Modification of Waste Polypropylene by Styrene-isoprene Block-copolymers

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The paper presents a study on the waste polypropylene modification with styrene-isoprene block-copolymers in correlation with elastomers molecular weight. The modification of this polyolefin improves the mechanical properties, especially the impact strength.

Keywords: styrene-isoprene block-copolymers, waste polypropylene, melt blending

The more diversified properties and the lower price of plastic materials compared to other materials lead to a considerable expansion of their areas of use, and consequently exponentially increased their consumption, that is estimated to exceed 100 kg /capita in 2015 in European Community [1]. The same rate of increase in the amount of waste from obsolescence of plastic products is estimated, which forcefully impose recycling for environmental depollution. Considering that the synthesis of 90 % of plastics uses fossil non-renewable resources, also not inexhaustible, recycling, especially the mechanical one, becomes increasingly necessary [2, 3].

At European level, polypropylene has an important percentage, of about 18% of total recovered plastics [1], which explains the large number of articles and patents on the subject of its reintroduction in the economic circuit, both through individual recycling and through blending with other plastics. Because it leads to the obtaining of polypropylene composites with an assured using domain, individual recycling is preferred also by using a minimum amount of modifiers [1, 2, 4].

It is well known that most of polypropylene sorts have low impact strength, property that becomes even more deficient in case of waste of obsolete objects. This deficiency is most commonly corrected through polypropylene modification by melt blending with different elastomers. The intense research has established that styrene-diene block-copolymers, as such or hydrogenated, with or without various fillers, are the most effective impact modifiers for native polypropylene and especially for recovered one, leading to composites with performance properties compared to the original polymer, mainly with higher impact strengths [5-12]. In some patents and papers, styrene-isoprene block-copolymers, as such or hydrogenated, are mentioned to have a superior modification effect compared to styrene-butadiene block-copolymers [13, 14].

Based on these considerations, this paper presents the study on waste polypropylene modification by melt blending with styrene-isoprene block-copolymers, aiming mainly to reveal the molecular mass effect of thermoplastic elastomers on the polyolefin modification degree.

Experimental part

The linear styrene-isoprene block-copolymers used in waste polypropylene modification were synthesized by sequential anionic polymerization of the monomers in cyclohexane solution, reaction initiated with n-butyl lithium [15-19]. Styrene-isoprene block-copolymers (SIS) were stabilized after polymerization with 1 % 2,6-di-tert-butyl-4-methylphenol (TOPANOL-OC), directly in the cyclohexane solution from synthesis. SIS elastomers were separated from cyclohexane solution by a desolvation process based on solvent with stripping hot water and steam, the polymer final drying being accomplished in an oven under reduced pressure, at a temperature not exceeding 60°C.

The molecular weight of SIS elastomers and of the component blocks was determined by gel permeation chromatography (GPC). Physico - mechanical properties were determined on polymer films obtained by centrifugal casting from toluene solution, according to the specific characterization requirements of styrene-diene block-copolymers.

The styrene-isoprene block-copolymers were used for the melt modification of a polypropylene sort recovered mainly from food transport crates, which presented the following properties:

Density, Kg/cm^3: 0.8966
Crystallinity, %: 77
Impact strength at 20°C, kJ/ m^2: 6.4
Impact strength at -20°C, kJ/m^2: 3.8
Tensile strength, MPa: 17.8
Elongation at break, %: 166
Hardness, °Sh D: 72
Melt flow index, 190°C, 5 Kg, g/10 min: 7.8

The recovered polypropylene modification with styrene-isoprene block-copolymers was performed using a roller at optimum load capacity. The compounding recipes complied this load, the amount of styrene-isoprene block-copolymer being varied from 5 to 30%. The working temperature was 180-190 °C and a friction coefficient of 1.18 to 1.20 was used. Plates were made from the rolled sheets by pressing them at a temperature of 185-190°C for 15 min, under a pressure of 196 N/m^2, followed by a sudden cooling of the mold under pressure. During pressing, 2-3

