European Polymer Journal 45 (2009) 996–1001

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Effect of filling mixtures of sepiolite and a surface modified fumed silica on the mechanical and swelling behavior of a styrene–butadiene rubber

Liliane Bokobza [a,*], Eric Leroy [b], Valérie Lalanne [b]

[a] Laboratoire PPMD, E.S.P.C.I., 10 rue Vauquelin, 75231 Paris Cedex, France
[b] CNRS, Laboratoire de Chimie Métallurgique des Terres Rares, 2 à 8 rue Henri Dunant, 94320 Thiais Cedex, France

ARTICLE INFO

Article history:
Received 17 September 2008
Received in revised form 11 December 2008
Accepted 17 December 2008
Available online 25 December 2008

Keywords:
Elastomers
Nanocomposites
Reinforcement
Silica
Sepiolite

ABSTRACT

A styrene–butadiene copolymer is filled with mixtures of pyrogenic silica combined with a silane coupling agent and fibers of organophilic sepiolite. The mechanical properties of the composites reveal that a mixture of double fillers impart to the elastomeric matrix a higher degree of reinforcement than that which would result from a simple addition of the two types of fillers. The swelling ratio of the composite containing the two types of fillers was found to highly decrease with regard to the pure polymer reflecting strong interactions with the matrix. The changes in the state of dispersion by adding the second filler were evaluated by transmission electron microscopy.

1. Introduction

In most of their industrial applications, elastomers are compounded with reinforcing fillers for improvement of their mechanical properties.

Owing to its strong interactions with hydrocarbon rubbers, carbon black has been shown to yield strong reinforcement effects but its presence makes rubber compound black and decreases their processability at high filler loadings. Silica is the other important reinforcing filler used in the rubber industry today. But silica particles are less compatible with hydrocarbon polymers than carbon black and tend to form a filler–filler network by hydrogen bonding through silanol groups present on their surface. On the other hand, ingredients of formulation used in sulfur cure systems can react with filler particles leading to a reduced state of cure. The use of silane coupling agents in combination with silica, brings a chemical coupling between the filler and the polymer that increases modulus and tensile strength and shifts the stress–strain curve closer to that obtained with carbon black [1–3].

The last few years have seen the extensive use of nanoparticles because of the small size of the filler and the corresponding increase in the surface area allowing to achieve the required mechanical properties at low filler loadings. Nanometer-scale particles including spherical particles such as silica generated in situ by the sol–gel process [4–8], layered silicates [9–13], carbon [14] or clay fibers [15–17] and multiwall or single-wall carbon nanotubes [18–22], have been used to reinforce rubber matrices.

Another alternative to conventionally filled elastomers that has not been exploited much in the literature, is the use of a blend of two fillers of different morphologies. Wang [23] showed that vulcanizates filled with blended filler systems (carbon black and silica without coupling agent, at different filler compositions) display a weaker Payne effect than that would result from a simple addition of the two single fillers. That suggests a less developed filler network in the filler blend compounds due to a weaker interaction between silica and carbon black aggregates than between two aggregates of any single filler. One of

---

* Corresponding author.
E-mail address: Liliane.Bokobza@espci.fr (L. Bokobza).

0014-3057/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2008.12.028

the most important commercial hybrid fillers is carbon–silica phase dual filler produced by pyrolyzing petroleum based feedstocks and silicon based feedstocks, a unique co-fuming technology developed by Cabot Corporation. This material, which consists of individual composite aggregates containing carbon and silica phases (a dual phase aggregate), was shown, when added to hydrocarbon rubber, to have higher polymer–filler interaction than a blend of silica and carbon black of equivalent silicon rubber [24]. Low-density polyethylene was filled with carbon black and carbon fibers in order to move the percolation threshold to a reduced filler content [25]. The authors reported that the incorporation of carbon fibers into polyethylene/carbon black composites provides long conductive pathways to bridge uncontacted carbon black aggregates. In a previous paper [26], we showed that filling an elastomeric matrix with two different types of fillers was a promising way to achieve a good reinforcement level at fairly low filler loading since it allows a better use of the filler capabilities and synergetic effects between both of them. Results obtained on natural rubber submitted to a double loading (spherical silica particles generated in situ via the sol–gel process and nanofibers of sepiolite) were presented and discussed. Very recently, the reinforcement of a styrene–butadiene rubber by mixtures of carbon black and multiwall carbon nanotubes was also investigated [27]. A better dispersion of the fillers as well as a significant improvement in the tensile properties was observed for the sample containing a dual phase.

