

Effect of biodegradation conditions on morphology of ternary compositions of low density polyethylene with poly(lactic acid) and starch

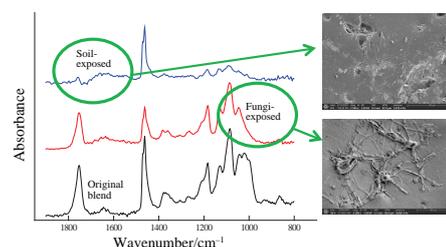
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Polyethylene–poly(lactic acid)–starch ternary compositions were obtained in a rotor disperser under conditions of shear deformation. Their biodegradation under the action of mold fungus spores and soil was investigated using IR spectroscopy and SEM. The changes under the fungal action revealed that the ternary blends represented a nutrient medium, while the exposure to soil led to alteration in morphology due to the whole range of numerous environmental factors.



Keywords: low density polyethylene, poly(lactic acid), starch, biodegradation, morphology.

Mixing of synthetic polymers with the natural ones or the polymers derived from naturally occurring raw materials represents an efficient approach towards biodegradable compositions.^{1–9} Low density polyethylene (LDPE) represents a widely used large tonnage synthetic polymer and can be mixed with biodegradable components to result in promising LDPE-based materials containing polysaccharides^{10–17} or poly(lactic acid) (PLA).^{18–22} Although the LDPE–polysaccharide blends possess some biodegradability, the introduction of rigid carbohydrates leads to deterioration of mechanical properties.^{10,11} In turn, the mixing of PLA with LDPE leads to a new type of biodegradable materials owing to a promising set of PLA properties including limited degradability in aggressive media like seawater or compost. Growing attention to the PLA–polysaccharide compositions, especially their cheapest PLA–starch variant, is related to the natural origin.^{23–27} The introduction of starch into PLA, particularly in combination with a plasticizer, results in systems with high biodegradability and good elasticity.^{23,28} Therefore, it seems reasonable to explore new LDPE–PLA–starch ternary blends. These systems with a total mass fraction of PLA and starch equal to 60% exhibit high biodegradability.²⁹ In this work, we investigated the degradation and morphology of LDPE–PLA–starch compositions under two different test conditions using Scanning Electron Microscopy (SEM) and Fourier-Transform Infrared (FTIR) spectroscopy methods.

The ternary compositions were obtained in a rotor disperser under shear deformation according to the technique described.¹⁰ Film samples had been formed by pressing and used in the biodegradability tests employing two independent approaches, namely destruction in wet soil as a model for environmental conditions and in the presence of mold fungus (for details, see Online Supplementary Materials).²⁹ As a result, the intensive pigmentation, changes in texture and formation of a rough surface of samples were observed.

According to our works,^{10,18,25,29} the degradation-induced mass loss of binary and ternary compositions based on LDPE, PLA and starch depended mainly on the starch content (Figure S1, see Online Supplementary Materials), while there was no biodegradation for the binary LDPE–PLA blends.

The difference in mechanisms of degradation resulting from the tests were first unraveled using SEM with preferably low voltage and the sample surface covered by a 10 nm layer of gold. The surface of the films before the tests was smooth and homogeneous. The material degradation upon exposure to soil led to the formation of holes that covered the whole film surface (Figures 1–3). As was expected, the higher the starch content, the more intensive was the material destruction. After the tests with mold fungus, a prominent network of fiber-like growth zones appeared due to the fungus vital activity (Figure 3). At the same

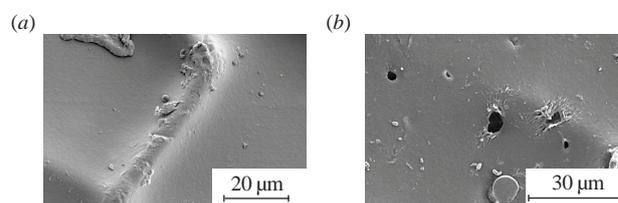


Figure 1 SEM images of the surface of LDPE–PLA–starch composition (60 : 20 : 20 wt) (a) before and (b) after exposure to soil.