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Crt. no.	Property	20 SIS – 1	20 SIS – 2	20 SIS – 3
1	Polystyrene content, %	19,8	20,1	19,9
2	Total molecular weight, g/mol	79600	102300	121200
3	Polystyrene block molecular weight, g/mol	7900	10300	12000
4	Polyisoprene block molecular weight, g/mol	63800	81700	97200
5	Tensile strength, MPa	7,20	7,25	7,70
6	Elongation at break, %	1520	1550	1580
7	Hardness, °Sh A	34	34	34
8	Melt flow index (190 °C, Kg), g/10 min.	9,4	8,3	7,1
9	T_g of the polystyrene phase, °C	90	90	91
10	T_g of the polyisoprene phase, °C	-61	-61	-60

Tabel 1
STYRENE-ISOPRENE BLOCK-COPOLYMERS PROPERTIES

short depressurizations were made to eliminate air bubbles. In these conditions, plates of 1 mm thickness were obtained for dynamic physico-mechanical properties and thermal behaviour (DSC), and plates of 4 mm thickness for hardness tests. From these 4 mm plates, were stamped unnotched specimens necessary for Izod impact strength determination.

Tensile properties were carried out using a FPZ 100 dynamometer, with an elongation rate of 50 mm/min , on type 5A specimens stamped from the 1 mm plates, according to SR EN ISO 527-96.

Shore hardness in D scale was measured on the 4 mm pressed plates.

Izod impact strength was determined at +20 °C and -20 °C, on unnotched specimens stamped from the 4 mm plates, according to SR EN ISO 180-2009, using a Ceast instrument.

The melt flow index was determined on a laboratory plastometer, according to SR EN ISO 1133-93, at 190 °C, under 5 kg loading.

Results and discussions

The melt blending of recovered polypropylene with styrene-isoprene block copolymers led to polyolefin morphological changes, regarding both crystalline and amorphous phases. It was found that the change of amorphous phase plays the main role in the impact strength improvement for polyolefins with high crystallinity, the effect depending on the dispersion degree and size of the elastomeric particles scattered in the amorphous polyolefin matrix [20-23]. In melt blending of incompatible polymers or polymers with low compatibility, it has been shown that the uniform and optimal dimensional dispersion is achieved most likely when the components melt viscosity are close [24-29]. In order to meet this blending criterion, the molecular weight variation for the styrene-isoprene block-copolymers was limited to the range 80.000-100.000 g/mol. This range of molecular weight gives to SIS elastomers a melt rheological behaviour similar to that of recovered polypropylene, as confirmed by the melt flow indexes from table 1.

The synthesized styrene-isoprene block-copolymer had 20% polystyrene, composition that gives them performance physico-mechanical properties (table 1).

Introducing styrene-isoprene block-copolymers in the polyolefin matrix leads to a decrease of the crystallinity of polyolefin composites, the effect being amplified with increasing their amount in the system, as can be seen in figure 1. There is a linear decrease of the crystallinity degree correlated with increasing the styrene-isoprene block-copolymers content in the composite, this indicating a

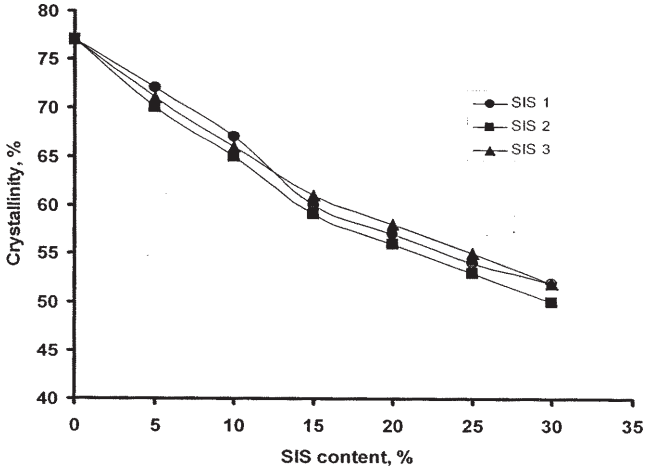

Fig. 1 Variation of the crystallinity degree of polypropylene composites depending on styrene-isoprene block-copolymers content

