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Modification of styrene-isoprene-styrene triblock copolymer with a core-shell filler

RAPID COMMUNICATION

Summary — Mechanical properties of composite materials based on triblock poly(styrene-*b*-isoprene-*b*-styrene) copolymers (SIS) and modified with two different grades of core-shell fillers (core — silsesquioxane microgel, shell — grafted polystyrene, particle diameters 15.7 and 17.7 nm, respectively). Significant improvement — almost 60 % increase in tensile strength, relative elongation at break reaching 700 % — was observed in case of a high molecular weight (M_w) copolymer at the maximal filler concentration of about 2 wt. % and longer chains of the polystyrene-shell. The rheological properties of nanocomposites differed with respect to the non-modified copolymer — softening of the material at higher temperatures was noticed.

Key words: thermoplastic elastomers, nanocomposites, microgels grafted with polymers, rheological properties, mechanical properties.

TRÓJBLOKOWY KOPOLIMER STYREN–IZOPREN–STYREN MODYFIKOWANY NAPEŁNIACZEM O STRUKTURZE RDZEŃ–OTOCZKA

Streszczenie — Zbadano właściwości mechaniczne kompozytów trójblokowych kopolimerów poli(styren-*b*-izopren-*b*-styren) (SIS) modyfikowanych dwoma różnymi napełniaczami o strukturze rdzeń-otoczka (rdzeń — mikrożel polisilseskwioksanowy, powłoka — zaszczepiony polistyren, średnice nanocząstek, odpowiednio 15,7 lub 17,7 nm). Zaobserwowano poprawę właściwości badanych materiałów na skutek napełniania, zwłaszcza w przypadku kopolimerów o dużym ciężarze cząsteczkowym (M_w) (tabela 1), zawartości napełniacza nieprzekraczającej 2 % mas. i dłuższych łańcuchach w polistyrenowej otoczce (tabela 3, rys. 1 i 2). Stwierdzono wystąpienie różnic we właściwościach reologicznych nanokompozytów w stosunku do wyjściowych kopolimerów (rys. 3). W podwyższonej temperaturze zaobserwowano mięknienie materiału.

Słowa kluczowe: elastomery termoplastyczne, nanokompozyty, mikrożele zaszczepione polimerem, właściwości reologiczne, właściwości mechaniczne.

The substantial progress observed lately in the field of material science became particularly apparent in case of block copolymers and polymer-based nanocomposites [1—3]. Within the first group of materials thermoplastic elastomers (TPE) — like triblock copolymers of styrene and dienes (styrene-isoprene-styrene, styrene-butadiene-styrene) — have gained the highest attention mainly due to their commercial significance [4]. Physical properties of the TPE can be easily improved by introducing a filler, particularly in form of nanoparticles [5]. However, the inherent incompatibility of organic (polymer) and mainly inorganic (filler) compounds can severely hinder the proper dispersion of additive and, in consequence, lead to property deterioration [2, 3, 6, 7]. In order to reduce this risk chemical treatment of filler surface utilizing appropriate low-molecular weight compounds (*e.g.* silanes) is usually suggested [7]. At last high interest is also related to the methods of nanoparticle modification *via* polymer grafting that could ensure almost perfect compatibility between the matrix and a filler [8, 9]. Modifications in the controlled manner — like atom transfer radical polymerization (ATRP) are especially interesting.

In case of block copolymers such hybrid, core-shell nanoparticles (with hard inorganic core and soft, polymer shell) can be used for selective modification of chosen domains. This relatively new issue has been extensively studied by several research teams mainly with respect to achieve the defined spatial arrangements of nanostructures that result in *e.g.* unique electrical pro-

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perties [10]. The matrix-filler interactions depend on the properties of both: the copolymer (molecular weight, block length and sequence) and polymer-grafted nanoparticles (diameter, molecular weight and grafting density of polymeric chains) [10, 11]. Due to spatial limitations imposed by the copolymer matrix (ratio of particle-domain dimensions [D/L] must remain as low as possible, at least smaller than 1 [10]) silsesquioxane-derived nanostructures constitute the appropriate filler. Good examples are polyhedral oligosilesquioxanes (POSS) [12, 13] or silsesquioxane microgels [14, 15].

