

# COMPARATIVE ANALYSIS OF POLYLACTIDE THERMAL DESTRUCTION IN THE PRESENCE OF LAYERED SILICATES CLOISITE NA AND CLOISITE 30B

E. V. Koverzanova<sup>1</sup>, N. G. Shilkina<sup>1</sup>, S. V. Usachev<sup>1</sup>, and S. M. Lomakin<sup>2</sup>

<sup>1</sup>N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation

<sup>2</sup>N. M. Emanuel Institute of Biochemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119334, Russian Federation

**Abstract:** The effect of mineral fillers with a nanostructure on the mechanism of thermal destruction of polylactide (PLA) was studied. The layered silicates Cloisite Na and Cloisite 30B were used, differing in the cation contained in the interlayer space: inorganic —  $\text{Na}^+$  and organic — quaternary ammonium salt. To study the effect of fillers, the compositions with three different concentrations for each filler were prepared. The PLA/nanoclay compositions were obtained by drying solutions of components in methylene chloride. Pyrolysis of solid composites was carried out in a flow tubular reactor and volatile decomposition products were condensed in methylene chloride. Analysis by gas chromatography with mass spectrometric detection showed a significant effect of each of the fillers on the mechanism of thermal destruction of PLA. Based on the obtained results, a mechanism of thermal transformations of PLA in the presence of nanoclays is proposed.

**Keywords:** polylactide; nanoclays; thermal destruction; pyrolysis; gas chromatography – mass spectrometry

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## Figure Captions

**Figure 1** Chemical structure of the Cloisite 30B cation where T is an alkyl substituent ( $\sim 65\%$   $\text{C}_{18}$ ,  $\sim 30\%$   $\text{C}_{16}$ , and  $\sim 5\%$   $\text{C}_{14}$ )

**Figure 2** Total ion current chromatograms of pyrolysis products: PLA without additives (a) and PLA / Closite Na composite (b)–(d) with a filler content of 1%, 5%, and 10%, respectively

**Figure 3** Total ion current chromatograms of pyrolysis products: PLA without additives (a) and PLA / Closite 30B composite (b)–(d) with a filler content of 1%, 5%, and 10%, respectively

**Figure 4** Scheme of possible directions of lactides formation and cyclic oligomers during PLA pyrolysis: thermal decomposition of the polymer chain with free end groups (a) and the hindrance of these decomposition directions after interaction with nanoclays (b)

**Figure 5** Scheme of 1,3-dimethyldioxalan-4-one's formation in the case of free end groups of PLA (a) and the difficulty of this direction after interaction with nanoclays (b)

## Table Captions

**Table 1** Pyrolysis products of PLA and its composites PLA / Closite Na with indication of yield times and percentage content of mixture components calculated using Eq. (1) relative to the total peak area

**Table 2** Pyrolysis products of PLA and its composite PLA / Closite 30B with indication of yield times and percentage content of mixture components calculated using Eq. (1) relative to the total peak area

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## References

1. Dana, R., and F. Ebrahimi. 2023. Synthesis, properties, and applications of polylactic acid-based polymers. *Polym. Eng. Sci.* 63(1):22–43. doi: 10.1002/pen.26193.
2. Farah, S., D. G. Anderson, and R. Langer. 2016. Physical and mechanical properties of PLA, and their functions in widespread applications — a comprehensive review. *Adv. Drug Deliver. Rev.* 107:367–392. doi: 10.1016/j.addr.2016.06.012.
3. Naser, A. Z., I. Deiaba, and B. M. Darras. 2021. Poly(lactic acid) (PLA) and polyhydroxyalkanoates(PHAs), green alternatives to petroleum-based

