Selective localization of titanium dioxide nanoparticles at the interface and its effect on the impact toughness of poly(L-lactide)/poly(ether)urethane blends

H. Xiu, H. W. Bai, C. M. Huang, C. L. Xu, X. Y. Li, Q. Fu*

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, 610065 Chengdu, P. R. China

Received 12 September 2012; accepted in revised form 10 November 2012

Abstract. Inorganic nanofillers are often added into polymer/elastomer blends as a third component to modify their performance. This work aims to clarify the role of interface-localized spherical nanoparticles in determining the impact toughness of polymer blends. The selective distribution of titanium dioxide (TiO₂) nanoparticles in poly(L-lactide)/poly(ether)urethane (PLLA/PU) blends was investigated by using scanning electron microscope. It is interesting to find that, regardless of the method of TiO₂ introduction, nano-TiO₂ particles are always selectively localized at the phase interface between PLLA and PU, leading to a significant improvement in notched Izod impact toughness. The moderately weakened interfacial adhesion induced by the interfacially-localized nano-TiO₂ particles is believed to be the main reason for the largely enhanced impact toughness.

Keywords: biodegradable polymers, poly(L-lactide), mechanical properties, toughness, microstructure

1. Introduction

With increasing environmental concerns and decreasing petroleum resources, bio-based and biodegradable polymers have gained growing interest during recent years. As one of the most promising biodegradable polymers derived from renewable sources (e.g. corn and sugar beets), poly(L-lactide) (PLLA) exhibits great potential to replace traditional petroleum-based plastics (e.g. polypropylene (PP) and polystyrene (PS)) in a wide variety of applications due to its excellent transparency, good mechanical strength and easy processability [1–7]. Furthermore, similar to poly(ε-caprolactone) (PCL) [8, 9], PLLA has been already used in biomedical fields owing to its good biocompatibility [2, 5]. However, the practical applications of PLLA are far from as widespread as expected because there are some drawbacks such as its inherent brittleness. Therefore,

considerable efforts have been devoted to toughen PLLA [10–22]. Blending PLLA with other rubbery polymers, such as poly(ether)urethane (PU) elastomer [15], polyamide elastomer (PAE) [16], PCL [17, 18], poly(butylene succinate) (PBS) [18, 19], and ethylene-co-vinyl acetate (EVA) [20], provides a practical and economical way to improve the toughness of PLLA. Unfortunately, a substantial elastomer concentration of about 15–20 wt% is required to achieve effective toughening, which, in turn, leads to a significant deterioration in strength and stiffness [15, 17, 20]. To overcome this problem, inorganic nanofillers are often added into these blends as a third component to enhance the strength and stiffness, while maintaining or even further improving the obtained toughness [23–35]. Hitherto numerous studies have demonstrated that the key issue in achieving the optimal combination

*Corresponding author, e-mail: qiangfu@scu.edu.cn
© BME-PT

of mechanical properties of polymer/elastomer/filler ternary nanocomposites is to tailor the phase morphology, especially the distribution of nanofillers in the matrix blends [28, 29]. Generally, when nanofillers are introduced into an immiscible or partially miscible polymer blend, they often distribute heterogeneously, i.e. selectively dispersed in polymer matrix, in elastomer phase or at the interface between the two polymer phases, thus forming separated dispersion, rigid core-soft shell and soft core-rigid shell structures, respectively. In most cases, the formation of the rigid core-soft shell structure is found to be more favorable to achieve satisfactory toughness at lower elastomer concentration and, consequently, a good balance between toughness and stiffness as compared to the separated dispersion structure [23–25]. However, much less attention has been paid to the soft core-rigid shell structure possibly because it is difficult to realize the exclusive localization of nanofillers at the phase interface [33–37]. More importantly, to the best of our knowledge, so far very little information has been obtained about its effect on the mechanical properties of such nanocomposites. Excitedly, in the present work, we find that isotropic titanium dioxide (TiO_2) nanoparticles have a strong tendency to preferentially distribute at the interface of PLLA/PU blends with ‘sea-island’ morphology, forming a unique soft core-rigid shell structure, i.e. PU particles are closely surrounded by a large amount of nano- TiO_2 particles, which gives us a good chance to gain full insight into the role of the interface-localized nanoparticles in determining the performance of polymer blends, especially the impact toughness. To this aim, the relationship between microstructure and impact toughness of PLLA/PU/ TiO_2 nanocomposites is analyzed carefully and then several possible toughening mechanisms are discussed.

2. Experimental

2.1. Materials

PLLA (4032D, D-isomer content = 1.2–1.6%) used as the matrix polymer was purchased from Nature-Works Co. Ltd, USA. It has a density of 1.25 g/cm^3 , weight-averaged molecular weight (M_w) of 207 kDa, and polydispersity of 1.74, respectively. PU (WHT-1570, Yantai Wanhua Polyurethanes Co., Ltd, China) with a density of 1.21 g/cm^3 was selected as the impact modifier in this work. Nano-sized titanium dioxide (TiO_2 , purity >98%, density = 4.25 g/cm^3 ,

average particle size = 200 nm) without any surface modification was produced by Chengdu Kelong Chemical Reagent Factory, China.