In the current report we mainly concentrate on defining and optimizing of the conditions favoring selective modification of the styrene-isoprene-styrene (SIS) triblock copolymer using a core-shell, silsesquioxane microgel based nanofiller. The spatial distribution of filler depends just on the entropic factors (related to dimensions of nanoparticles, grafting density and molecular weight of the polymeric shell, *etc.*) in contrast to the systems described elsewhere [16] where the regulary shaped POSS cubes (so called T8-POSS particles defined by chemical structure $R_4Si_8O_{12}$, where R denotes organic substituent) were grafted onto block copolymer chain affecting directly mobility of matrix chain. Subsequently the effect of modification was evaluated with respect to the mechanical and rheological properties.

EXPERIMENTAL

Materials

Two styrene-isoprene-styrene triblock copolymers (SIS) were used as matrices:

— Vector 4411A which is commercial product of Dexco Polymers,

— TB-2 prepared *via* sequential anionic polymerization at the Max Planck Institut für Polymerforschung (MPIP) in Mainz.

Core-shell nanostructures were used as a filler. The silsesquioxane colloids (core) were synthesized in an O/W microemulsion. While optimizing preparative route [15] we referred to the method described by Baumann *et. al.* [14] and Lindenblatt *et. al.* [17]. Microgel nanoparticles with diameters ranging from 11.4 to about 23.4 nm and exhibiting low polydispersity index *PDI* = 1.07—1.42 were obtained. The surface of colloid was modified with silane compounds bearing functional groups' activity in ATRP processes [15].

The polystyrene (PS) chains constituting the shell were grafted in surface-initiated, controlled free-radical polymerization of styrene according to the ATRP mechanism [with catalyst CuBr/$CuBr_2$, toluene as solvent and pentamethyldiethylenetriamine (PMDTA) as a ligand] [15, 18]. Changing the ratio of copper salts and amount of particular initiator used (microgel) we were able to synthesize core-shell particles differing in M_w values of grafted chains and grafting density. However, taking into consideration the influence of D/L ratio we decided to use for further investigation the smallest particles denoted P18 and P20 (diameters 15.7 and 17.7 nm, respectively, based on the microgel MG17 as it was described in details in [15]) as they were believed to fulfill this requirement.

Sample preparation

Nanocomposite samples were prepared *via* solution mixing (in toluene) and film casting. The toluene solutions (with average solid content of about 4—5 wt. %) were cast into the polytetrafluoroethylene (PTFE) dishes and left for slow solvent evaporation (about 8—9 days). Afterwards, the obtained films were dried under normal and reduced pressure (~30 mbar). In the latter case, the temperature was slowly rising from about 60 to almost 120 °C.

Methods of testing

The structure and some physical properties of the synthesized ATRP initiators, microgels, core-shell structures and SIS block copolymers were investigated directly after reactions using ^1H and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC) and small angle X-ray scattering (SAXS). All these methods were described in detail elsewhere [15].

The samples for tensile tests (thickness of 0,8—1,5 mm, width of 2 mm) were cut out directly from the films using appropriate die. The evaluation of the tensile strength (σ_r), stresses at 100 and 300 % relative elongation (σ_{100} and σ_{300}, respectively) and elongation at break (ε_r) was carried out using the Instron testing machine. The crosshead speed and gap were set for 100 mm/min and 14 mm, respectively.

The rheological properties were examined using RMS-800 rheometer and parallel plate setup (6 mm of diameter). The isochronal measurements were recorded for constant shear rate of 10 rad/s, within the temperature range 75—260 °C and at heating rate of 2K/min. In consequence, the temperature dependence of the components of complex shear modulus G^*, *i.e.* storage (G') and loss (G'') moduli, was obtained. The mastercurves of G' and G'' were calculated using the RSI Orchestrator software.