- plastics: A review. *RSC Adv.* 11:17151–17196. doi: 10.1039/D1RA02390J.
4. DeStefano, V., S. Khan, and A. Tabada. 2020. Applications of PLA in modern medicine. *Engineered Regeneration* 1:76–87. doi: 0.1016/j.engreg.2020.08.002
  5. Shao, L., Y. Xi, and Y. Weng. 2022. Recent advances in PLA-based antibacterial food packaging and its applications. *Molecules* 27(18):5953. doi: 10.3390/molecules27185953.
  6. Standau, T., C. Zhao, S. M. Castellón, C. Bonten, and V. Altstädt. 2019. Chemical modification and foam processing of polylactide (PLA). *Polymers – Basel* 11(2):306. doi: 10.3390/polym11020306.
  7. Wang, C., Z. Ren, S. Li, and X. Yi. 2018. Effect of ramie fabric chemical treatments on the physical properties of thermoset polylactic acid (PLA) composites. *Aerospace* 5(3):93. doi: 10.3390/aerospace5030093.
  8. Trivedi, A. K., M. K. Gupta, and H. Singh. 2023. PLA based biocomposites for sustainable products: A review. *Advanced Industrial Engineering Polymer Research* 6(4):382–395. doi: 10.1016/j.aiepr.2023.02.002.
  9. Horváth, T., T. J. Szabó, and K. Marossy. 2020. Polylactic acid as a potential alternatives of traditional plastic packagings in food industry. *Int. J. Management Science Engineering Management* 5(2):123–129. doi: 10.21791/IJEMS.2020.2.16.
  10. Réti, C., M. Casetta, S. Duquesne, S. Bourbigot, and R. Delobel. 2008. Flammability properties of intumescent PLA starch and lignin. *Polym. Advan. Technol.* 19:628–635. doi: 10.1002/pat.1130.
  11. Li, S., H. Yuana, T. Yua, W. Yuana, and J. Rena. 2009. Flame-retardancy and anti-dripping effects of intumescent flame retardant incorporating montmorillonite on poly(lactic acid). *Polym. Advan. Technol.* 20:1114–1120. doi: 10.1002/pat.1372.
  12. Zhan, J., X. Liu, T. Yang, and C. Cao. 2019. Flammability properties of intumescent flame retardant polylactic acid /layered silicate nanocomposites. *IOP C. Ser. Earth Env.* 332:032046. doi: 10.1088/1755-1315/332/3/032046.
  13. Maqsood, M., and G. Seide. 2020. Biodegradable flame retardants for biodegradable polymer. *Biomolecules* 10:1038. doi: 10.3390/biom10071038.
  14. Gilman, J. W. 1999. Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. *Appl. Clay Sci.* 15(1-2):31–49. doi: 10.1016/S0169-1317(99)00019-8.
  15. Lomakin, S. M., and G. E. Zaikov. 2005. Flame-resistant polymer nanocomposites based on layered silicates. *Polymer Science Ser. B* 47(1-2):9–21. EDN: KFWCP.
  16. Kalendova, A., J. Smotek, P. Stloukal, K. M. Kracalik, M. Slouf, and S. Laske. 2019. Transport properties of PLA/clay nanocomposites. *Polym. Eng. Sci.* 59:2498–2501. doi: 10.1002/pen.25251.
  17. Singha, S., and M. S. Hedenqvist. 2020. A review on barrier properties of poly(lacticacid)/clay nanocomposites. *Polymers* 12(5):1095. doi: 10.3390/polym12051095.
  18. Lai, S.-M., S.-H. Wub, G.-G. Lin, and T.-M. Don. 2014. Unusual mechanical properties of melt-blended poly(lactic acid) (PLA)/clay nanocomposites. *Eur. Polym. J.* 52:193–206. doi: 10.1016/j.eurpolymj.2013.12.012.
  19. Ibrahim, N., M. Jollands, and R. Parthasarathy. 2017. Mechanical and thermal properties of melt processed PLA/organoclay nanocomposites. *IOP Conf. Ser. — Mat. Sci.* 191(1):012005. doi: 10.1088/1757-899X/191/1/012005.
  20. Krishnamachari, P., J. Zhang, J. Lou, J. Yan, and L. Uitenham. 2009. Biodegradable poly(lactic acid)/clay nanocomposites by melt intercalation: A study of morphological, thermal, and mechanical properties. *Int. J. Polym. Anal. Ch.* 14(4):336–350. doi: 10.1080/10236660902871843.
  21. Bourbigot, S., and G. Fontaine. 2010. Flame retardancy of polylactide: An overview. *Polym. Chem. — U.K.* 1:1413–1422. doi: 10.1088/1757-899X/191/1/012005.
  22. Brevnov, P. N., L. A. Novokshonova, V. G. Krasheninnikov, M. V. Gudkov, E. V. Koverzanova, S. V. Usachev, N. G. Shilkina, and S. M. Lomakin. 2019. Influence of the chemical nature and structural characteristics of nanofillers on the mechanism of polyethylene pyrolysis. *Russ. J. Phys. Chem. B* 13(5):825–830. doi: 10.1134/S1990793119050026.
  23. McNeill, I. C., and H. A. Leiper. 1985. Degradation studies of some polyesters and polycarbonates-2. Polylactide: Degradation under isothermal conditions, thermal degradation mechanism and photolysis of the polymer. *Polym. Degrad. Stabil.* 11:309–326. doi: 10.1016/0141-3910(85)90035-7.
  24. Kopinke, F. D., and K. Mackenzie. 1997. Mechanistic aspects of the thermal degradation of poly(lactic acid) and poly( $\beta$ -hydroxybutyric acid). *J. Anal. Appl. Pyrol.* 40-41:43–53. doi: 10.1016/S0165-2370(97)00022-3.
  25. Usachev, S. V., S. M. Lomakin, E. V. Koverzanova, N. G. Shilkina, E. V. Prut, S. Z. Rogovina, A. A. Berlin, and I. I. Levina. 2022. Thermal degradation of various types of polylactides research. The effect of reduced graphite oxide on the composition of the PLA4042D pyrolysis products. *Thermochim. Acta* 712:179227. doi: 10.1016/j.tca.2022.179227.
  26. Lomakin, S., P. Brevnov, E. Koverzanova, S. Usachev, N. Shilkina, L. Novokshonova, V. Krasheninnikov, N. Berezhkina, I. Gajlewicz, and M. Lenartowicz-Klik. 2017. The effect of graphite nanoplates on the thermal degradation and combustion of polyethylene. *J. Anal. Appl. Pyrol.* 128:275–280. doi: 10.1016/j.jaat.2017.09.023.

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## Contributors

**Koverzanova Elena V.** (b. 1962) — senior research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; koverlena@list.ru

**Shilkina Nataliya G.** (b. 1973) — research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; tashi05@list.ru

**Usachev Sergey V.** (b. 1969) — Candidate of Science in chemistry, senior research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; usachevsv@inbox.ru

**Lomakin Sergey M.** (b. 1953) — Candidate of Science in chemistry, head of laboratory, N. M. Emanuel Institute of Biochemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119334, Russian Federation; lomakin@sky.chph.ras.ru