2.2. Sample preparation

PLLA/PU/ TiO_2 ternary nanocomposites were prepared by melt blending various amounts of TiO_2 (0–25 wt%) with PLLA/PU blend matrix (90:10 or 75:25 w/w) in a Haake mixer (XSS-300, USA) at a temperature of 190°C and rotor speed of 50 rpm for 5 min. In this case, TiO_2 , PLLA, and PU were loaded to the mixing chamber simultaneously. For comparison, PLLA/PU binary blends were blended under the same conditions. Specially, in order to investigate the effect of mixing procedure on the distribution of TiO_2 in the nanocomposites, the other two blending procedures were also employed: blending of precompounded PU/ TiO_2 or PLLA/ TiO_2 with the second polymer (PLLA or PU) during a second blending step. All raw materials including PLLA, PU and TiO_2 were dried under vacuum before using. To obtain standard specimens for mechanical testing, the obtained materials were then compression molded at 190°C for 5 min and then quenched to room temperature.

2.3. Scanning electron microscopy (SEM)

The phase morphologies of PLLA/PU blends with and without TiO_2 were observed using an FEI Inspect F scanning electron microscope (SEM, USA) with an accelerating voltage of 5.0 kV. The specimens for the SEM observation were prepared by cryogenic fracture in liquid nitrogen. The impact fractured surfaces of the specimens after the impact testing were also observed by SEM.

2.4. Surface energy measurement

Contact angles measurement is a traditional and valid method to evaluate the surface energy of solids [38]. The surface energy of a solid or a liquid and its dispersive and polar components can be calculated from the contact angle data by using Owens-Wendt method [39] (Equation (1) and (2)):

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (1)$$

$$\gamma_l(1 + \cos\theta) = 2\sqrt{\gamma_s^d\gamma_l^d} + 2\sqrt{\gamma_s^p\gamma_l^p} \quad (2)$$

where θ is the contact angle, γ is the surface energy, subscripts ‘s’ and ‘l’ indicate solid and liquid, respec-

tively, while superscripts ‘d’ and ‘p’ indicate the dispersive and polar components, respectively. Generally, in order to obtain the surface energy γ_s of the measured solid from Equations (1) and (2), at least two liquids, usually a polar and a nonpolar liquid, should be used. Here, two test liquids (i.e. distilled water (H_2O) and diiodomethane (CH_2I_2)) were selected as widely reported in the literature [28, 40]. The values of surface energy of the two test liquids are $\gamma^p = 50.7$ mN/m and $\gamma^d = 22.1$ mN/m for H_2O , and $\gamma^p = 6.7$ mN/m and $\gamma^d = 44.1$ mN/m for CH_2I_2 [28].

The contact angle tests were conducted on a DSA100 apparatus (Krüss GmbH, Germany) based on the sessile drop method, i.e. depositing a drop of test liquid onto the sample surface. At least six replicates were performed for each sample to ensure the reproducibility of the measured data. Prior to the measurements, TiO_2 powders were compression molded by using a home-made metal mold at room temperature under a pressure of 15 MPa, while PLLA and PU specimens were compression molded at 190°C for 5 min and then quenched to 25°C.

2.5. Mechanical testing

The notched Izod impact strength was measured using an impact tester (XJU-5.5, China), according to ISO180/179 standard. Pendulum impact velocity is 3.5 m/s. Tensile testing was performed with a SANS universal tensile testing machine (China) at a cross-head speed of 5 mm/min, according to ISO 527-3 standard. For each sample, the measurements were carried out at room temperature (23°C) and the results obtained were averaged at least five specimens.

2.6. Differential scanning calorimetry (DSC)

The degree of crystallinity (X_c) of the PLLA matrix in the compression molded samples was evaluated using differential scanning calorimetry (DSC, Perkin-Elmer pyris-1, USA) in a dry nitrogen atmosphere. For each measurement, about 5 mg of the sample was directly heated from 0 to 200°C at a heating rate of 10°C/min. The value of ΔH_m were determined using the most commonly used Equation (3) [21, 22, 41]:

$$X_c = \frac{\Delta H_m - \Delta H_c}{w_f \Delta H_m^0} \cdot 100\% \quad (3)$$

where ΔH_m and ΔH_c are the enthalpies of melting and cold crystallization, respectively; w_f is the weight percent of the PLLA matrix, and ΔH_m^0 is the melting enthalpy of completely crystalline PLLA (93.7 J/g [42]).