RESULTS AND DISCUSSION

The physicochemical properties of the SIS triblock copolymers and core-shell structures used in experiments are summarized in Table 1 and 2, respectively. These copolymers, differing in M_w value and internal structure of diene block, were characterized by the styrene content of over 40 wt. % and lamellar morphology. The Vector copolymer exhibited better elastic properties as a result of higher content of cis-1,4 monomer units, whereas the

TB-2 contained bigger PS domains. Mainly due to higher styrene content the shape of stress-strain curves (Figures 1 and 2) differed from those observed for standard elastomers [19].

T a b l e 1. Properties of the investigated SIS copolymers

SIS	PS content[a] wt. %	M_w of PI block[b]	M_w of PS block[a]	*PDI* of copolymer[b]	Content of particular units in polyisoprene block[c], wt. %	
					cis-1,4	1,2./3,4
Vector	42.82	50000[d]	37 450[d]	1.25	76.09	7.16
TB-2	47.59	86640	78 680	1.06	38.42	42.49

[a] Calculated from ^{1}H NMR spectra. [b] Measured by GPC.
[c] Calculated from ^{13}C NMR spectra. [d] Estimated value.

T a b l e 2. Properties of the investigated core-shell fillers

Core-shell filler	Microgel (core)			Grafting density of the PS-shell[a] nm^{-2}	M_w of the grafted PS[b]	Core-shell diameter[a] nm
	diameter[a] nm	density g/cm^3	*PDI*[b]			
P18	11.4	1.70	1.06	0.54	11 750	15.7
P20			1.09	0.59	17 240	17.5

[a] Calculated from SAXS images.
[b] Measured with the GPC.

The core shell fillers were based on the same silsesquioxane core (11.4 nm average diameter) and differed in M_w and grafting density of PS chains (Table 2). By using of grafted chains of different lengths we wanted to evaluate the influence of this parameter on final nanocomposite performance. The silsesquioxane microgel MG17 (please refer to [15] for more details) was chosen due to specific properties of block copolymer matrices.

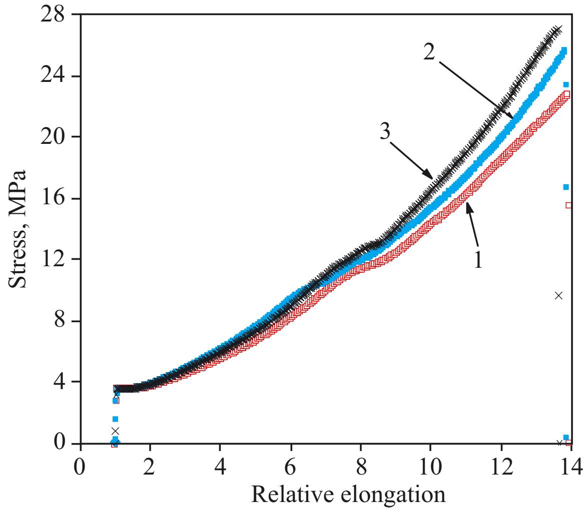

Fig. 1. Stress-strain curves of typical low-filled nanocomposites based on the Vector SIS copolymer: 1 — without filler, 2 — with 2 wt. % of P18, 3 — with 1.5 wt. % of P20

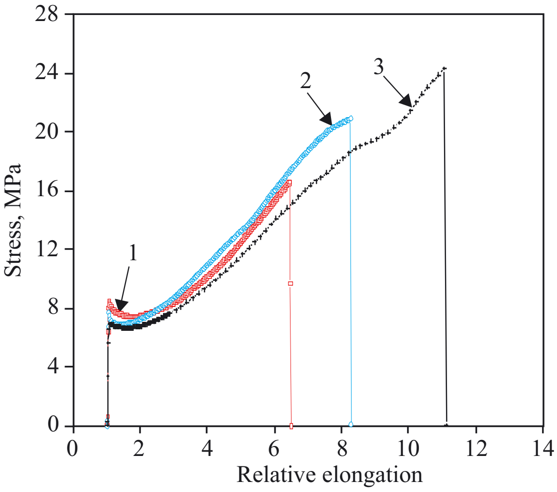

Fig 2. Stress-strain curves of typical low-filled nanocomposites based on the TB-2 SIS copolymer: 1 — without filler, 2 — with 2 wt. % of P18, 3 — with 1.5 wt. % of P20

The dimensions of the introduced filler and modified domains should at least be comparable.

