties of biodegradable poly(L-lactic acid)\*)

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**Abstract:** Modified calcite  $\text{CaCO}_3$  (M- $\text{CaCO}_3$ ) was synthesized from calcium nitrate, sodium carbonate, ethylene diamine tetraacetic acid and sodium dodecyl sulfate. Then, poly(L-lactic acid) (PLLA)/M- $\text{CaCO}_3$  composites were fabricated using melt blending and hot-press forming technologies. The effect of M- $\text{CaCO}_3$  on the thermal and mechanical performance of PLLA was investigated. The results showed that the crystallization temperature and M- $\text{CaCO}_3$  content significantly affected the crystallization of PLLA but the effect of M- $\text{CaCO}_3$  on the crystallization of PLLA was very complicated. Compared to neat PLLA, 1 % M- $\text{CaCO}_3$  decreased the  $t_{1/2}$  from 3999.4 s to 342.7 s at 100 °C. The melt index measurements indicated that a small amount of M- $\text{CaCO}_3$  could block the fluidity of PLLA. However, the addition of a high content M- $\text{CaCO}_3$  increased the fluidity of PLLA. The results of tensile strengths and elongation at break of PLLA/M- $\text{CaCO}_3$  composites showed that both M- $\text{CaCO}_3$  content and defective modification  $\text{CaCO}_3$  affected the mechanical performance of the PLLA/M- $\text{CaCO}_3$  composites.

**Keywords:** poly(L-lactic acid), calcium carbonate, thermal behavior, mechanical performance.

## Wpływ modyfikowanego węgla wapnia na termiczne i mechaniczne właściwości biodegradowalnego poli(kwasu L-mlekowego)

**Streszczenie:** Z zastosowaniem azotanu wapnia, węgla sodu, kwasu etylenodiaminotetraoctowego i dodecylosiarczanu sodu syntezowano modyfikowany kalcyt (M- $\text{CaCO}_3$ ), a następnie mieszając składniki w stanie stopionym wytwarzano kompozyty poli(kwas L-mlekowy)/M- $\text{CaCO}_3$ . Badano zależność właściwości termicznych i mechanicznych wytworzonych kompozytów (z matrycą polilaktydową) od zawartości M- $\text{CaCO}_3$ . Wykazano, że istotny wpływ na krystalizację PLLA wywiera temperatura oraz zawartość modyfikowanego kalcytu. W temperaturze 100 °C czas połowicznej krystalizacji ( $t_{1/2}$ ) kompozytu z udziałem 1 % M- $\text{CaCO}_3$  znacznie się zmniejszył (342,7 s) w porównaniu do wartości  $t_{1/2}$  czystego PLLA (3999,4 s). Pomiar masowego wskaźnika szybkości płynięcia (MFR) dowodzi, że dodatek modyfikowanego kalcytu (powyżej 3 %) do matrycy polilaktydowej wpływa na zwiększenie wartości MFR. Wyniki wytrzymałości na rozciąganie i wydłużenia przy zerwaniu kompozytów PLLA/M- $\text{CaCO}_3$  wykazały, że zarówno zawartość węgla wapnia, jak i jego modyfikacja wpływają na wytrzymałość mechaniczną wytworzonych kompozytów PLLA/M- $\text{CaCO}_3$ .

**Słowa kluczowe:** poli(kwas L-mlekowy), węgiel wapnia, właściwości termiczne, właściwości mechaniczne.

Calcium carbonate ( $\text{CaCO}_3$ ), as a very crucial inorganic material, is one of the most widely added fillers to po-