The present work reports investigations performed on a styrene–butadiene copolymer filled with mixtures of an organophilic sepiolite and fumed silica used with a coupling agent. Mixtures of fumed silica and sepiolite have been already used by Martínez-Ruiz et al. [28] as fillers of solvent-based polyurethane, especially for the low cost of sepiolite with regard to that of fumed silica. The purpose of the authors was to obtain, with sepiolite + fumed silica mixtures, rheological, mechanical and adhesion properties of polyurethane adhesives, similar to those obtained by using fumed silica alone but without specific treatment of sepiolite to separate the fiber aggregates.

The main objective in our work is to analyze, by transmission electron microscopy, how mutual effects between the two types of fillers can modify the arrangement of particles within the matrix. Stress–strain measurements and swelling behavior of the composites are used to assess the extent of reinforcement.

2. Experimental section

2.1. Materials

The styrene–butadiene rubber contains 25 wt% of styrene units. The microstructure of the butadiene phase is the following: 10% cis, 17% trans, 73% 1,2. The formulations used in this work are shown in Table 1.

Silica (Aerosil 300 from Degussa) is a hydrophilic fumed silica with silanol groups on the surface and with a specific area of 300 m^2/g. The silane coupling agent, the bis-(3-triethoxysilylpropyl) tetrasulfide (also supplied by Degussa), commonly abbreviated 'Si69', is a bifunctional sulfur-containing organosilane used in the rubber industry in combination with fillers that carry silanol groups.

Table 1
Formulations of the rubber compounds.

Ingredients (phr)	
Rubber	100
Sulfur	1.1
Diphenyl guanidine (DPG)	1.45
Zinc oxide	1.82
Stearic acid	1.1
Cyclohexyl benzothiazole sulfenamide (CBS)	1.3
SiO_2	0, 5, 10
Si69	0, 0.4, 0.8
Sepiolite	0, 1, 3, 4, 5, 10

All the ingredients are in parts per hundred parts of rubber (phr).

Sepiolite (Pangel B20 from Tolsa) was kindly offered by le Comptoir des Minéraux et Matières Premières (France). Sepiolite, which belongs to phyllosilicate group, is a hydrous magnesium silicate, with a crystal structure formed by two sheets of tetrahedral silica units bonded to a central sheet of magnesium atoms. Internal channels run along the entire length of the structure. The microfibres of sepiolite stick together and form bundles. The Pangel B20 is an organophilic sepiolite, obtained from pristine sepiolite by means of specific physico-chemical purification, micronization and chemical modification processes developed and patented by Tolsa. The micronization leads essentially to a disagglomeration of the bundles of microfibres thus favoring interactions between sepiolite particles and polymer chains. On the other hand, the hydrophilic surface of sepiolite was modified with surfactants (unspecified quaternary ammonium salt) in order to make it more compatible with low polarity polymers. The infrared spectrum of sepiolite (Pangel B20) displays bands located at 2927 and 2856 cm^{-1} associated with the C–H stretching vibrations of methylene groups that proves that the clay particles have been organically modified.

2.2. Preparation of the composites

In this study, the fillers (single filler or mixtures of double fillers) were incorporated into the polymer before the cross-linking process by the usual technique of blending. The mixing sequence was the following:

- One single filler (silica or sepiolite) was dispersed in toluene with a magnetic stirrer for half an hour. Dispersion of silica is followed by addition of the silane coupling agent, 'Si69' (8% by weight of silica as recommended by the supplier [1]), incorporated in order to increase the interaction between filler and rubber. In the case of double filling, sepiolite is added to the toluene solution about 30 mn after the introduction of the coupling agent and the mixture is further stirred for a homogeneous dispersion.

– The gum containing the styrene–butadiene copolymer and all the ingredients of formulation was dissolved separately in toluene under magnetic stirring for about 12 h then mixed with the filler dispersion. The solvent was then carefully evaporated at room temperature then under vacuum at 50 °C.

The unfilled and filled samples were cured into plaques at 170 °C during 10 mn under a pressure of 150 bar in a standard hot press. The resulting films were around 200 μm thick.

2.3. Analysis and characterization

The morphology, structure and state of dispersion of the filler particles within the elastomeric matrix were observed on a FEI Tecnai F20 and on a JEOL 2000EX Transmission Electron Microscopes, operating at 200 kV. Ultra-thin sections (50–60 nm) were prepared using a Leica Ultracut UCT ultramicrotome fitted with a 35° diamond knife. During the preparation, the samples were cooled at −80 °C by liquid nitrogen and put onto copper grids.