3. Results and discussion

3.1. Phase morphology and selective localization of nano- TiO_2 particles

In order to elucidate the microstructure and morphology of PLLA/PU blends with and without TiO_2 , SEM experiment was carried out and the results are shown in Figure 1. Obviously, all samples exhibit typical ‘sea-island’ morphologies, where discrete PU spherical domains are uniformly dispersed in the PLLA matrix. Unexpectedly, with the introduction of 15 phr nano- TiO_2 particles into the blend of PLLA/10PU, the size of the PU domains increases slightly (Figure 1b). This result is opposite to that usually seen in polymer blends filled with other nanofillers, such as silicon dioxide (SiO_2), clay and multi-walled carbon nanotubes (MWCNTs), where the size of dispersed-phase domains decreases significantly with adding small amounts of nanofillers [43–45]. Recently, Cai *et al.* [46] confirmed that morphology evolution of immiscible polymer blends is strongly dominated by the self-agglomerating pattern of nanoparticles in polymer melts. An increase in the size of PA6 domains is observed as high loading of nano- TiO_2 (e.g. 25 phr) is added into PS/30PA6 blend due to its unique self-agglomerating pattern completely different from other nanofillers. Similarly, the increased size of the PU domains may be associated with the unique self-agglomerating pattern of the TiO_2 , which needs further investigation in our future work. Very interestingly, almost all nano- TiO_2 particles are selectively located at the phase interface between PLLA and PU in PLLA/10PU/15 TiO_2 ternary nanocomposite, which can be observed more clearly in the ternary samples containing relatively high content of PU, such as PLLA/25PU/15 TiO_2 nanocomposite (Figure 1c). In this case, spherical PU domains are surrounded by a large number of nano- TiO_2 particles, forming a special soft core-rigid shell structure in the PLLA matrix. More interestingly, the distribution of nano- TiO_2 particles in the obtained PLLA/PU/ TiO_2 nanocomposites is independent on the method of TiO_2 introduction, as shown in Figure 2. In all cases, nano- TiO_2 particles are mainly located at the interface

Figure 1. SEM micrographs of the cryofractured surfaces of PLLA/PU blends with and without TiO₂: (a) PLLA/10PU, (b) PLLA/10PU/15TiO₂, and (c) PLLA/25PU/15TiO₂

and almost no nano-TiO₂ particles can be found in the two blend components (PLLA and PU), suggesting that the nano-TiO₂ particles should be thermodynamically driven into the phase interface during mixing process. This conclusion can be further confirmed by theoretical calculation using the wetting coefficient ω_a defined by Equation (4) [47]:

$$\omega_a = \frac{\gamma_{\text{PLLA-TiO}_2} - \gamma_{\text{PU-TiO}_2}}{\gamma_{\text{PLLA-PU}}} \quad (4)$$

where $\gamma_{\text{PLLA-TiO}_2}$, $\gamma_{\text{PU-TiO}_2}$, and $\gamma_{\text{PLLA-PU}}$ are the interfacial energies between PLLA and TiO₂, between PU and TiO₂, between PLLA and PU, respectively. ω_a has been widely used to predict the thermodynamic equilibrium distribution of nanofillers in polymer blends [25, 40]. Generally, for $\omega_a > 1$, TiO₂

particles are only found in PU; for $\omega_a < -1$, TiO₂ particles are present only in PLLA and for $-1 < \omega_a < 1$, TiO₂ particles are selectively located at the interface between PLLA and PU.

The interfacial energy can be obtained from surface energies of the corresponding components and their dispersive and polar parts, based on the two most commonly used methods, i.e. harmonic-mean Equation (5) and geometric-mean Equation (6) [38]:

Harmonic-mean equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right) \quad (5)$$

Geometric-mean equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p}) \quad (6)$$

Figure 2. SEM micrographs of the cryofractured surfaces of PLLA/10PU/15TiO₂ composites prepared by different blending procedures: (a) direct blending of all three components, (b) blending of premixed PU/TiO₂ with PLLA, and (c) blending of premixed PLLA/TiO₂ with PU

Table 1. The measured contact angles and calculated surface energy data of PLLA, PU and TiO₂

Sample	Contact angles[°]		Surface energy [mN/m]		
	H ₂ O	CH ₂ I ₂	γ	γ^d	γ^p
PLLA	78.5	37.7	47.74	38.37	9.37
PU	78.1	55.2	41.69	30.36	11.33
TiO ₂	19.7	10.1	80.70	46.40	34.30

where γ_i is the surface energy of component i , γ_i^d and γ_i^p are the dispersive and polar contributions to the surface energy of component i , respectively.

In this work, the values of surface energies were calculated from the contact angle data by using Equation (1) and Equation (2) and the results are summarized in Table 1. The values of interfacial

Table 2. Interfacial tensions and wetting coefficient as calculated using harmonic-mean and geometric-mean equations

Component couple	Based on harmonic-mean equation [mN/m]	Based on geometric-mean equation [mN/m]
PLLA/PU	1.06	0.56
PLLA/TiO ₂	15.00	8.20
PU/TiO ₂	14.91	7.89
ω_a	0.08	0.55

energies and are listed in Table 2. As expected, the value of is 0.08 based on Harmonic-mean equation, and 0.55 based on Geometric-mean equation, indicating that the state of thermodynamic equilibrium distribution of nano-TiO₂ particles should be selec-

tively concentrated at the interface between PLLA and PU.

3.2. Mechanical properties

As discussed in the introduction, the distribution of nanofillers plays a decisive role in controlling the performance of polymer/elastomer/filler nanocomposites. In order to know the effect of such interfacially-localized nano-TiO₂ particles on the mechanical properties of PLLA/PU blends, notched Izod impact toughness and tensile properties were evaluated. Figure 3 shows the impact strength of PLLA

and PLLA/10PU blends as a function of nano-TiO₂ content. It is very interesting to observe that, although no obvious toughening effect on PLLA matrix can be obtained by only adding low content (e.g. 10 wt%) of nano-TiO₂ or PU, the presence of nano-TiO₂ particles at the interface gives rise to a largely improved impact toughness of PLLA/10PU blend. For example, the impact strength of PLLA/10PU blend increases remarkably from 5.61 to 30.41 kJ/m² with increasing nano-TiO₂ content up to 15 phr. This indicates that realizing selective distribution of nano-TiO₂ particles at the interface is an effective method to toughen PLLA/PU blends. Meanwhile, it should be noted that there is a saturation of the toughening effect. With further increasing nano-TiO₂ content, the high-concentration (e.g. 25 phr) nano-TiO₂ induces a slight decrease of impact toughness due to the serious aggregation of nano-TiO₂ particles in this condition (as discussed below). Unfortunately, the nano-TiO₂ induces dramatic improvement in the impact toughness, but evident deterioration in tensile strength and elongation at break, as can be observed in Figure 4 and Table 3. This can be explained as follows. On one hand, the existence of large amounts of nano-TiO₂ around PU domains can lead to a moderate increase in the effective vol-