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lymers because of its low cost and good performance [1]. Furthermore, greater scientific and technological attention has been paid to polymer/inorganic composites with low cost and good performance in recent years [2, 3], which significantly has promoted the development of the  $\text{CaCO}_3$  industry and also makes studies on  $\text{CaCO}_3$  a hot research field again. For example, to achieve the synthesis and morphological control of  $\text{CaCO}_3$  crystals with complex structures, Mao *et al.* [4] reported that vaterite  $\text{CaCO}_3$  with a flowerlike appearance was synthesized by a nanoparticle-mediated self-organization process and research further showed that the total carbonate content and the volume ratio of ethanol/double-distilled water

could significantly affect the polymorphs and morphologies of the  $\text{CaCO}_3$  crystals. Zebarjad *et al.* [5] investigated the effects of  $\text{CaCO}_3$  on the mechanical properties of polypropylene. The addition of  $\text{CaCO}_3$  decreased the yield strength of polypropylene while increasing modulus. Similarly, the effect of high-density polyethylene and  $\text{CaCO}_3$  on the crystallization of polypropylene has been reported [6]. This result indicated that  $\text{CaCO}_3$  was dispersed in the polypropylene and  $\text{CaCO}_3$  could improve the crystallization of polypropylene. However, the high-density polyethylene and polypropylene was phase separated in their blends.

Poly(L-lactic acid) (PLLA) as a typical biodegradable polymer material is paid more and more attention by scientists [7, 8]. Moreover, many excellent properties of materials based on PLLA have been obtained by utilizing advantageous technologies. To further improve the degradation rate of PLLA,  $\text{SiO}_2$  was introduced into PLLA to evaluate the hydrophilicity of PLLA/ $\text{SiO}_2$  nanocomposites. The experimental results indicated that  $\text{SiO}_2$  had a good dispersion in the PLLA matrix and that the hydrolytic degradation of PLLA was accelerated with an increased content of  $\text{SiO}_2$ . At the same time, the addition of  $\text{SiO}_2$  can promote the microstructure reorganization of PLLA [9]. Liang *et al.* investigated the tensile properties of PLLA/PCL/nano- $\text{CaCO}_3$  composites at different tensile rates, and the tensile rates affected slightly the tensile elastic modulus and tensile strength [10]. Besides, the results showed that PCL could improve the tensile fracture toughness of the composites [10]. Graphene oxide grafted with PLLA was added into PLLA matrices as a promising reinforcement. Measurements showed that the dispersion of graphene oxide and interfacial interactions between PLLA and graphene oxide were enhanced because of the functionalization of graphene oxide. Furthermore, compared to neat PLLA, the flexural and tensile strength of PLLA/graphene oxide grafted with PLLA materials were increased by 114.3 % and 105.7 % [11]. However, to the best of our knowledge, it is still a major challenge to improve the thermal and mechanical performance of PLLA for wider applications.

In this paper, to further reinforce the thermal and mechanical performance of PLLA,  $\text{CaCO}_3$  modified by EDTA and SDS (M- $\text{CaCO}_3$ ) was first synthesized, then PLLA/M- $\text{CaCO}_3$  composites were prepared by a simple melt blending method, and the thermal and mechanical performance of PLLA/M- $\text{CaCO}_3$  composites were evaluated by a comparative study.

## EXPERIMENTAL PART

### Materials

Poly(L-lactic acid) (2002D) was purchased from Nature Works LLC (USA). Calcium nitrate and sodium

dodecyl sulfate (SDS) were purchased from Mianyang Rongshen Chemical Reagents Company (Sichuan Province, China), ethylene diamine tetraacetic acid (EDTA) and sodium carbonate were purchased from Beijing Chemical Reagents Company (Beijing, China).

### Synthesis of M- $\text{CaCO}_3$

EDTA (0.001 mol) and SDS (0.001 mol) were added into 100 cm<sup>3</sup> the calcium nitrate solution [0.1 mol/dm<sup>3</sup>  $\text{Ca}(\text{NO}_3)_2$ ]. Then, the mixture was heated (80 °C) to make EDTA and SDS dissolve with stirring. Then sodium carbonate solution (0.1 mol/dm<sup>3</sup>  $\text{Na}_2\text{CO}_3$ , 200 cm<sup>3</sup>) was added slowly (dropwise add) into the mixture solution, the white precipitate was obtained after 1h (this is the time to complete the reaction after the addition of the  $\text{Na}_2\text{CO}_3$ ), and the obtained precipitate was washed four times by water and then four times by 99.7 % ethanol at room temperature. The resulting product M- $\text{CaCO}_3$  was dried in vacuum at 80 °C for 24 h.