preferential partition of elastomers in polyolefin amorphous phase. Also the effect of the molecular weight on the crystallinity degree, at the same dosage of block-copolymer, is smaller due to the elastomers minimal presence in the polyolefin crystalline phase, but it can still been observed that the styrene-isoprene block-copolymer with the molecular weight of 100.000 g/mol (SIS 2) disturbs more the crystalline lattice of the polyolefin composites, throughout the melt blending domain.

Crystalline lattice weakening leads also to hardness decreasing of polypropylene composites, as can be seen from figure 2. The decrease of composites hardness is relatively uniform, following a simple, linear expansion rule of a hard material (polypropylene) with an elastic one (SIS bloc-copolymers).

As expected, the composites based on SIS 2 block-copolymer show the lowest hardness values because, as mentioned above, the percentage of crystalline phase in the system is the most reduced for this material.

The preferential distribution of styrene-isoprene block-copolymers in the polypropylene amorphous phase produces the material expansion, the effect being clearly highlighted by composites variation of tensile strength (fig. 3) and elongation at break (fig. 4) correlated with elastomers dosage.

The presence of small amounts of elastomer (up to 10 %) in the polyolefin matrix has a very favorable effect increasing both tensile strength and elongation at break. This can be explained by the balanced dispersion as domains of the styrene-isoprene block-copolymers in both

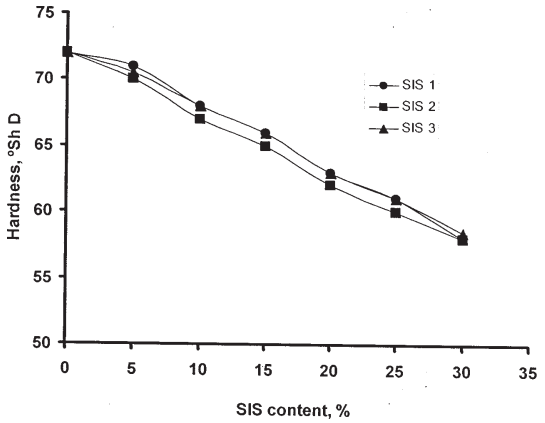

Fig. 2. Hardness variation of polypropylene composites depending on styrene-isoprene block-copolymers content

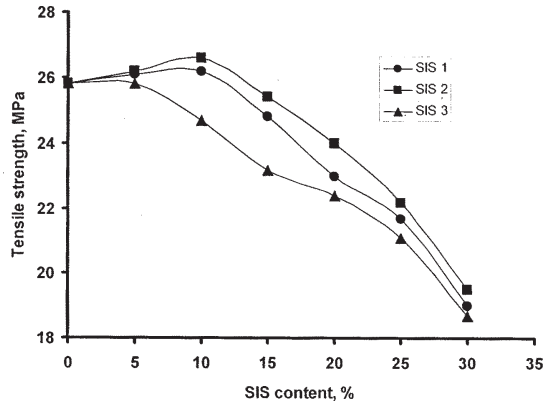

Fig. 3. Tensile strength variation of polypropylene composites depending on styrene-isoprene block-copolymers content

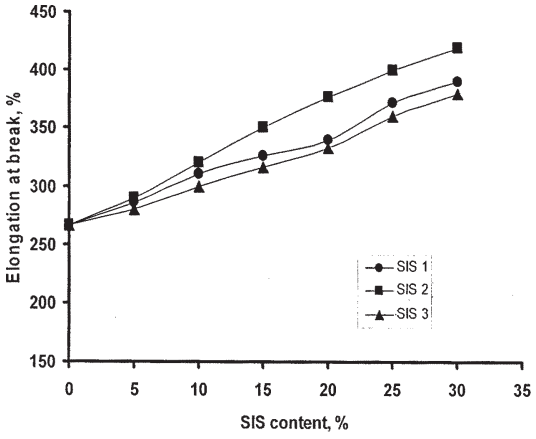

Fig. 4. Elongation at break variation of polypropylene composites depending on styrene-isoprene block-copolymers content

