IMPROVEMENT OF MECHANICAL, THERMAL AND MORPHOSTRUCTURAL PROPERTIES OF SBS THERMOPLASTIC ELASTOMER USING KAOLIN AND DOLOMITE MICROPARTICLES WITH MODIFIED SURFACE

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The aim of this paper was to assess the influence of the modification of the surface of dolomite and kaolin with SiO₂ and TiO₂ precursors, on the block copolymer styrene-butadiene-styrene (SBS) type thermoplastic rubber properties. These composite materials were obtained by compounding SBS with various ratio of powders. Based on the SEM images it can conclude that the powders were homogeneously dispersed in to the SBS matrix. The dolomite particles can be clearly identified in the SEM images as particles of 10 micrometers. The samples obtained with modified dolomite have similar morphology. The EDS elemental distribution confirming a good corroboration between the elements of the dolomite, kaolin and titanium or silicon elements. Based on the thermal analysis according to the residual mass, the presence of 20% mineral phase can be confirmed. According to the DSC curves a strong stabilization of the composite appears, because of the presence of the mineral component. According to the physical-mechanical data all the composite materials exhibit improved mechanical properties. Additionally, the modification of the kaolin and/or dolomite bring important improvements in mechanical properties. The samples 13 and 14 exhibit high tensile and tear strength. These composites can be used for various applications, such as, for instance, soles for firefighters' footwear.

Keywords: SBS thermoplastic rubber, interface, functionalization.

INTRODUCTION

Styrene-butadiene block copolymers are an important class of synthetic rubber, composed of central rubber blocks and polystyrene ends. Hard styrene blocks induce mechanical and abrasion resistance, while butadiene improves flexibility and toughness. SBS rubber is widely used as an impact modifier in various plastics and adhesives, sealing materials, gaskets, rubber bands for wires and cables, shoe soles, toy parts and bitumen-based products for road paving and roofing applications, etc. (Jin *et al.*, 2021). To improve performance (mechanical, thermal, etc.), styrene-butadiene-styrene (SBS) rubber is often compounded with other polymers (PP, PS, etc.) and/or other reinforcing agents (TiO₂, SiO₂, carbon black, clay, talcum, graphene, CaCO₃, MgCO₃, multi-walled carbon nanotubes-MWCNTs, fullerene (C60), nanodiamond, etc.) (Bicy *et al.*, 2018; Abdelsalam *et al.*, 2019; Das *et al.*, 2019; Sönmez *et al.*, 2019; Costa *et al.*, 2014; Perov, 2018). However, the interaction between the rubber matrix/filler is affected by several factors such as the chemical/physical interactions between the surface of the filler/polymer particles, the structure of the filler network, the shape, size, proportion of the filler, etc.

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(Abdelsalam *et al.*, 2019). In the literature, there are no studies on the effect of dolomite and/or kaolin microparticles functionalized with SiO₂ and TiO₂ precursors on the physical-mechanical, morpho-structural and thermal properties of SBS rubber. Improving the properties of SBS rubber is of major importance in the industry, as it is used in a wide range of applications and by using low cost and high availability fillers, improved properties can be obtained.

MATERIALS AND METODS

Materials

The following raw materials were used for the processing of composites: Styrene-butadiene-styrene rubber (SBS) - type Eurruber from Tecnofil SME, Italy; Kaolin - calcined (Snowpague), with particle size from 2 to 50 µm and layer thickness from 13.2 nm to 19.25 nm, purchased from Bridgexim SRL; DOLOFLOR dolomite powder, with the following composition: CaO - 30-33%, MgO - 18-20%, pH = 9.67, neutralization number - 59.55% CaO, particle size of several tens of µm, manufacturer SC CEMROM SA.

Method

Composites based on SBS reinforced with 5g kaolin powder and/or varying amounts (30-75g) of modified/unmodified dolomite relative to 100g SBS were obtained according to Table 1.