### Preparation of PLLA/M- $\text{CaCO}_3$ composites

PLLA and M- $\text{CaCO}_3$  were dried before blending and the blending process of PLLA and M- $\text{CaCO}_3$  was similar to that performed in our previous paper [12].

### Methods of testing

#### Wide angle X-ray diffraction (WAXD)

WAXD experiments were performed on a diffractometer (D/MAX2550, Rigaku, Japan) using  $\text{Cu K}_\alpha$  radiation (wavelength, 1.54 Å) at room temperature in the range of  $2\theta = 5\text{--}80^\circ$  with a scanning rate of 2°/min.

#### Isothermal crystallization measurement

The isothermal crystallization of PLLA/M- $\text{CaCO}_3$  composites were investigated on a GJY-III optical depolarizer (Donghuang university, China) in the region from 100 °C to 120 °C. The values were directly measured by optical depolarizer.

#### Thermogravimetric analysis (TGA)

TGA measurements of M- $\text{CaCO}_3$  were carried out using thermal analysis Q500 from TA Instruments-Waters LLC with a heating rate of 10 °C/min under air flow of 50 cm<sup>3</sup>/min from room temperature to 950 °C.

#### Melt index

The fluidity of melting PLLA/M- $\text{CaCO}_3$  composites was measured by a melt index instrument (Beijing Guance Testing Instrument Co., LTD, China), the measurement temperature was 180 °C and load 10 kg.

### Mechanical performance testing

Normal tensile tests were conducted on a M-4010 electronic tensile tester (Shenzhen Reger Instrument Co., LTD, China) at the speed of 50 mm/min at room temperature. The tensile strength and elongations at break were obtained by averaging over four specimens.

## RESULTS AND DISCUSSION

### Structure of M-CaCO<sub>3</sub>

The structure of M-CaCO<sub>3</sub> was investigated by WAXD. As shown in Fig. 1, the M-CaCO<sub>3</sub> exhibits a strong, characteristic diffraction peak at  $2\theta = 29.5^\circ$  due to diffraction from (104) plane and other peaks at  $2\theta = 23.1^\circ$ ,  $35.9^\circ$ ,  $43.2^\circ$  and  $48.6^\circ$  occurring from the (012) plane, (110) plane, (202) plane and (116) plane, respectively [13]. The appearance of these relevant characteristic peaks confirms that the crystal phase of M-CaCO<sub>3</sub> is calcite CaCO<sub>3</sub>.

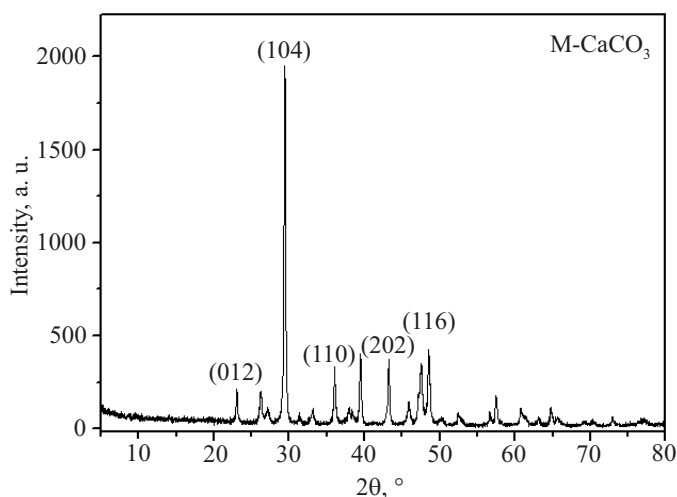


Fig. 1. WAXD analysis of M-CaCO<sub>3</sub>

The thermal properties of M-CaCO<sub>3</sub> were also investigated using TGA. Figure 2 shows the TGA curve of M-CaCO<sub>3</sub> at a heating rate of 10 °C/min under air flow, it is clear that the mass loss is about 3 % at 600 °C, resulting from the combustion of organic materials on the surface of M-CaCO<sub>3</sub> under air flow. Then, M-CaCO<sub>3</sub> begins to decompose at higher temperatures and the onset decomposition temperature ( $T_0$ ) of M-CaCO<sub>3</sub> is 712.1 °C, which indicated that the decomposition temperature of M-CaCO<sub>3</sub> is lower than that of ultra-fine CaCO<sub>3</sub> synthesized using a solid-state reaction at supersonic speed airflow [14], the possible reason is that the addition of EDTA and SDS makes the crystal of synthesized CaCO<sub>3</sub> imperfect. However, this imperfect structure of M-CaCO<sub>3</sub> may result in a larger specific area that can improve the performance of the polymer [15]. The final mass loss was 46.2 %, inclu-