Figure 3. Notched Izod impact strength of PLLA and PLLA/10PU blends with various amounts of TiO₂

Figure 4. (a) Stress-strain curves of PLLA and PLLA/10PU blends with various amounts of TiO₂, and (b) enlarged part of the curves

Table 3. Mechanical properties of PLLA and PLLA/10PU blends with various amounts of TiO₂

Sample	Yield stress [MPa]	Modulus MPa[	Elongation at break [%]	Notched impact strength [kJ/m ²]
PLLA	68.36±0.67	2452.80±29.69	5.67±0.18	3.10±0.12
PLLA/10TiO ₂	67.21±0.98	2730.10±22.65	4.17±0.07	3.23±0.23
PLLA/10PU	53.35±0.63	1946.75±59.75	313.42±32.81	5.61±0.32
PLLA/10PU/5TiO ₂	49.02±0.36	2143.17±62.43	235.37±59.77	11.39±1.78
PLLA/10PU/10TiO ₂	47.04±0.58	2099.11±23.87	41.24±20.00	17.95±1.44
PLLA/10PU/15TiO ₂	41.21±0.68	1969.38±20.90	69.04±37.04	30.41±0.16
PLLA/15PU	46.87±0.10	1939.78±27.39	294.09±29.11	23.19±2.93

ume of PU dispersed phase. On the other hand, unlike bridge effect of MWCNTs with high aspect ratio, the interfacially-localized nano-TiO₂ particles are most likely to weaken the interfacial bonding strength between PLLA and PU because of the shielding effect, thus promoting debonding of PU domains from PLLA matrix during deformation. Both factors are believed to contribute to the substantially reduced tensile strength, based on the fact that, although the true volume fraction of PU phase (18.4%) in PLLA/15PU blend is higher than the effective volume fraction of PU phase (14.9%) in PLLA/10PU/15TiO₂ nanocomposite, the former sample exhibits a much higher tensile strength as compared with the latter one (Table 3). With regard to the remarkably decreased extensibility, undoubtedly, the latter factor is the main reason. Furthermore, one thing should be stressed that tensile testing and notched Izod impact testing were carried out at remarkably different test speeds. Thus, the materials are most likely to exhibit different mechanical responses when they are subjected to different loading conditions. For the tensile testing, the tensile speed is only 5 mm/min, indicating a quasi-static loading condition. In this case, the presence of nano-TiO₂ particles at the interface is unfavorable to the stress transferring between PLLA and PCL because of the reduced interfacial adhesion, thus giving rise to the notably reduced extensibility. However, for the notched Izod impact testing, the impact speed is as high as 3.5 m/s, indicating a dynamic loading condition. In this case, the interfacially-localized nano-TiO₂ particles seem to be favorable to the toughening.

3.3. Toughening mechanism

To make clear the role of the interfacially-localized nano-TiO₂ particles in the toughening of PLLA/PU blends, the impact fractured surfaces of PLLA/10PU blends with and without TiO₂ particles were characterized by SEM, and the results are given in Figure 5. Clearly, the blank PLLA/10PU blend exhibits a typical brittle failure. The fractured surface is very smooth and no evident deformation of PLLA matrix appears (Figure 5a). This suggests that fast crack propagation occurs during impact fracture process. In contrast, after adding 10–15 phr TiO₂, many fibrils as a result of crazing of PLLA matrix can be clearly observed on the whole surface (Figure 5b and 5c), indicating that the interfacially-

localized nano-TiO₂ particles effectively facilitate the deformation of PLLA matrix through crazing mechanism. Moreover, these highly stretched fibrils can prevent the crack initiation and propagation, allowing for a considerable plastic deformation to develop [48]. As a result, substantial energy is consumed, leading to the high impact toughness. Now it is logical to ask how the nano-TiO₂ particles induce the stable crazes in PLLA matrix. In fact, it has been widely accepted that the role of elastomer in toughening polymers is mainly associated with the cavitation of elastomer particles and the cavitation caused by interfacial debonding can promote energy dissipation through relaxing the locally tri-axial stress that favors brittle failure [49–51]. Here, since spherical nano-TiO₂ particles located at the interface can weaken the interfacial adhesion between PLLA matrix and PU dispersed phase to a certain extent (evidenced by the decreased tensile strength as discussed above), the interfacial debonding and, consequently, the plastic deformation of PLLA matrix become easier to be triggered as compared to the blank PLLA/PU blends. This mechanism has been successfully used to explain the reason for the enhanced toughness of epoxy/acrylic rubber blends induced by the interfacially-localized clay [52]. On the other hand, Shi *et al.* [35] have demonstrated that the introduction of interfacially-localized MWCNTs causes a decrease in the impact strength of PLLA/EVA blends, suggesting that the enhanced interfacial adhesion seems to be unfavorable to the toughening of PLLA/elastomer blends. Furthermore, by considering that the impact strength of PLLA/10PU/15TiO₂ nanocomposite with a lower effective volume fraction of PU phase (14.9%) is much higher than PLLA/15PU blend with a higher true volume fraction of PU phase (18.4%) (Table 3), we believe that the increase in the effective volume fraction of PU phase has little influence on the improvement in the impact toughness. Therefore, the largely enhanced impact toughness of PLLA/PU blends induced by the interfacially-localized nano-TiO₂ is mainly attributed to the moderately reduced interfacial debonding. Most importantly, it should be noted that appropriate concentration of TiO₂ is the prerequisite to obtain the blends with good impact toughness. At high concentrations (e.g. 25 phr), some of nano-TiO₂ particles aggregate together and form large aggregates at the phase interface and, subsequent, only small amounts of

