Influence of vulcanizing systems on the properties of polymer composites based on grafted block copolymers and dispersed crumb rubber

Volodymyr Myshak, Vita Seminog

Institute of Macromolecular Chemistry of National Academy of Sciences of Ukraine,
UKRAINE, Kyiv, 48 Kharkivske shausse, E-mail : myshak_vd@ukr.net

Abstract - Investigation of the influence of type vulcanizing system on the structuring of various types of grafted block copolymers based on functionalized oligomers of soybean oil, linseed oil, or low molecular weight synthetic rubber and their composites with crumb rubber was conducted.

Keywords - graft block copolymer, composites, vulcanizing system, crumb rubber, vegetable oils, ethylene-vinyl acetate copolymer.

Introduction

In modern conditions of growing deficit of hydrocarbon polymer raw materials the creation and production of polymer composite materials based on recycled polymeric materials [1, 2] and vegetable raw materials [3, 4] get the increasing urgency and importance. In particular, studies on the establishment of oligomers, polymers, block copolymers based on vegetable oils are developing intensively. Previously, we [5, 6] presented the possibility of synthesizing hydroxyl-containing oligomers based on linseed or soybean oils and synthesizing grafted block copolymers (GBC) on their basis by the reaction of urethane formation. The resulting block copolymers are of interest from the point of view of being used as compatibilizing additives in the creation of polymer composite materials and as polymer matrices. Taking into account that GBC contains oligomers based on vegetable oils (linseed or soybean) or synthetic low molecular weight rubber, and containing unsaturated double bonds, both in the composition of diglycerides and ethanolamides of fatty acids in vegetable oils, and in polybutadiene, this opens up the possibility obtaining vulcanized composite materials. The reactivity of double bonds of unsaturated diglycerides is the same as that of polybutadiene; therefore, the vulcanization methods successfully used in the formation of rubber can also be used for the polymerization of composites based on GBC, which contains oligomeric components based on linseed or soybean oils of low molecular weight butadiene rubber. Such composites differ fundamentally from ordinary filled thermoplastics in terms of their characteristics, features of production and processing, since they combine the properties of vulcanized rubbers (during operation) and thermoplastics.

The process of vulcanization of grafted block copolymers containing oligomeric blocks based on linseed or soybean oils or blocks of low molecular weight rubber is based on the reactions of unsaturated bonds and hydrogen atoms in the α position of GBC blocks with the components of vulcanizing systems. In this case, the rate of formation of cross-links depends primarily on the nature of the vulcanizing agent and the vulcanization accelerator.

Based on the above, the aim of this work was to study the effect of vulcanizing systems on the physical and mechanical properties of grafted block copolymers based on ethylene-vinyl acetate copolimer and vegetable oil oligomers or low molecular weight synthetic rubber and polymer composites based on them filled with crumb rubber.

Research results and discussion

Studies obtaining of hydroxyl-containing oligomers based on vegetable oils (linseed and soybean) and synthesis of graft block copolymers based on hydroxyl-containing oligomers and ethylene-vinyl acetate copolymer have been carried out by us. The presence in the obtained GBC

fragments of vegetable oils, which contain double bonds, allows the use of vulcanizing components for obtaining composite materials based on them. For research and the creation of composites, as a filler a crumb rubber (CR) obtained by grinding of depreciated tires were used. Composite materials based on 50% of GBC, 50% CR and a vulcanizing systems was prepared by mechanically mixing of the components with subsequent homogenisation of the obtained mixture in the extruder, under appropriate strain and temperature conditions.

Two types of vulcanizing systems were used for the vulcanization of the GBC. These were a sulfur-containing vulcanizing system which included sulfur - vulcanizing agent, accelerator of high activity type altaks (di (2-benzothiazolyl) disulfide), and vulcanization activator - zinc oxide (ZnO); and vulcanizing system, which did not contain sulfur and included tertrametilthiuramdisulfide (TMTD), Dithiodimorpholine (DTDM) and zinc oxide (ZnO). Passage of the vulcanization reaction and the chemical structure of the obtained samples were studied by FTIR spectroscopy.

The results show that both sulfur-containing and thiuramdisulfide-containing vulcanizing systems affect the process of structuring compositions, their physico-mechanical and thermal characteristics. In particular, when we introduce a cross-linking system in the GBC, the glass transition temperature interval and the specific heat capacity of the obtained copolymers decrease, and the glass transition temperature and the melting temperature increase. Tensile strength of the obtained copolymers increases up to 12%, Shore hardness increases too, while relative elongation decreases to 80%. This is due to the influence of formed crosslinks.

Conclusions

The obtained results can serve as an example for the industrial production of vulcanized composite material, using as a matrix graft copolymers based on functionalized oligomers of vegetable oils or low molecular weight synthetic rubber and vulcanizing systems such as sulfur-containing and thiuramdisulfide-containing. The selection of suitable accelerators, vulcanization activators, vulcanizing agents can significantly change the properties of polymer composite materials and obtain composites with a given set of physical and mechanical properties.

References

[1]. Rahimi, A., Garcia, J.M. (2017). Chemical recycling of waste plastics for new materials production. Nature Reviews Chem., 6 (1), 1-11. https://doi.org/10.1038/s41570-017-0046.

[2]. Maris, J., Bourdon, S., Brossard, J-M., Cauret, L., Fontaine, L., Montembault, V. (2018). Mechanical recycling: Compatibilization of mixed thermoplastic wastes. Polymer Degradation and Stability, 147, 245-266. https://doi.org/10.1016/j.polymdegradstab.2017.11.001.

[3]. Desroches, M., Escouvois, M., Auvergne, R., Caillol, S., Boutevin, B. (2012). From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products. Polymer Reviews, 52 (1), 38-79.

[4]. Changqing, F., Xiaoting, Q., Ruien, Y., Xin, Y., Jianjun, L., Jiang, Y., Ronghou, X. (2016). Influence of modification process parameters on the properties of crumb rubber/ ethylene-vinyl acetate copolimer modified. Journal of Applied Polymer Science, 133, 43598. https://doi.org/10.1002/app.435958.

[5]. Siryk O.M., Myshak V.D., Grishchenko V.K., Lebedev E.V. (2012). Synthesis and structural features of reactive oligomers based on vegetable oils. Polimerniy zhurnal, 34, (3), 293-297.

[6]. Myshak V.D., Siryk O. M., Grishchenko V.K., Syrovets A.P., Lebedev E.V. (2013). Graft block copolymer based on functionalized ethylene-vinyl acetate copolymer and reactive olygomers of soybean oil. synthesis, structure and properties. Polimerniy zhurnal, 35, (3), 312-320.