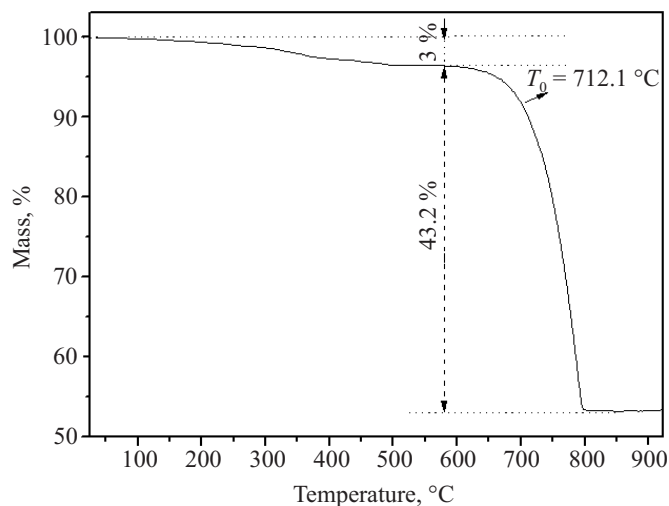


Fig. 2. TGA curve of M-CaCO<sub>3</sub>

ding organic materials, and the remaining product was calcium oxide.

### Isothermal crystallization of PLLA/M-CaCO<sub>3</sub> composites

CaCO<sub>3</sub> is an important additive of polymers. The addition of CaCO<sub>3</sub> can significantly reduce the cost and improve the performance of polymer matrices, particularly the thermal performance [16, 17]. Thus, the isothermal crystallization behavior of PLLA/M-CaCO<sub>3</sub> composites was investigated with an optical depolarizer. Figure 3 shows the effect of crystallization temperature and M-CaCO<sub>3</sub> content on the crystallization of PLLA. With increasing crystallization temperature, the half-time of overall crystallization ( $t_{1/2}$ ) of neat PLLA becomes shorter, and the  $t_{1/2}$  has a minimum value of 2359.9 s at 115 °C. Then, the  $t_{1/2}$  of neat PLLA becomes longer at higher crystallization temperatures. In contrast, higher crystalliza-

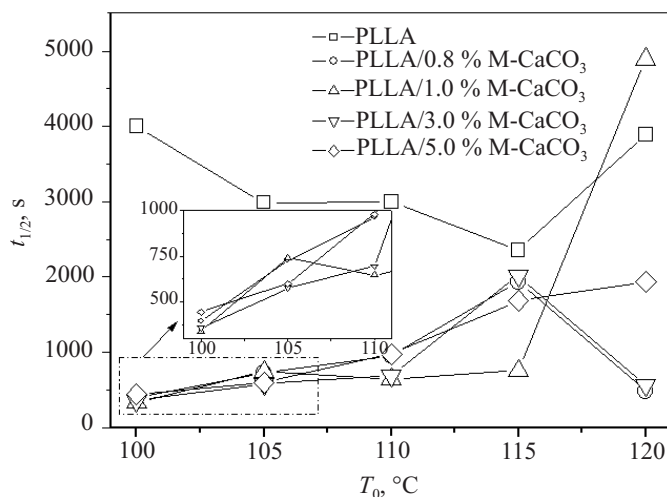


Fig. 3. The effect of M-CaCO<sub>3</sub> content on the crystallization temperature and half-time of overall crystallization of PLLA