Figure 5. SEM micrographs of impact fractured surfaces of PLLA/10PU blends with and without TiO₂: (a) PLLA/10PU, (b) PLLA/10PU/10TiO₂, (c) PLLA/10PU/15TiO₂, and (d) PLLA/10PU/25TiO₂

Figure 6. DSC heating curves of PLLA/10PU blends with various amounts of TiO₂

highly stretched fibrils and less evident matrix deformation can be observed on the impact fractured surface (Figure 5d). This observation is well consistent with the deteriorated impact toughness of the blends with high-concentration TiO₂ as mentioned above.

In addition, our previous work has shown that the crystallinity of PLLA matrix may influence the impact toughness of PLLA/elastomer blend [53]. However, it can be disregarded completely in this work. All the samples present the same low level of the PLLA matrix crystallinity (~10%), as displayed in Figure 6.

4. Conclusions

In this work, PLLA/PU/TiO₂ ternary nanocomposites were prepared by three different mixing procedures. Regardless of the method of TiO₂ introduction, almost all nano-TiO₂ particles are located around spherical PU domains, forming a unique soft core-rigid shell structure in the PLLA matrix. The results show that the addition of nano-TiO₂ leads to a largely enhanced impact toughness of PLLA/PU blend mainly due to the weakened interfacial debonding in the presence of the interfacial-localized nano-TiO₂ particles. During the impact process, nano-TiO₂ particles induce interfacial debonding, promoting the plastic deformation of PLLA matrix through crazing rather than crack, thus dissipating large amounts of energy. This work not only provides a simple and effective method to largely improve the impact toughness of polymer blends, but also gives a comprehensive understanding of the role of interfacial-localized spherical

Acknowledgements

We would like to express our great thanks to the National Natural Science Foundation of China (50903048 and 51121001) for Financial Support.