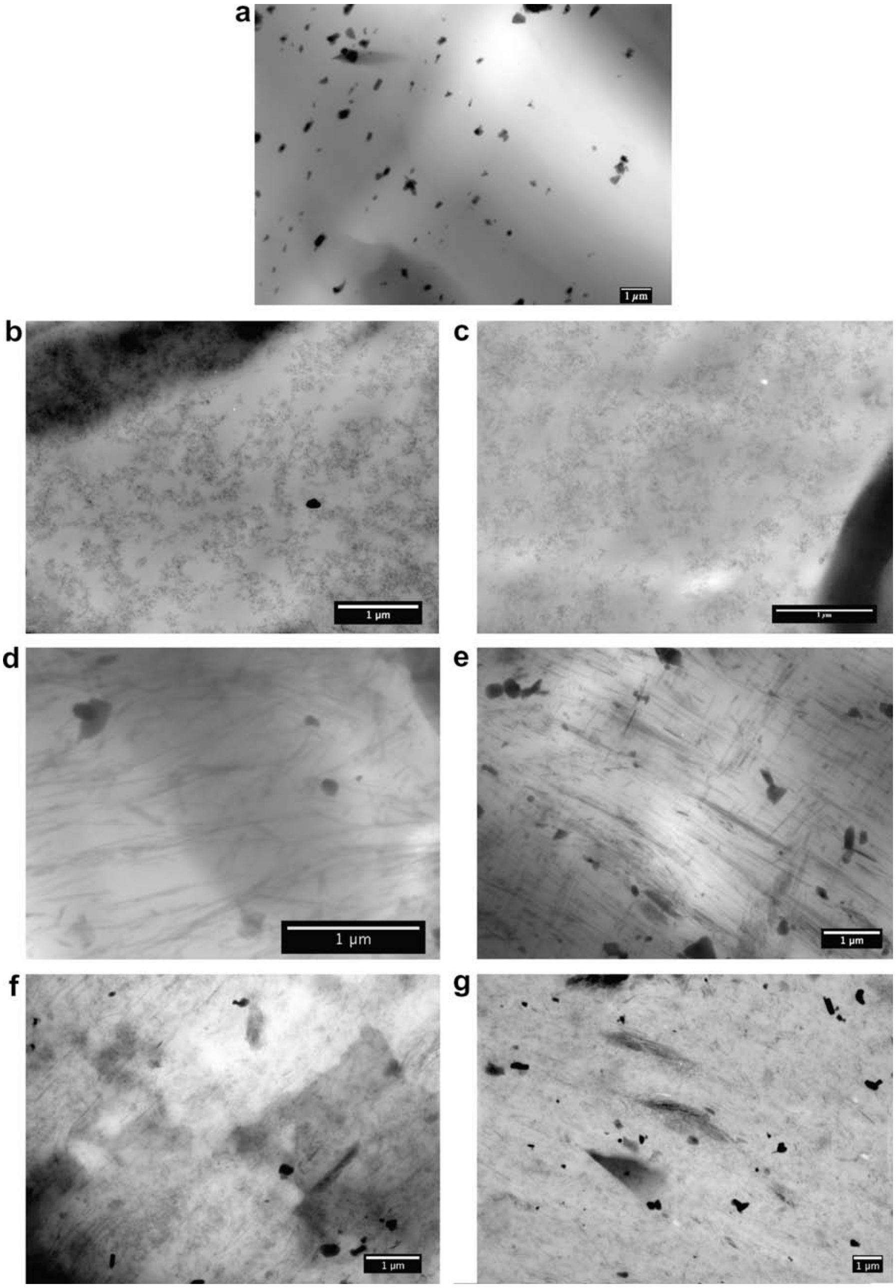

Fig. 1. Typical TEM micrographs of: (a) pure SBR, (b) SBR + 5 phr SiO_2, (c) SBR + 10 phr SiO_2, (d) SBR + 5 phr sepiolite, (e) SBR + 10 phr sepiolite, (f) and (g) SBR + 5 phr SiO_2 + 5 phr sepiolite.

The strain–stress measurements were carried out at room temperature on strips of $50 \times 5 \times 0.2\ \text{mm}^3$ between two clamps by means of a sequence of increasing weights attached to the lower clamp. The distance between two marks on the sample was measured with a cathetometer after allowing sufficient time (10 min after adding a weight) for equilibration.