Table 1. Formulation based on SBS rubber reinforced with modified/unmodified particles, wt ratio

Sample code / Raw materials	SBS	11	12	13	14	15
SBS Rubber	100	100	100	100	100	100
Kaolin	-	5	-	-	-	-
Kaolin/10%PDMS	-	-	5	-	-	-
Kaolin/10%TiO ₂	-	-	-	5	-	-
Dolomite	-	30	-	-	-	-
Dolomite/5%TEOS+5% PDMS	-	-	30	-	-	20
Dolomite/5%TEOS+5% TiO ₂	-	-	-	30	20	-
Dolomite/10%TiO ₂	-	-	-	-	55	-
Dolomite/10%PDMS	-	-	-	-	-	55

The surface of kaolin and dolomite was modified by a methodology similar to the one described in the article published by Sönmez *et al.* (2019). Prior to the actual processing on the Brabender, the first step was assigned to drying the raw materials at 100°C in a hot air oven for several hours. The second stage consisted of processing the composites on a Brabender mixer, at 160°C and at different rotational speeds (30 rpm, ~1 minute, and at 130 rpm, ~3 minutes). Depending on the amount of powder added (mixtures 14 and 15), the processing time increased by 2-3 minutes or until the total and uniform incorporation of the powders into the SBS mass took place. From the processed mixtures, plates with the size of 150x150x4 mm (length x width x thickness) were obtained in a metal mold, by the hot compression method. Press processing parameters: the temperature of the platters (upper and lower) was set at 170°C, preheating and pressing time – 4 minutes, cooling the platters – 10 minutes. From the resulting composite plates, specimens with standardized dimensions

and shapes were stamped (dumbbell specimen – tensile strength, elongation at break, modulus, and from the trouser-type specimen – tear strength was determined), in order to perform physical-mechanical tests. Following the physical-mechanical determinations, the tested specimens were used for thermal (DSC-TG) and morpho-structural analyses (SEM, EDS).

RESULTS AND DISCUSSION

Energy Dispersive Spectroscopy (EDS) and SEM Analysis

Figure 1. SEM image, EDS spectra and map of: Sample 11 (A, A' and B); Sample 12 (C, C' and D) and Sample 13 (E, E' and F)

Figure 1, image A for sample 11 in which the reinforcing agents are not chemically modified, kaolin and/or dolomite particles can be observed but also defects (of the order of tens of μm) due to the detachment of the dispersed phase, which denotes a weak interaction between phases. In image C of sample 12, due to surface modification, the large defects visible in sample 11 are not specific, probably due to a better matrix/reinforcing agent interaction. In sample 13 the morphology changes considerably, the polyhedral reinforcing agent particles seem to be better embedded in the polymer matrix,

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and the rupture takes place mainly through the SBS matrix. The EDS elemental distribution (Figure 1, images B, D and F) confirming a good corroboration between the elements of the dolomite and titanium or silicon elements. The EDS spectra (images A', C' and E') highlight the presence of component elements in dolomite (mainly Ca, Mg), kaolin (Al, Si, Fe) (Sönmez *et al.*, 2019) and functionalizing agents (and additionally from PDMS, and/or silica from TEOS, Ti element).

DSC-TG Thermal Analysis

Figure 2. Thermal analysis of SBS rubber (left) and Sample 14 (right)

Thermal analysis performed on SBS rubber shows a relatively good stability up to 190°C (0.5% mass loss being caused by the elimination of traces of solvent – endothermic effect with a minimum of 75.4°C). In the interval 190-250°C there is a mass loss of 2.44%, accompanied by an exothermic effect with a maximum of 217.6°C, which indicates an oxidation phenomenon. The main stage of mass loss (78.89%) takes place in the range of 250-490°C and is accompanied in the first part by an exothermic effect with a maximum of 359°C, then by an endothermic effect generated by breaking some bonds and eliminating fragments such as C₁₁H₁₂ (1-cyclopentene-1-yl-benzene). In the range 490-635°C there is a mass loss of 3.85%, the process being accompanied by two separate effects with maximums at 494.9 and 611.7°C (both exothermic effects are wide and asymmetric indicating several overlapping reactions). In principle, in this interval the residual carbon mass is oxidized. The last stage, between 635-820°C represents an endothermic decomposition process (mass loss is 5.56% and the minimum effect is at 781.1°C). The residual mass is 8.75% and can most likely be associated with the filler used in SBS stabilization.