References

- [1] Auras R., Harte B., Selke S.: An overview of polylactides as packaging materials. *Macromolecular Bioscience*, **4**, 835–864 (2004). DOI: [10.1002/mabi.200400043](https://doi.org/10.1002/mabi.200400043)
- [2] Nampoothiri K. M., Nair N., R., John R. P.: An overview of the recent developments in polylactide (PLA) research. *Bioresource Technology*, **101**, 8493–8501 (2010). DOI: [10.1016/j.biortech.2010.05.092](https://doi.org/10.1016/j.biortech.2010.05.092)
- [3] Gross R. A., Kalra B.: Biodegradable polymers for the environment. *Science*, **297**, 803–807 (2002). DOI: [10.1126/science.297.5582.803](https://doi.org/10.1126/science.297.5582.803)
- [4] del Valle L. J., Díaz A., Royo M., Rodríguez-Galán A., Puiggali J.: Biodegradable polyesters reinforced with triclosan loaded polylactide micro/nanofibers: Properties, release and biocompatibility. *Express Polymer Letters*, **6**, 266–282 (2012). DOI: [10.3144/expresspolymlett.2012.30](https://doi.org/10.3144/expresspolymlett.2012.30)
- [5] Rasal R. M., Janorkar A. V., Hirt D. E.: Poly(lactic acid) modifications. *Progress in Polymer Science*, **35**, 338–356 (2010). DOI: [10.1016/j.progpolymsci.2009.12.003](https://doi.org/10.1016/j.progpolymsci.2009.12.003)
- [6] Drumright R. E., Gruber P. R., Henton D. E.: Polylactic acid technology. *Advanced Materials*, **12**, 1841–1846 (2000). DOI: [10.1002/1521-4095\(200012\)12:23<1841::AID-ADMA1841>3.0.CO;2-E](https://doi.org/10.1002/1521-4095(200012)12:23<1841::AID-ADMA1841>3.0.CO;2-E)
- [7] Lim L-T., Auras R., Rubino M.: Processing technologies for poly(lactic acid). *Progress in Polymer Science*, **33**, 820–852 (2008). DOI: [10.1016/j.progpolymsci.2008.05.004](https://doi.org/10.1016/j.progpolymsci.2008.05.004)
- [8] De Santis R., Catauro M., Di Silvio L., Manto L., Raucci M., Ambrosio L., Nicolais L.: Effects of polymer amount and processing conditions on the in vitro behaviour of hybrid titanium dioxide/polycaprolactone composites. *Biomaterials*, **28**, 2801–2809 (2007). DOI: [10.1016/j.biomaterials.2007.02.014](https://doi.org/10.1016/j.biomaterials.2007.02.014)
- [9] Russo T., Gloria A., D-Antò V., D'Amora U., Ametrano G., Bollino F., De Santis R., Ausanio G., Catauro M., Rengo S., Ambrosio L.: Poly(ϵ -caprolactone) reinforced with sol-gel synthesized organic-inorganic hybrid fillers as composite substrates for tissue engineering. *Journal of Applied Biomaterials and Biomechanics*, **8**, 146–152 (2010). DOI: [10.5301/jabb.2010.6094](https://doi.org/10.5301/jabb.2010.6094)
- [10] Liu H., Zhang J.: Research progress in toughening modification of poly(lactic acid). *Journal of Polymer Science Part B: Polymer Physics*, **49**, 1051–1083 (2011). DOI: [10.1002/polb.22283](https://doi.org/10.1002/polb.22283)
- [11] Martin O., Avérous L.: Poly(lactic acid): Plasticization and properties of biodegradable multiphase systems. *Polymer*, **42**, 6209–6219 (2001). DOI: [10.1016/S0032-3861\(01\)00086-6](https://doi.org/10.1016/S0032-3861(01)00086-6)
- [12] Kulinski Z., Piorkowska E., Gadzinowska K., Stasiak M.: Plasticization of poly(L-lactide) with poly(propylene glycol). *Biomacromolecules*, **7**, 2128–2135 (2006). DOI: [10.1021/bm060089m](https://doi.org/10.1021/bm060089m)
- [13] Ljungberg N., Wesslén B.: Preparation and properties of plasticized poly(lactic acid) films. *Biomacromolecules*, **6**, 1789–1796 (2005). DOI: [10.1021/bm050098f](https://doi.org/10.1021/bm050098f)
- [14] Ljungberg N., Wesslén B.: Tributyl citrate oligomers as plasticizers for poly(lactic acid): Thermo-mechanical film properties and aging. *Polymer*, **44**, 7679–7688 (2003). DOI: [10.1016/j.polymer.2003.09.055](https://doi.org/10.1016/j.polymer.2003.09.055)
- [15] Li Y., Shimizu H.: Toughening of polylactide by melt blending with a biodegradable poly(ether)urethane elastomer. *Macromolecular Bioscience*, **7**, 921–928 (2007). DOI: [10.1002/mabi.200700027](https://doi.org/10.1002/mabi.200700027)
- [16] Zhang W., Chen L., Zhang Y.: Surprising shape-memory effect of polylactide resulted from toughening by polyamide elastomer. *Polymer*, **50**, 1311–1315 (2009). DOI: [10.1016/j.polymer.2009.01.032](https://doi.org/10.1016/j.polymer.2009.01.032)
- [17] López-Rodríguez M., López-Arraiza A., Meaurio E., Sarasua J. R.: Crystallization, morphology, and mechanical behavior of polylactide/poly(ϵ -caprolactone) blends. *Polymer Engineering and Science*, **46**, 1299–1308 (2006). DOI: [10.1002/pen.20609](https://doi.org/10.1002/pen.20609)