tion temperatures do not make the  $t_{1/2}$  of PLLA/M-CaCO<sub>3</sub> composites shorter. Generally, the  $t_{1/2}$  of PLLA/M-CaCO<sub>3</sub> composites in the low crystallization zone is smaller than that in the high crystallization zone. That is to say, there exists a minimum  $t_{1/2}$  of PLLA/M-CaCO<sub>3</sub> composites at 100 °C. Compared to neat PLLA, 1 % M-CaCO<sub>3</sub> can decrease the  $t_{1/2}$  from 3999.4 s to 342.7 s at 100 °C. It is clear from Fig. 3 that the M-CaCO<sub>3</sub> content also affects the crystallization of PLLA, the  $t_{1/2}$  significantly becomes shorter after addition of M-CaCO<sub>3</sub>, which indicates that M-CaCO<sub>3</sub> as nucleating agent could improve the crystallization of PLLA, and increase the crystallization rate of PLLA. The  $t_{1/2}$  of PLLA with high M-CaCO<sub>3</sub> content is shorter than that of PLLA with low M-CaCO<sub>3</sub> content. However, 1 % M-CaCO<sub>3</sub> gives the minimum  $t_{1/2}$  at 100 °C. The possible reason is that 100 °C can improve the formation of nuclei although 1 % M-CaCO<sub>3</sub> as nucleating agent can significantly increase the crystallization rate of PLLA. However, 1 % M-CaCO<sub>3</sub> does not hinder the movement of PLLA molecular chains. The isothermal crystallization results indicate that the effect of M-CaCO<sub>3</sub> on the crystallization of PLLA is very complicated.

#### Melt index and mechanical performance of PLLA/M-CaCO<sub>3</sub> composites

The addition of functional additives can affect the fluidity of polymers [18]. Thus, the melt index was investigated, using a melt index instrument, as an important parameter of fluidity of the polymer. As shown in Fig. 4, the melt mass flow rate (MFR) is lowered with increased M-CaCO<sub>3</sub> content, and with 1 % M-CaCO<sub>3</sub> there is a minimum of value 0.912 g/10 min of PLLA/M-CaCO<sub>3</sub> composites. Then, the MFR begins to increase with larger amounts of M-CaCO<sub>3</sub>. These results indicate that a small amount of M-CaCO<sub>3</sub> can block the fluidity of PLLA. However, the addition of a high content M-CaCO<sub>3</sub> can increase the fluidity of PLLA. The possible reason of this

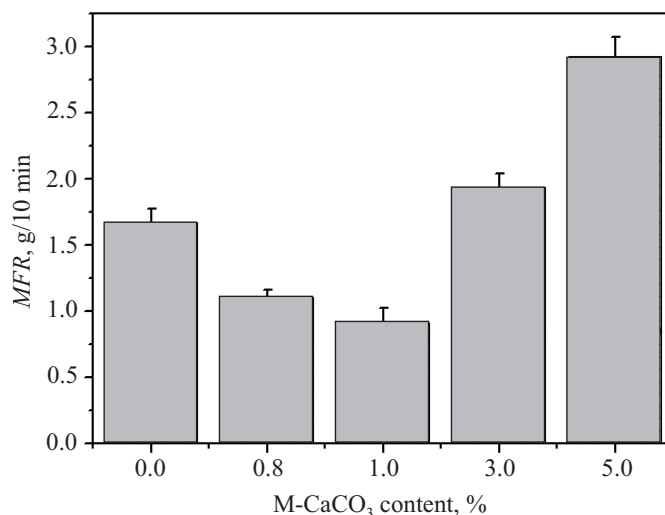


Fig. 4. The effect of M-CaCO<sub>3</sub> content on the MFR of PLLA

phenomenon is that a low content of M-CaCO<sub>3</sub> with a small amount of EDTA and SDS mainly serves as a nucleating agent of PLLA for the crystallization to decrease the chain movements of PLLA. However, a high content M-CaCO<sub>3</sub> can improve the chain movements because of a larger amount of EDTA and SDS that serve as a plasticizer of PLLA.