T a b l e 3. Mechanical properties of the chosen nanocomposite materials based on Vector or TB-2 SIS copolymers

Type of core-shell filler	Filler content wt. %	σ_r MPa	σ_{100} MPa	σ_{300} MPa	ε_r %
Vector					
—	0	24.07	3.92	5.89	1255
P18	2.0	25.35	3.94	5.92	1253
	5.0	16.66	3.66	5.34	1167
P20	1.5	25.61	3.86	5.92	1241
	5.0	19.81	3.88	5.76	1180
SIS TB-2					
—	0	14.11	7.54	10.66	449
P18	2.0	20.08	7.35	8.78	642
	5.0	17.86	7.26	8.68	594
P20	1.5	22.19	6.73	7.79	864
	5.0	13.59	7.05	8.30	472

The nanocomposites based on the Vector copolymer containing up to 2.0 wt. % of nanoparticles were transparent, whereas at higher filler loadings traces of agglomeration could be observed. Unfortunately, the mechanical tests revealed that even in case of the low-filled mixtures the observed reinforcement was rather poor. Limited σ_r increase by 5.32 and 6.40 % was found for filler concentrations of 1.5 wt. % (P20) and 2.0 wt. %. (P18) (Table 3, Fig. 1). Significant deterioration of σ_r was observed at higher filler content, whereas ε_r remained almost unaffected. The results obtained for the Vector-based nanocomposites suggest that the nanoparticles remained predominantly agglomerated. In our opinion it could be related to disadvantageous M_w ratio of the PS blocks and grafted chains along with the unfavorable filler domain dimension ratio.

However, in case of the TB-2- based systems different effects were observed. The composite materials filled with up to 2 wt. % of the core-shell particles stood out with respect to the non-modified copolymer due to noticeably better mechanical performance. The addition of 1.5 wt. % of P20 nanoparticles led to reduction of the σ_{100} and σ_{300} stresses and concurrently significant reinforcement as manifested by the 60 % increase in σ_r value. Interestingly, in case of these low-filled systems the ε_r values simultaneously increased reaching the value of even 864 % (for 1.5 wt. % of the P20 filler). In comparison, the nanocomposite materials containing the P18 particles were characterized by slightly worse mechanical properties (optimal values of σ_{max} at 2 wt. % of nanoparticles), what led to conclusion that the reinforcement effect depended on the length of the grafted shell chains. From our point of view, the improved mechanical properties may suggest successful selective modification of the PS domains in the block copolymer matrix. This could originate from the growing number of entanglements that are formed between PS-blocks of the copolymer and shell chains.

The isochronal measurements were conducted for chosen nanocomposites based on TB-2 copolymer in order to investigate rheological effects of modification (Figure 3). The forms of G', G'' and tanδ curves were typical for the microphase-separated materials. Due to the internal structure of polyisoprene (PI) characterized by relatively low content of 1,4-units, the investigated nanocomposites exhibited the storage modulus G' of about 10^9 Pa already at about -30 °C. Owing to high styrene content G' decreased to only 10^7 Pa at the elastic plateau. Additionally, this copolymer showed no flow behavior at elevated temperatures probably due to the increased number of entanglements and high M_w value [19]. In case of the composite with 2 wt. % of P18 (short shell PS chains, M_w = 11750) a slight increase in the storage modulus was observed, however over about 140 °C one could observe faster softening of the material (compared to the neat TB-2 copolymer). The fact was clearly manifested by G' and G'' drop. In case of the composite with 5 wt. % of P20 (long shell PS chains, M_w = 17240) other effect was observed — over whole temperature range the measured G' and G'' values were reduced with respect to the base copolymer. At temperature below the glass transition temperature (T_g) of PS G' value was even 30 % lower. Compared to TB-2/P18 nanocomposite faster softening of the material was observed.