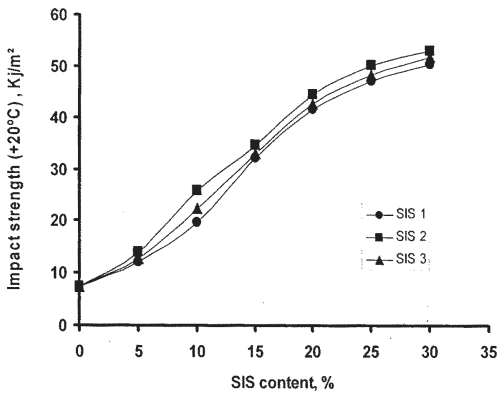

Fig. 5. Izod impact strength variation of polypropylene composites at +20 °C depending on styrene-isoprene block-copolymers content

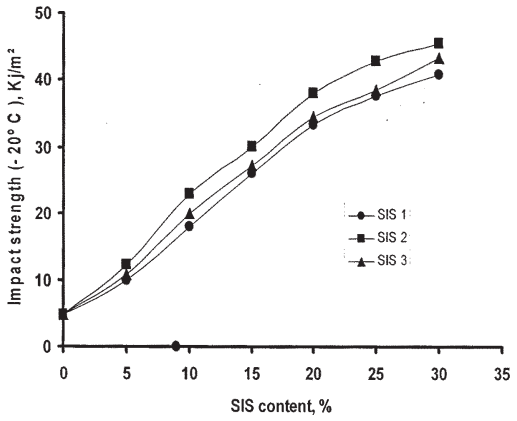

Fig. 6. Izod impact strength variation of polypropylene composites at -20 °C depending on styrene-isoprene block-copolymers content

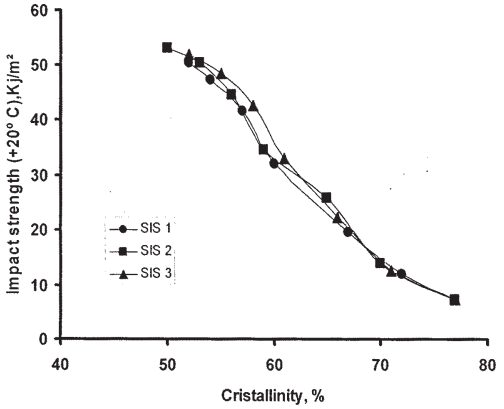

Fig. 7. Izod impact strength variation of polypropylene composites at +20 °C depending on the crystallinity degree

crystalline and amorphous polypropylene phase. The presence of elastic domains in the crystalline phase induces a decrease of its brittleness and allows a more uniform takeover of the mechanical tensile stress, leading to an increase of composites tensile strength.

The elastomeric domains dispersed in polypropylene amorphous phase acts as a plasticizer at these first dosages allowing a better material stretching and thus also the increase of elongation at break. At a higher dosage of styrene-isoprene block-copolymers in composites, to more than 15 %, their expansion effect in prevalent and consequently increases the elongation at break and decreases the tensile strength. Maximum values were obtained for composites with block-copolymer SIS 2, as expected.

The appreciable increase of alloys impact strength at positive temperatures (fig. 5) and especially at negative ones (fig. 6) is the most important consequence of the increseas of the elasticity of polyolefin composites due to styrene-isoprene block-copolymers. The phenomenon can be strictly correlated with the decrease of crystallinity degree, as can be seen in figure 7 and 8.