The influence of M-CaCO<sub>3</sub> on the mechanical performance of PLLA was investigated. The tensile strengths and elongation at break of PLLA with different M-CaCO<sub>3</sub> contents are presented in Fig. 5a) and Fig. 5b), respectively (the fitted lines was made using origin7.0, and the mechanical properties of PLLA/M-CaCO<sub>3</sub> with increasing of M-CaCO<sub>3</sub> content is not linear. Thus, we used non linear fitting. The error bars is different of four specimens measurement).

The tensile strength moderately increased with the larger M-CaCO<sub>3</sub> contents. Upon the addition of 0.8 % M-CaCO<sub>3</sub>, compared with neat PLLA, the tensile

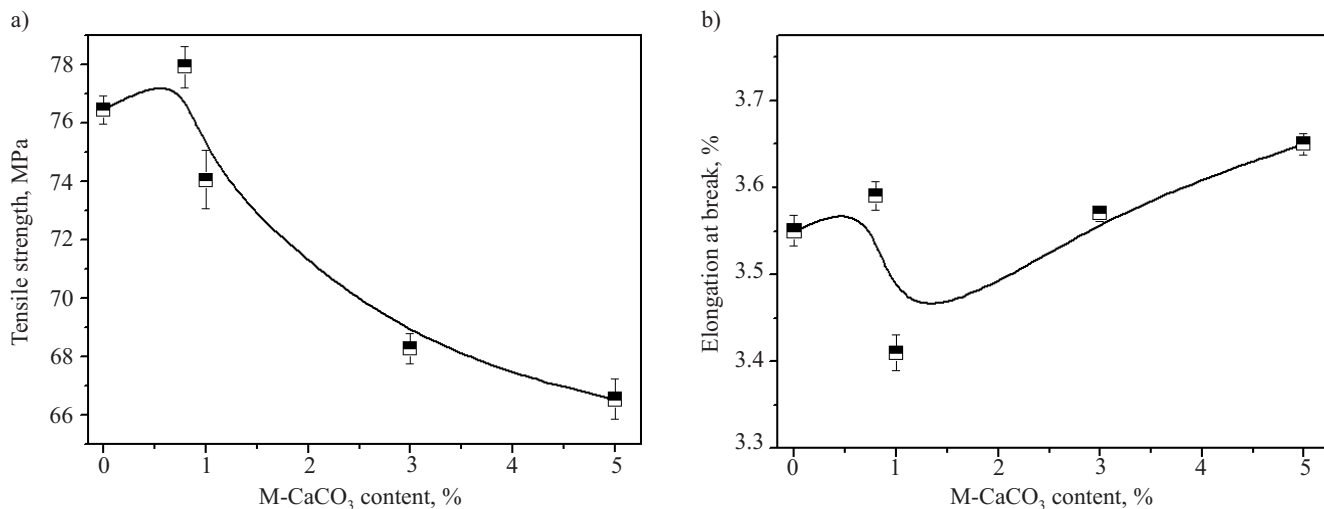


Fig. 5. Mechanical properties of PLLA/M-CaCO<sub>3</sub> composites



strength increases from 76.4 MPa to 77.9 MPa. And the tensile strength of PLLA/M-CaCO<sub>3</sub> composites with other M-CaCO<sub>3</sub> content is lower than that of neat PLLA. It is clear that the trend of elongation at break of PLLA with different M-CaCO<sub>3</sub> contents is irregular, which shows that the mechanical performance of PLLA/M-CaCO<sub>3</sub> composites is not only affected by M-CaCO<sub>3</sub>. This irregular trend may result from the defective modification of CaCO<sub>3</sub> with EDTA and SDS.

### CONCLUSION

The effect of M-CaCO<sub>3</sub> on the thermal and mechanical properties of PLLA was investigated. The isothermal crystallization behavior indicated that M-CaCO<sub>3</sub> as a nucleating agent could improve the crystallization of PLLA and the M-CaCO<sub>3</sub> content and crystallization temperature significantly affected the crystallization of PLLA. The addition of M-CaCO<sub>3</sub> also could affect the melt index and mechanical performance of PLLA/M-CaCO<sub>3</sub> composites.