For swelling experiments, strips of dimensions $20 \times 10 \times 0.2$ mm were immersed in toluene at room temperature for three days and the lengths and the widths changes were measured in the immersed state by means of a Digimatic Caliper from Mitutoyo, with an accuracy of 0.01 mm. The swelling ratio Q, defined as the ratio of the volume of the swollen to unswollen composite, were expressed as:

$$Q = [L_{\text{swollen}}/L_{\text{unswollen}}]^3 \ \text{or}\ [l_{\text{swollen}}/l_{\text{unswollen}}]^3,$$

L and l being related to the length and width of the sample.

3. Results and discussion

3.1. Transmission electron microscopy

Fig. 1 represents typical TEM micrographs for the different samples observed. On pure SBR, the presence of large particles arising from the ingredients of formulation can be noted.

Typical TEM images of composite filled with silica aggregates are shown in Fig. 1b and c. The silica particles have a spherical shape with a diameter of about 10 nm. They are arranged in larger structures (agglomerates) of approximately 50–100 nm connected to each other and forming a continuous network. The space is not completely filled with the SiO_2 particles leaving some parts of the sample free of filler.

Fig. 1d and e shows the typical TEM images of composite filled with 5 and 10 phr of sepiolite. The particles are relatively well dispersed in the sample and exhibit their characteristic needle shape despite the occurrence of some bundles of microfibers. On the other hand, an orientation of the fibers along a given direction is clearly revealed. When the concentration of sepiolite increases, larger bundles are observed together with a tendancy to form an orthogonal network of fibers (Fig. 1e).

For the sample filled with a mixture of sepiolite and silica (Fig. 1f and g), the dispersion of both particles is totally different: the sepiolite fibers, still oriented, seem more separated and the space between them is filled with silica particles (Fig. 1f). A synergy between the two types of the filler phase is clearly evidenced.

3.2. Mechanical properties

Fig. 2 displays stress–strain curves for the pure styrene–butadiene rubber (SBR) and for SBR composites and the mechanical properties are summarized in Table 2. Each single filler (silica + Si69 or sepiolite) incorporated in the matrix, imparts almost the same extent of stiffness which increases with the filler content. The results differ from those already published on the reinforcement of natural rubber provided by nanofillers such as in situ generated silicas and nanofibres of sepiolite [15]. It was shown that sepiolite fibers impart to natural rubber (NR) a higher degree of reinforcement than the spherical silica particles on account of their high aspect ratio. In styrene–butadiene

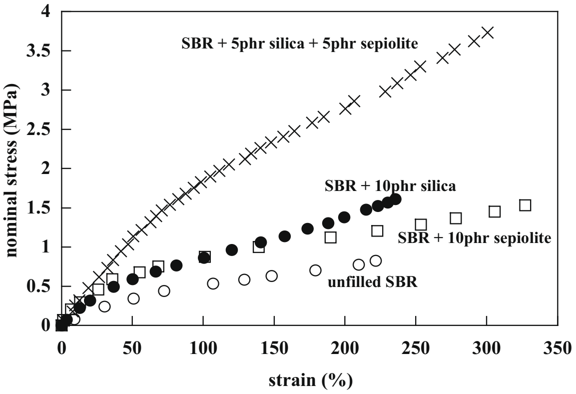

Fig. 2. Stress–strain curves for pure SBR and SBR composites. The filler content is expressed in phr (phr = parts per hundred parts of rubber).

Table 2
Mechanical properties of SBR and SBR composites.

Sample	Stress at 200% (MPa)	Tensile strength (MPa)	Elongation at break (%)	(Q_{rubber})[b,c]
Pure SBR	0.75	0.82	222	6.7
SBR + 5 phr silica[a]	1.08	1.45	274	5.5
SBR + 10 phr silica[a]	1.38	1.61	236	4.7
SBR + 5 phr sepiolite	0.93	1.41	353	5.8
SBR + 10 phr sepiolite	1.12	1.53	327	5.2
SBR + 5 phr silica[a] + 1 phr sepiolite	1.01	1.40	272	[d]
SBR + 5 phr silica[a] + 3 phr sepiolite	1.86	3.35	353	[d]
SBR + 5 phr silica[a] + 4 phr sepiolite	2.25	3.22	291	[d]
SBR + 5phr silica[a] + 5 phr sepiolite	2.76	3.73	301	2.8

[a] Used in combination with the coupling agent 'Si69'.