Within the experimental temperature window three maxima of tanδ were observed suggesting presence of different relaxation processes — the segmental relaxations of PI and PS blocks, respectively, followed by the terminal chain relaxation (around 195 °C). The latter process is strongly affected by the number of entanglements related to M_w of the matrix [20].

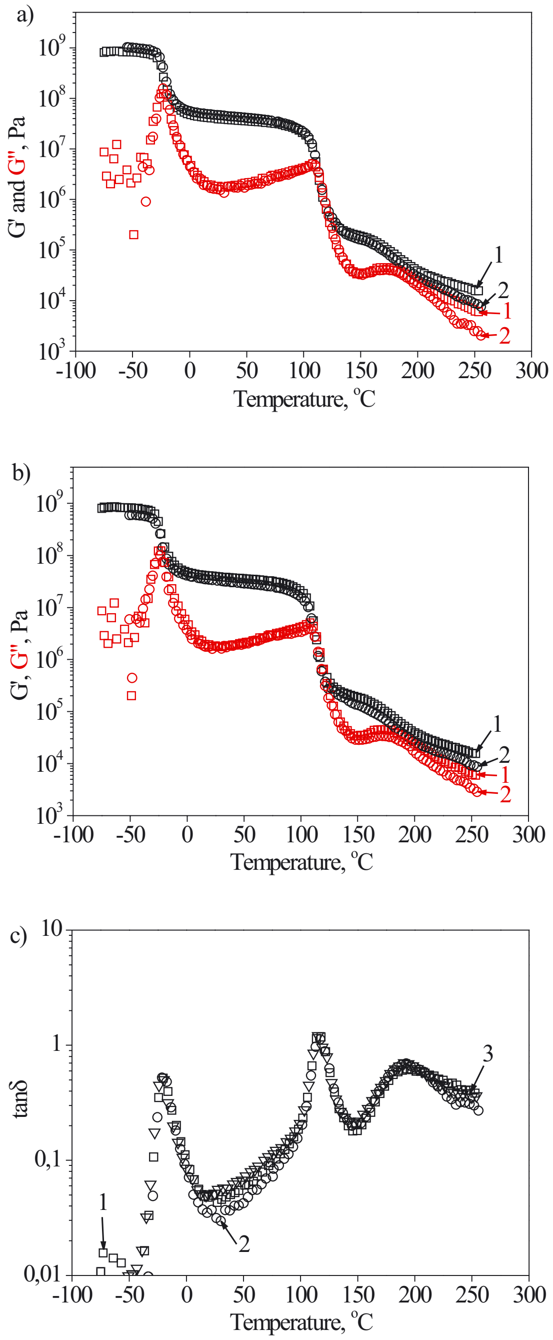

Fig. 3. G', G'' (a and b) and tanδ (c) mastercurves obtained during isochronal measurements of the nanocomposites based on TB-2 copolymer: 1 — without filler, 2 — with 2 wt. % of P18, 3 — with 5 wt. % of P20

The observed mechanical reinforcement and changes in rheological properties of TB-2 based nanocomposites must be related to the matrix-filler interactions. In our opinion, the suitable M_w ratio of grafted PS-chains and PS-blocks of copolymer favors the matrix molecules to migrate into the filler shell. However, further investigation is necessary in order to identify all factors defining the performance of the reported nanocomposites [21].

CONCLUSIONS

The presented results suggest that selective modification with hybrid fillers (compatible with a chosen block) can lead to distinct property improvement of the block copolymer matrix. However, in case of matrix-filler interactions numerous factors (M_w, grafting density, filler concentration, *etc.*) must be taken into consideration.

Below certain filler concentration (up to max. 2.0 wt. % in case of the P18 and P20 particles) positive effect of modification manifested by the almost 60 % increase in σ_r and distinct improvement of ε_r can be observed. The changes are accompanied by the simultaneous reduction of σ_{100} and σ_{300}. Additionally, the observed modification effects depend on M_w of the shell chains. Utilization of a high M_w immobilized PS chains causes *e.g.* faster material softening.

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