- [18] Vilay V., Mariatti M., Ahmad Z., Pasomsouk K., Todo M.: Characterization of the mechanical and thermal properties and morphological behavior of biodegradable poly(L-lactide)/poly(ϵ -caprolactone) and poly(L-lactide)/poly(butylene succinate-co-L-lactate) polymeric blends. *Journal of Applied Polymer Science*, **114**, 1784–1792 (2009). DOI: [10.1002/app.30683](https://doi.org/10.1002/app.30683)
- [19] Shibata M., Inoue Y., Miyoshi M.: Mechanical properties, morphology, and crystallization behavior of blends of poly(L-lactide) with poly(butylene succinate-co-L-lactate) and poly(butylene succinate). *Polymer*, **47**, 3557–3564 (2006). DOI: [10.1016/j.polymer.2006.03.065](https://doi.org/10.1016/j.polymer.2006.03.065)
- [20] Yoon J-S., Oh S-H., Kim M-N., Chin I-J., Kim Y-H.: Thermal and mechanical properties of poly(L-lactic acid)-poly (ethylene-co-vinyl acetate) blends. *Polymer*, **40**, 2303–2312 (1999). DOI: [10.1016/S0032-3861\(98\)00463-7](https://doi.org/10.1016/S0032-3861(98)00463-7)
- [21] Liu H., Chen F., Liu B., Estep G., Zhang J.: Super toughened poly(lactic acid) ternary blends by simultaneous dynamic vulcanization and interfacial compatibilization. *Macromolecules*, **43**, 6058–6066 (2010). DOI: [10.1021/ma101108g](https://doi.org/10.1021/ma101108g)
- [22] Liu H., Song W., Chen F., Guo L., Zhang J.: Interaction of microstructure and interfacial adhesion on impact performance of polylactide (PLA) ternary blends. *Macromolecules*, **44**, 1513–1522 (2011). DOI: [10.1021/ma1026934](https://doi.org/10.1021/ma1026934)
- [23] Matonis V. A., Small N. C.: A macroscopic analysis of composites containing layered spherical inclusions. *Polymer Engineering and Science*, **9**, 90–99 (1969). DOI: [10.1002/pen.760090204](https://doi.org/10.1002/pen.760090204)
- [24] Matonis V. A.: The interfacial stresses in particulate composite systems. *Polymer Engineering and Science*, **9**, 100–104 (1969). DOI: [10.1002/pen.760090205](https://doi.org/10.1002/pen.760090205)
- [25] Jancar J., Dibenedetto A. T.: The mechanical properties of ternary composites of polypropylene with inorganic fillers and elastomer inclusions. *Journal of Materials Science*, **29**, 4651–4658 (1994). DOI: [10.1007/BF00376292](https://doi.org/10.1007/BF00376292)
- [26] Jancar J., Dibenedetto A. T.: Effect of morphology on the behaviour of ternary composites of polypropylene with inorganic fillers and elastomer inclusions. *Journal of Materials Science*, **30**, 1601–1608 (1995). DOI: [10.1007/BF00375271](https://doi.org/10.1007/BF00375271)
- [27] Jancar J., Dibenedetto A. T.: Failure mechanics in ternary composites of polypropylene with inorganic fillers and elastomer inclusions. *Journal of Materials Science*, **30**, 2438–2445 (1995). DOI: [10.1007/BF01184598](https://doi.org/10.1007/BF01184598)
- [28] Yang H., Zhang X., Qu C., Li B., Zhang L., Zhang Q., Fu Q.: Largely improved toughness of PP/EPDM blends by adding nano-SiO₂ particles. *Polymer*, **48**, 860–869 (2007). DOI: [10.1016/j.polymer.2006.12.022](https://doi.org/10.1016/j.polymer.2006.12.022)
- [29] Yang H., Zhang Q., Guo M., Wang C., Du R., Fu Q.: Study on the phase structures and toughening mechanism in PP/EPDM/SiO₂ ternary composites. *Polymer*, **47**, 2106–2115 (2006). DOI: [10.1016/j.polymer.2006.01.076](https://doi.org/10.1016/j.polymer.2006.01.076)
- [30] Chow W. S., Leu Y. Y., Mohd Ishak Z. A.: Effects of SEBS-g-MAH on the properties of injection moulded poly(lactic acid)/nano-calcium carbonate composites. *Express Polymer Letters*, **6**, 503–510 (2012). DOI: [10.3144/expresspolymlett.2012.53](https://doi.org/10.3144/expresspolymlett.2012.53)
- [31] Gao X., Qu C., Zhang Q., Peng Y., Fu Q.: Brittle-ductile transition and toughening mechanism in POM/TPU/CaCO₃ ternary composites. *Macromolecular Materials and Engineering*, **289**, 41–48 (2004). DOI: [10.1002/mame.200300222](https://doi.org/10.1002/mame.200300222)
- [32] Premphet K., Horanont P.: Phase structure of ternary polypropylene/elastomer/filler composites: Effect of elastomer polarity. *Polymer*, **41**, 9283–9290 (2000). DOI: [10.1016/S0032-3861\(00\)00303-7](https://doi.org/10.1016/S0032-3861(00)00303-7)
- [33] Wu D., Zhang Y., Zhang M., Yu W.: Selective localization of multiwalled carbon nanotubes in poly(ϵ -caprolactone)/polylactide blend. *Biomacromolecules*, **10**, 417–424 (2009). DOI: [10.1021/bm801183f](https://doi.org/10.1021/bm801183f)
- [34] Shi Y. Y., Li Y. L., Wu J., Huang T., Chen C., Peng Y., Wang Y.: Toughening of poly(L-lactide)/multiwalled carbon nanotubes nanocomposite with ethylene-co-vinyl acetate. *Journal of Polymer Science Part B: Polymer Physics*, **49**, 267–276 (2011). DOI: [10.1002/polb.22177](https://doi.org/10.1002/polb.22177)
- [35] Shi Y. Y., Li Y. L., Xiang F. M., Huang T., Chen C., Peng Y., Wang Y.: Carbon nanotubes induced microstructure and mechanical properties changes in cocontinuous poly(L-lactide)/ethylene-co-vinyl acetate blends. *Polymers for Advanced Technologies*, **23**, 783–790 (2011). DOI: [10.1002/pat.1959](https://doi.org/10.1002/pat.1959)
- [36] Li W., Karger-Kocsis J., Schlarb A. K.: Dispersion of TiO₂ particles in PET/PP/TiO₂ and PET/PP/PP-g-MA/TiO₂ composites prepared with different blending procedures. *Macromolecular Materials and Engineering*, **294**, 582–589 (2009). DOI: [10.1002/mame.200900123](https://doi.org/10.1002/mame.200900123)
- [37] Li W., Karger-Kocsis J., Thomann R.: Compatibilization effect of TiO₂ nanoparticles on the phase structure of PET/PP/TiO₂ nanocomposites. *Journal of Polymer Science Part B: Polymer Physics*, **47**, 1616–1624 (2009). DOI: [10.1002/polb.21752](https://doi.org/10.1002/polb.21752)
- [38] Wu S.: *Polymer interface and adhesion*. Marcel Dekker, New York (1982).
- [39] Owens D. K., Wendt R. C.: Estimation of the surface free energy of polymers. *Journal of Applied Polymer Science*, **13**, 1741–1747 (1969). DOI: [10.1002/app.1969.070130815](https://doi.org/10.1002/app.1969.070130815)