Sample 14 is relatively stable up to 190°C (0.57% mass loss being caused by the elimination of traces of solvent – endothermic effect with a minimum of 68.9°C). In the interval 190-250°C there is a mass loss of 2.13%, accompanied by an exothermic effect with a maximum of 231.5°C, which indicates an oxidation phenomenon. This process takes place at a slightly higher temperature than in the control SBS sample, indicating that the incorporation of dolomite has a protective role against this oxidation process. The main stage of weight loss (42.19%) takes place in the range of 250-470°C and is accompanied by two exothermic effects, partially overlapping with maximums at 363°C

and 430.5°C. Basically, the addition of dolomite delays the first oxidation process and modifies the decomposition mechanism, intervening in this interval a second oxidation process. In the range 470-625°C there is a mass loss of 6.35%, the process being accompanied by two separate effects with maximums at 520.6 and 594.4°C (both exothermic effects are wide and asymmetric indicating several overlapping reactions). In principle, in this interval the residual carbon mass is oxidized. Although we have less organic matter, we have more residual carbon mass burned during this time. A possible explanation is given by the fact that in the previous stage, instead of the elimination of some large organic molecules, only a partial oxidation took place. The last stage, between 625-860°C, represents an endothermic decomposition process (mass loss is 20.71% and the minimum effect is at 805.2 and 826.4°C plus a shoulder at a lower temperature). The endothermic effect is clearly formed by the superposition of at least 3 individual endothermic effects. The lower temperature shoulder is also associated with the existing filler in SBS. The other two effects are specific to dolomite. It is normal for the mass loss at this stage to be higher, because in addition to the decomposition that was present in SBS, we also have the decomposition of dolomite in the sample. The residual mass is 28.06%, white-gray, consisting mainly of metal oxides. Considering approximately 8% the residual mass related to SBS and based on the thermal analysis of dolomite (Sönmez *et al.*, 2020), it can be estimated that the mass of the reinforcing agent is ~40% which is in accordance with the proposed working method.

Physical-Mechanical Characterisation

Table 2 shows the physical-mechanical values obtained for SBS-based composites reinforced with kaolin and/or various amounts of dolomite. In the case of mixtures containing kaolin and modified/unmodified dolomite (samples 11-13) respectively modified dolomite powder (samples 14-15) tensile strength, presents values with 130, 141, 212, 182 and 94% higher compared to the control sample – SBS. A similar trend was observed in the case of the module at 300%, elongations at break and tear strength, these being clearly higher compared to the control test – SBS. This clearly demonstrates that the modification of the surface of kaolin and/or dolomite with SiO₂ and TiO₂ precursors contributes to the reduction of the surface energy between phases, which leads to a good compatibility and implicitly to improved mechanical properties.

Table 2. Values of physical-mechanical characteristics of SBS and composites

Symbol /Property	SBS	11	12	13	14	15
Hardness, °ShA	60±0.05	80±0.05	85±0.1	89±1	91±0	96±2.1
Tensile strength, N/mm ²	1.29±0.13	2.97±0.26	3.11±0.07	4.03±0.08	3.64±0.07	2.5±0.13
Modulus at 300%	-	2.87±0	2.89±0.04	4.03±0.08	-	2.23±0.3
Elongation at break, %	120±57.73	320±34.64	340±20	300±0	300±0	360±3
Tear strength, N/mm	8.97±1.84	17.11±0.71	17.79±0.17	21.52±1.15	23±0.01	16±0.19

These improved mechanical properties are maintained even at high amounts of dolomite, compared to the data presented in the literature, where even the addition of 5% dolomite in PC/ABS reduces tensile strength and elongation at break, and the amounts between 10-15% almost completely compromise the properties due to the high susceptibility of dolomite to the phenomenon of agglomeration and void formation

(Ezenkwa *et al.*, 2019). Similar observations of diminishing elongation at break were also reported in the case of SBS/nanoCaCO₃ composites (at a loading degree of only 1-3 phr), attributed to the restriction of polymer chain mobility (Vahidi and Azizi, 2017).

CONCLUSIONS

Composite materials based on SBS and modified or unmodified kaolin and/or dolomite were obtained. According to the mechanical properties, it can be concluded that surface modification of the fillers can bring important improvements especially for tensile and tear strength. Furthermore, the presence of the filler leads to important thermal stabilization. These composites can be used for various applications, such as, for instance, soles for firefighters' footwear.

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