SIS 2 styrene-isoprene block-copolymer gives to polypropylene composites the best impact strength values throughout the entire blending domain, the effect being more evident at negative temperatures. This property can be explained by the fact that SIS 2, showing the closest melt rheological behavior to that of polypropylene, assures an optimal dispersion in the polyolefin matrix, forming elastomer particles with the most suitable dimensions, able to absorb the energy, to redistribute the internal stresses and thus to more efficiently prevent the propagation of microcracks which appeared when the material is subject to mechanical shocks.

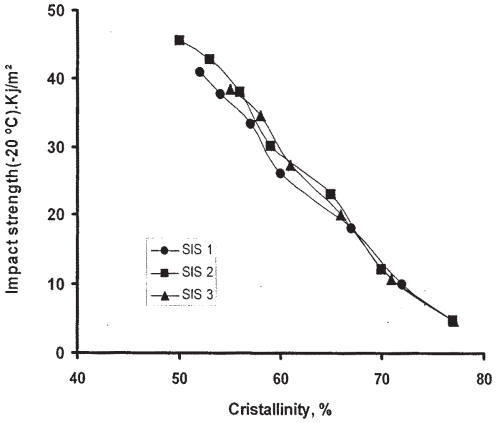

Fig. 8. Izod impact strength variation of polypropylene composites at -20 °C depending on the crystallinity degree

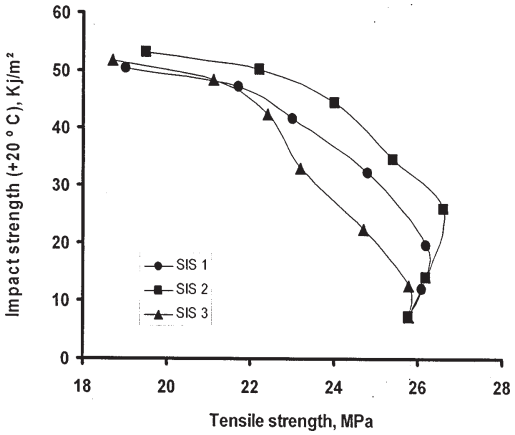

Fig. 9. Izod impact strength variation of polypropylene composites at +20 °C depending on the tensile strength

Patrick diagrams, charts that make correlations between the most important physico-mechanical properties of composites: impact and tensile strength are presented in figures 9 and 10, the dosage of the styrene-isoprene block-copolymers being increased gradually with 5 % from right to left.

Patrick diagrams allow an easy selection of styrene-isoprene block-copolymers dosage which provides an optimal balance between these two properties depending on the application of domain requirements. The highest values composites impact and tensile strength, given by the styrene-isoprene block-copolymer of 100.000 g/mol molecular weight on the recovered polypropylene, is also evidenced by these charts as the most favorable effect.

Conclusions

The study of recovered polypropylene blending with styrene-isoprene block-copolymers revealed that the modification effect depends on the viscosity of thermoplastic elastomers, property that was controlled and guided through the molecular weight during their synthesis.

Polypropylene composites of all styrene-isoprene block-copolymers presented an optimal balance between tensile and impact strength for current applications for these materials at a content of 10 % SIS elastomers. The best properties of recovered polypropylene composites were given by the styrene-isoprene block-copolymer of 100.000 g/mol molecular weight and with 20 % polystyrene.

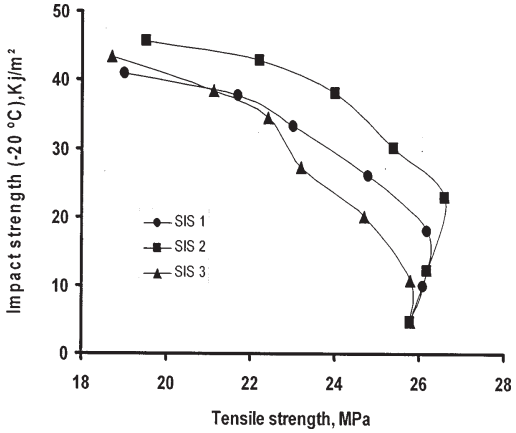

Fig. 10. Izod impact strength variation of polypropylene composites at -20 °C depending on the tensile strength

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