[b] Q_{rubber} represents the equilibrium swelling ratio of the rubber phase in toluene. It is calculated from the expression: $Q_{\text{rubber}} = (Q - \phi)/(1 - \phi)$, where Q is the equilibrium swelling ratio of the composite and ϕ is the volume fraction of filler.

[c] Determined with an experimental error of ±0.2.

[d] Not determined.

rubber, a comparable reinforcement is obtained for both silica and sepiolite filled composites. One reason may be that sepiolite has less interaction with SBR than with NR which causes a poor dispersion and consequently reduced interaction between the polymer and the filler. The presence of several agglomerates is revealed by transmission electron microscopy. On the other hand, silica used with Si69 produces a more significant reinforcement effect than that obtained with in situ generated particles which were growing within the preformed elastomeric network after hydrolysis of tetraethoxysilane used to swell the polymer. Moreover, the use of the coupling agent in this study, is expected to induce polymer–filler bonding that increases the modulus.

In recent papers of Bhattacharya et al. [16,17] dealing with rubber nanocomposites filled with a wide range of nanofillers, similar observations are reported concerning the effect of sepiolite on the two different hydrocarbon rubbers. The authors attribute the high extent of interaction between sepiolite and natural rubber to the fact that the linear chains of the polymer can get easily accommodated in the narrow channels of the sepiolite's structure. The lower interaction in the case of the styrene–butadiene copolymer can be ascribed to a reduced penetration of the macromolecular chains into the sepiolite's channels on account of the bulky styrenic side-chain substitutions with regard to the linear NR chains.

The most striking feature of the data presented in Fig. 2 and Table 2 is the strong reinforcement effect provided by the mixture of double fillers. The sample filled with a mixture of 5 phr of silanized-silica and 5 phr of sepiolite has a tensile strength of 3.73 MPa which is increased approximately 350% compared to pure SBR.

Adding increasing amounts of sepiolite to composites containing a constant silica content (5 phr) leads to larger increases in stress than adding increasing amounts of the same filler (Fig. 3 and Table 2). The increase in the modulus imparted by incorporation of sepiolite to silica, would reflect an increase in the cross-linking density created by polymer–fillers interactions. The obtained results lead to the belief that the mixture of fillers yields a better dispersion of sepiolite and thus a larger polymer–filler interface on account of the high aspect ratio of the clay fibers. This interpretation is confirmed by the examination of the equilibrium swelling ratios in toluene, listed in Table 2. The degree of adhesion between polymer chains and filler particles can be evaluated from equilibrium swelling of the composites in good solvents. The extent of swelling at equilibrium is reduced in the case of adsorption of polymer chains on particle surfaces and may be enhanced with non-adhering fillers due to a dewetting of the particles and vacuole formation [29]. Although swelling of the rubber phase decreases significantly with both single fillers, silica (used in combination with 'Si69') restricts a bit more than sepiolite as a result of improved interfacial properties and adhesion via the silane coupling agent. The mixture of fillers decreases strongly the swelling of the rubber, indicating enhanced polymer–filler interactions.

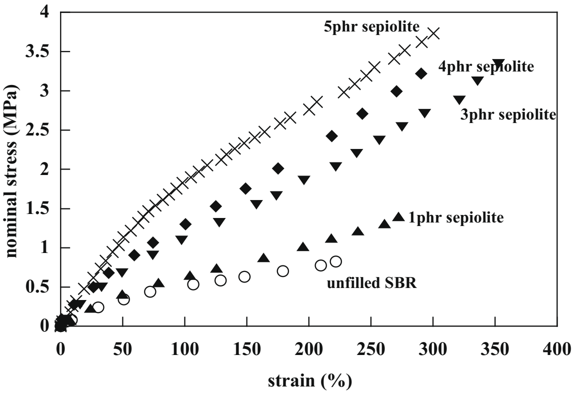

Fig. 3. Stress–strain curves of SBR filled with a constant silica content (5 phr) and different amounts of sepiolite.

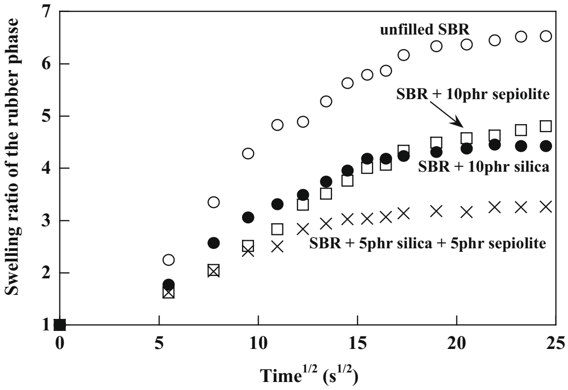

Fig. 4. Swelling behavior of the vulcanizates in toluene at room temperature.