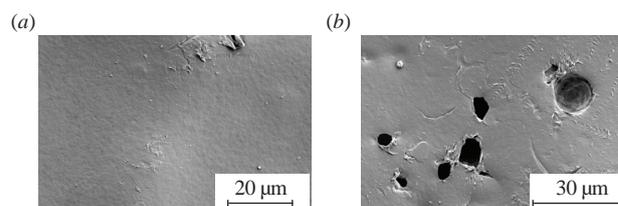


Figure 2 SEM images of the surface of LDPE–PLA–starch composition (50 : 20 : 30 wt) (a) before and (b) after exposure to soil.

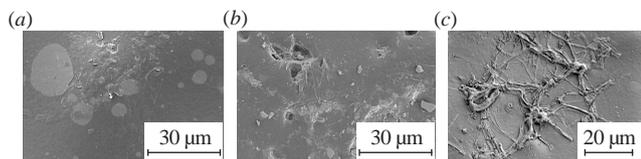


Figure 3 SEM images of the surface of LDPE–PLA–starch composition (40 : 20 : 40 wt) (a) before as well as after exposure to (b) soil and (c) fungi.

time, the surface degradation mechanism also included the formation of holes. The fungus penetration into the material resulted in erosion and roughening of the surface. Starch was supposed to be an initiator and was observed on the film surface, in contrast to the PLA–starch compositions.²³ In both soil and fungus tests, it was obvious that not only starch but also PLA as the polymer produced from natural monomer was involved in the destruction process.

To investigate details of the biodegradation, FTIR spectroscopy in the ATR mode was further applied. Figure 4 demonstrates spectra of the initial LDPE–PLA–starch composition as well as the blends after interaction with mold fungi and exposure to soil. For the initial composition, the spectrum reveals characteristic absorption bands of all the three components. For the sample treated by fungi, the changes in the region 1000–1130 cm^{-1} corresponding to the C–O and C–C stretching vibrations typical of starch are observed. This testifies the reduction of the starch content on surface of the film. According to the results of the tests on resistance to fungi, the intensity of fungal growth was high due to starch serving as a nutrient medium, and as a consequence significant destruction of the film was observed. At the same time, spectrum of the composition after exposure to soil for 12 months indicates a decrease in intensity of the characteristic bands for both starch and PLA, which is unambiguously confirmed by a substantial lowering of the intensity of the above-mentioned C–C and C–O vibrations as well as, more importantly, almost complete disappearance of the ester C=O stretches at $\sim 1750 \text{ cm}^{-1}$. The characteristic LDPE bands on the surface remained unaltered after the treatment. Thus, the sample morphology underwent changes during the biodegradation, starch was washed out from the composition as a result of the action of fungus spores and other microorganisms of the soil as well as water, while PLA was subjected to partial degradation. This process was accompanied by inversion of the ternary polymer matrix expressed in its decomposition into initial polymers since the film surface after treatment contained almost only LDPE bands.

The color reaction of starch with iodine was employed to confirm the results of FTIR spectroscopy. Some blue coloration on the initial composite surface unambiguously indicated the presence of starch. In contrast to the systems described in our work,²³ there was no starch encapsulation into the PLA matrix. Under the conditions of the tests reported here, starch on the surface disappeared (decomposed) completely, since there was

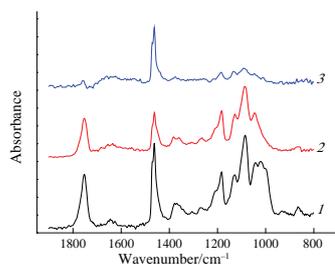


Figure 4 FTIR spectra of LDPE–PLA–starch composition (1) before as well as after action of (2) mold fungi and (3) soil.

no blue coloration with iodine for the samples both after exposure to soil and fungal action.

In summary, our experiments revealed the difference in biodegradation processes for LDPE–PLA–starch ternary compositions upon action of fungi and exposure to soil due to the effect of various factors on the process, including specific fungi species, other microorganisms in the soil or water. The fungal action led to changes, which revealed that the composition represented a nutrient medium, while the exposure to soil led to alteration in morphology under the action of the whole range of the above numerous environmental factors. The different mechanism of biodegradation, particularly the presence of a component initiating the destruction, is the main reason that affects morphology of the films under investigation.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.041.

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