- [40] Wu D., Sun Y., Lin D., Zhou W., Zhang M., Yuan L.: Selective localization behavior of carbon nanotubes: Effect on transesterification of immiscible polyester blends. *Macromolecular Chemistry and Physics*, **212**, 1700–1709 (2011).
DOI: [10.1002/macp.201100095](https://doi.org/10.1002/macp.201100095)
- [41] Wei J.-C., Sun J.-R., Wang H.-J., Chen X.-S., Jing X.-B.: Isothermal crystallization behavior and unique banded spherulites of hydroxyapatite/poly(L-lactide) nanocomposites. *Chinese Journal of Polymer Science*, **28**, 499–507 (2010).
DOI: [10.1007/s10118-010-9060-7](https://doi.org/10.1007/s10118-010-9060-7)
- [42] Garlotta D.: A literature review of poly(lactic acid). *Journal of Polymers and the Environment*, **9**, 63–84 (2002).
DOI: [10.1023/A:1020200822435](https://doi.org/10.1023/A:1020200822435)
- [43] Hong J. S., Namkung H., Ahn K. H., Lee S. J., Kim C. Y.: The role of organically modified layered silicate in the breakup and coalescence of droplets in PBT/PE blends. *Polymer*, **47**, 3967–3975 (2006).
DOI: [10.1016/j.polymer.2006.03.077](https://doi.org/10.1016/j.polymer.2006.03.077)
- [44] Si M., Araki T., Ade H., Kilcoyne A. L. D., Fisher R., Sokolov J. C., Rafailovich M. H.: Compatibilizing bulk polymer blends by using organoclays. *Macromolecules*, **39**, 4793–4801 (2006).
DOI: [10.1021/ma060125+](https://doi.org/10.1021/ma060125+)
- [45] Gubbels F., Jerome R., Teyssie Ph., Vanlathem E., Deltour R., Calderone A., Parente V., Bredas J. L.: Selective localization of carbon black in immiscible polymer blends: A useful tool to design electrical conductive composites. *Macromolecules*, **27**, 1972–1974 (1994).
DOI: [10.1021/ma00085a049](https://doi.org/10.1021/ma00085a049)
- [46] Cai X., Li B., Pan Y., Wu G.: Morphology evolution of immiscible polymer blends as directed by nanoparticle self-agglomeration. *Polymer*, **53**, 259–266 (2012).
DOI: [10.1016/j.polymer.2011.11.032](https://doi.org/10.1016/j.polymer.2011.11.032)
- [47] Bose S., Bhattacharyya A. R., Kodgire P. V., Misra A.: Fractionated crystallization in PA6/ABS blends: Influence of a reactive compatibilizer and multiwall carbon nanotubes. *Polymer*, **48**, 356–362 (2007).
DOI: [10.1016/j.polymer.2006.11.019](https://doi.org/10.1016/j.polymer.2006.11.019)
- [48] Jiang L., Zhang J., Wolcott M. P.: Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: Reinforcing effects and toughening mechanisms. *Polymer*, **48**, 7632–7644 (2007).
DOI: [10.1016/j.polymer.2007.11.001](https://doi.org/10.1016/j.polymer.2007.11.001)
- [49] Kayano Y., Keskkula H., Paul D. R.: Fracture behaviour of some rubber-toughened nylon 6 blends. *Polymer*, **39**, 2835–2845 (1998).
DOI: [10.1016/S0032-3861\(97\)00600-9](https://doi.org/10.1016/S0032-3861(97)00600-9)
- [50] Kim G.-M., Michler G. H., Gahleitner M., Fiebig J.: Relationship between morphology and micromechanical toughening mechanisms in modified polypropylenes. *Journal of Applied Polymer Science*, **60**, 1391–1403 (1996).
DOI: [10.1002/\(SICI\)1097-4628\(19960531\)60:9<1391::AID-APP15>3.0.CO;2-5](https://doi.org/10.1002/(SICI)1097-4628(19960531)60:9<1391::AID-APP15>3.0.CO;2-5)
- [51] Galeski A., Bartczak Z.: Cavitation and cavity-free deformation of filled crystalline polymer systems. *Macromolecular Symposia*, **194**, 47–62 (2003).
DOI: [10.1002/masy.200390105](https://doi.org/10.1002/masy.200390105)
- [52] Balakrishnan S., Start P. R., Raghavan D., Hudson S. D.: The influence of clay and elastomer concentration on the morphology and fracture energy of preformed acrylic rubber dispersed clay filled epoxy nanocomposites. *Polymer*, **46**, 11255–11262 (2005).
DOI: [10.1016/j.polymer.2005.10.053](https://doi.org/10.1016/j.polymer.2005.10.053)
- [53] Bai H., Xiu H., Gao J., Deng H., Zhang Q., Yang M., Fu Q.: Tailoring impact toughness of poly(L-lactide)/poly(ϵ -caprolactone) (PLLA/PCL) blends by controlling crystallization of PLLA matrix. *ACS Applied Materials and Interfaces*, **4**, 897–905 (2012).
DOI: [10.1021/am201564f](https://doi.org/10.1021/am201564f)