Fig. 4 displays the swelling behavior of the vulcanizates, obtained by plotting the equilibrium swelling ratio of the rubber phase in toluene at room temperature. The sorption curves exhibit differences in the initial rates of diffusion. In the unfilled sample, there is no restriction for penetration of solvent molecules, the solvent uptake is the highest at small times. The samples filled with sepiolite shows, at the beginning of the sorption curve, a lower rate of diffusion than that filled with silica only. The reason may be due to the orientation of the clay particles that strongly restricts the solvent penetration in the direction perpendicular to the particle alignment. Finally, the lowest solvent uptake is observed for the sample filled with the mixture of double fillers.

4. Conclusion

It has been demonstrated that composites filled with mixtures of double fillers (pyrogenic silica + sepiolite fibers) exhibit improved characteristics with regard to single filler materials. The morphologies, mechanical and swelling properties reveal synergistic effects arising between the two types of fillers.

References

[1] Byers JT. Rubber World 1998;218:38.
[2] Seo G, Kaang S, Hong CK, Jung DS, Ryu CS, Lee DH. Polym Int 2008;57:1101.

[3] Liu J, Wu C, Zhang P, Zhao S. J Macromol Sci B 2008;47:689.
[4] McCarthy DW, Mark JE, Schaffer DW. J Polym Sci B: Polym Phys 1998;36:1167.
[5] Kohjiya S, Murakami K, Iio S, Tanahashi T, Ikeda Y. Rubber Chem Technol 2001;74:16.
[6] Yoshikai K, Ohsaki T, Firukawa M. J Appl Polym Sci 2002;85:2053.
[7] Bandyopadhyay A, De Sarkar M, Bhowmick AK. J Polym Sci B: Polym Phys 2005;43:2399.
[8] Dewimille L, Bresson B, Bokobza L. Polymer 2005;46:4135.
[9] Arroyo M, López-Manchado MA, Herrero B. Polymer 2003;44:2447.
[10] Varghese S, Karger-Kocsis J. Polymer 2003;44:4921.
[11] Sadhu S, Bhowmick AK. J Appl Polym Sci 2004;92:698.
[12] Liao M, Zhu J, Xu H, Li Y, Shan W. J Appl Polym Sci 2004;92:3430.
[13] Joly S, Garnaud G, Ollitrault R, Bokobza L. Chem Mater 2002;14:4202.
[14] Gauthier C, Chazeau L, Prasse T, Cavaillé JY. Compos Sci Technol 2005;65:335.
[15] Bokobza L, Chauvin J-P. Polymer 2005;46:4144.
[16] Bhattacharya M, Bhowmick AK. Polymer 2008;49:4808.
[17] Bhattacharya M, Maiti M, Bhowmick AK. Polym Eng Sci, Published online in advance of print: October 22, 2008, doi:10.1002/pen.21224.
[18] López-Manchado MA, Biagiotti J, Valentini L, Kenny JM. J Appl Polym Sci 2004;92:3394.
[19] Bokobza L, Kolodziej M. Polym Int 2006;55:1090.
[20] Bokobza L. Polymer 2007;48:4907.
[21] De Falco A, Goyanes S, Rubiolo GH, Mondragon I, Marzocca A. Appl Surf Sci 2007;254:262.
[22] Bokobza L, Belin C. J Appl Polym Sci 2007;105:2054.
[23] Wang M-J. Rubber Chem Technol 1998;71:520.
[24] Murphy LJ, Wang M-J, Mahmud K. Rubber Chem Technol 1998;71:998.
[25] Di W, Zhang G, Xu J, Wang X, Xie Z. J Polym Sci B: Polym Phys 2003;41:3094.
[26] Bokobza L. Compos Interfaces 2006;13:345.
[27] Bokobza L, Rahmani M, Belin C, Bruneel J-L, El Bounia N-E. J Polym Sci B: Polym Phys 2008;46:1939.
[28] Martínez-Ruiz A, Torró-Palau AM, Orgilés-Barceló AC, Martín-Martínez JM. J Adhes Sci Technol 2000;14:833.
[29] Kraus G. Adv Polym Sci 1971;8:155.