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„Hybrid composites of polylactide and organosilicon derivatives”

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SUMMARY

The topic of my doctoral thesis is "Hybrid composites of polylactide and organosilicon derivatives". The aim of the research was to investigate the possibility of using organosilicon derivatives: polysilsesquioxanes and cyclotetrasiloxanes functionalized with substituents capable of supramolecular interactions (hydrogen bonds and $n-\pi^*$ interactions) as polylactide (PLA) modifiers. Polylactide, as a "double green" biopolymer, is of great interest due to the natural origin of the raw materials used for its production, biocompatibility, biodegradability and compostability. Such materials become extremely important due to the increasing pollution of the natural environment with polymer waste and the depletion of fossil resources. Despite the advantages, PLA requires modification in order to improve its thermal and mechanical performance. Therefore, the new methods of its modification are sought for the production of biodegradable composites with enhanced properties. Application of aryl amide or hydrazide derivatives as additives that can form nanocrystals on cooling of the PLA melt is an interesting example. Formation of hydrogen bonds between PLA chains and these supramolecular structures leads to an effective nucleation of PLA.

Linear poly(silsesquioxanes) (LPSQ-R) functionalized with substituents containing side groups (COOH, COOMe, OH, C₆H₄F, C₆H₄CF₃, C₆F₅), which can interact with polyesters were designed as PLA modifiers. Their unique feature is the presence of a double main chain of ladder structure. It allows controlling the spatial distribution of functional groups grafted to silicon atoms, analogously to the effect exerted by supramolecular crystals of aryl amido/hydrazide derivatives in PLA melt. Their small-molecule analogs - cyclotetrasiloxanes (CX-R) - were used to estimate the influence of the structure of ladder polysilsesquioxanes on the properties of hybrid materials. The organosilicon derivatives were partially miscible with PLA and the strength of their interactions with the polyester matrix as well as their morphology (macromolecules or low molecular weight compounds) determined the degree of dispersion in PLA. Hybrid composite materials obtained in this way exhibited various physicochemical and mechanical properties, depending on the type and content of LPSQ-R and CX-R. Addition of LPSQ-R, depending on the type of the R functional group, influenced the course of the crystallization of the amorphous phase during heating and stereocomplexation, as well as the optical and mechanical properties of the blends. It should be emphasized that the material toughness increased significantly in the presence of LPSQ with COOMe, C₆H₄F, C₆H₄CF₃ and C₆F₅ groups while maintaining the high yield point of PLA. In turn, the addition of LPSQ-COOH, LPSQ-COOMe and LPSQ-OH significantly improved the thermal resistance of PLA. It is worth noting that compounds forming hydrogen bonds with fluorine atoms and $n-\pi^*$ interactions were used for the first time for modification of PLA. As a result, a significant improvement of barrier properties in amorphous films of PLA-based composites was achieved.