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### REFERENCES

[1] Wang B., Wang Q., Li L.: *J. Appl. Polym. Sci.* **2013**, 130, 3050. <http://dx.doi.org/10.1002/app.39557>

- [2] Wang L., Ling X.L., Guo Z.X. *et al.*: *Chem. J. Chin. Univ.-Chin.* **2012**, 33, 2789. <http://dx.doi.org/10.7503/cjcu20120181>
- [3] Liang J.Z.: *J. Polym. Eng.* **2012**, 32, 401. <http://dx.doi.org/10.1515/polyeng-2012-0027>
- [4] Mao B.G., Chu D.Q., Wang A.X. *et al.*: *Eur. J. Inorg. Chem.* **2013**, 35, 5958. <http://dx.doi.org/10.1002/ejic.201300892>
- [5] Zebarjad S.M., Golmakaniyoon S.: *J. Vinyl Addit. Technol.* **2013**, 19, 271. <http://dx.doi.org/10.1002/vnl.21329>
- [6] Zhang Y., Zhang L., Liu H. *et al.*: *J. Macromol. Sci., Part B.* **2014**, 53, 13. <http://dx.doi.org/10.1080/00222348.2012.759019>
- [7] Furukawa T., Sato H., Murakami R. *et al.*: *Polymer* **2006**, 47, 3132. <http://dx.doi.org/10.1016/polymer.2006.03.010>
- [8] Dell'Erba R., Groeninckx G., Maglio G., *et al.*: *Polymer* **2001**, 42, 7831. [http://dx.doi.org/10.1016/S0032-3861\(01\)00269-5](http://dx.doi.org/10.1016/S0032-3861(01)00269-5)
- [9] Chen H.M., Wang Y.P., Chen J. *et al.*: *Polym. Degrad. Stab.* **2013**, 98, 2672. <http://dx.doi.org/10.1016/j.polymdegradstab.2013.09.033>
- [10] Liang J.Z., Duan D.R., Tang C.Y. *et al.*: *Polym. Test.* **2013**, 32, 617. <http://dx.doi.org/10.1016/j.polymertesting.2013.02.008>
- [11] Li W.X., Xu Z.W., Chen L. *et al.*: *Chem. Eng. J.* **2014**, 237, 291. <http://dx.doi.org/10.1016/j.cej.2013.10.034>
- [12] Cai Y.H.: *J. Chem. Soc. Pak.* **2013**, 35, 1174.
- [13] Dai J.J., Zhang Y.: *Modern Chem. Ind.* **2011**, 31, 228.
- [14] Cai Y.H., Peng R.F., Ma D.M. *et al.*: *Sci. Technol. Chem. Ind.* **2008**, 16, 7.
- [15] Cai Y.H.: "Studies on Synthesis of Novel Bisamides Nucleating Agents and Effect on Crystallization of Poly(L-lactic acid)", Shanghai University 2011, p. 37.
- [16] Shi N., Cai J., Dou Q.: *Adv. Mater. Res.* **2013**, 602, 768.
- [17] Nekhamanurak B., Patanathabutr P., Hongsriphan N.: *Plast. Rubber Compos.* **2012**, 41, 175. <http://dx.doi.org/10.1179/1743289811Y.0000000066>
- [18] Guan J.F., Chen Y., Wu H.D. *et al.*: *Non-Metallic Mines.* **2011**, 34, 26.

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### BAZĘ APARATURY DO OKREŚLANIA CHARAKTERYSTYKI I PRZETWÓRSTWA POLIMERÓW

będącej w posiadaniu uczelni, instytutów PAN i instytutów badawczych.

Baza jest wyposażona w funkcje umożliwiające wyszukiwanie wg zadanych parametrów: nazwy, typu lub modelu aparatu, roku produkcji, producenta, charakterystyki parametrów technicznych, zastosowania do badań, lokalizacji, słów kluczowych, sposobu wykonywania badań, numerów norm, wg których prowadzi się badania, oraz adresu i kontaktu z osobą odpowiedzialną za dany aparat. Baza jest ciągle uaktualniana.

Dostęp do danych i wyszukiwanie informacji w bazie jest bezpłatne.

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