



Macromolecular Nanotechnology

Studies of molecular dynamics of carboxylated acrylonitrile-butadiene rubber composites containing in situ synthesized silica particles

Joanna Pietrasik^{a,*}, Magdalena Gaca^a, Marian Zaborski^a, Lidia Okrasa^b, Gisèle Boiteux^c, Olivier Gain^c^a Technical University of Lodz, Institute of Polymer and Dye Technology, Stefanowskiego 12/16, 90 924 Lodz, Poland^b Technical University of Lodz, Department of Molecular Physics, Zeromskiego 116, 90 924 Lodz, Poland^c Université de Lyon, Lyon F-69003, France; Université Lyon 1, CNRS, UMR5223, Ingénierie des Matériaux Polymères, 43 bd du 11 Novembre, Villeurbanne F-69622, France

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ABSTRACT

The molecular dynamics of carboxylated acrylonitrile-butadiene rubber – silica hybrid materials was investigated. Silica hybrids were formed in situ rubber matrix using varied amounts of *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DAMS), serving also as a cross-linker. Filler–filler and filler–rubber interactions were present, due to the specific nature of these materials. It was found that the amounts of added aminosilane determined the cross-linking density of obtained materials and was the highest with 20 phr DAMS used. The cross-links had ionic nature. Dielectric relaxation spectroscopy (DRS) revealed β , α and α' relaxation processes. The β relaxation, correlated with the mobility of polymer side groups, was influenced by the weak interaction between both acrylonitrile and carboxylic groups of the rubber and silanol groups of silica. The activation energy for that relaxation was similar for all materials (~ 32 kJ mol⁻¹). Both DRS and dynamical mechanical analysis (DMA) demonstrated that the amount of in situ formed silica filler did not significantly influence either the temperature of the α relaxation (correlated with glass transition) or its activation energy. Therefore, that relaxation was caused by free polymer chains, not attached to the silica particles. Similar values of glass transition temperature (T_g) for all hybrids were confirmed by DSC. It appeared that the amplitude of tangent delta (DMA) within T_g was dependent on silica amount. Detected at higher temperature α' relaxation resulted from the presence of domains, where polymer chains were affected by silica network, geometrical restrictions and morphology of the silica-rich domains.

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1. Introduction

Polymer additives are used in order to improve such physical properties of rubbers as processability, tensile strength, wear resistance, and performance. In many applications fillers, such as silica, carbon black and zinc oxide, cross-linking agents, dispersants and anti-degradants are

used as additives [1–14]. The properties of the final composite can be tailored depending on the formulation used.

The properties of filled materials are critically dependent on the interphase between filler and the polymer matrix [15–17]. According to the theory of filler reinforcement of polymers, the boundary layer of a matrix material is formed on the surface of the filler. The properties of polymers in the boundary layer are different from those in the bulk of the matrix material, mainly due to the decreased mobility of the adsorbed chains on the filler surface.

When the polymer matrix is a blend of two or more polymers, rubber–rubber interactions can appear.

* Corresponding author. Tel.: +48 42 631 32 08; fax: +48 42 636 25 43.
E-mail address: joanna.pietrasik@p.lodz.pl (J. Pietrasik).

However, they are considered not to be as significant as the interactions between filler and rubber or filler–filler, respectively.

Filler–filler interactions contribute significantly in the reinforcement mechanism, especially at high filler loading. The character of these interactions can be either physical (van der Waals, hydrogen bonding) or can result from the chemical interactions between filler particle surfaces. It can also be influenced by the morphology of the filler network and filler volume fraction.

Filler particles, *i.e.* silica which is very useful filler, are mostly composed of the primary particles, but some particles can be strongly bonded to other primary particles to form aggregates and agglomerates, which is an undesired behavior [17–21]. The dispersion of silica particles, especially very fine ones is a difficult task. Forces holding individual particles together are sufficiently strong to resist even very intensive grinding or mixing. Agglomeration processes are very complex in nature, but their prevention is necessary for the optimum design of reinforced rubber. Numerous efforts have been made in order to obtain homogenous dispersion of primary particles in a polymer matrix. The use of coupling agents [22–24], surfactants [25–29] or synthesis of silica *in situ* [30–42], are the most common examples. The separation of the filler particles especially on the order of molecular dimensions may have consequences for the matrix behavior.

Our research is focused on *in situ* synthesis of silica filler particles in an elastomeric matrix by the sol–gel process using *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DAMS). From our previous studies it appeared that the silica particle formation can take place even without the addition of water or methanol [43]. Furthermore, the amino groups on the alkyl substituents of the silane act as cross-linking moieties for the carboxylated acrylonitrile-butadiene rubber [44].

Silane cross-linking was also successfully applied to polyethylene [45,46] and halogen-containing rubbers [47,48]. The cross-linking reaction is composed of two steps: the reaction of the silane compound with the polymer and the condensation of silanol groups produced by hydrolysis of the alkoxy groups. It was of interests to determine the mobility of the system cross-linked with ionic bonds, created by the interactions of amino groups of the silane and carboxyl groups of the rubber. Moreover, the subsequent hydrolysis and condensation reactions of methoxy groups provided the *in situ* formed silica filler. Therefore, filler–filler and filler–rubber interactions are considered to be significant. In this paper, we describe the molecular dynamics of the resulting organic–inorganic hybrid materials, containing varied amounts of cross-linker (aminosilane), and therefore, silica filler, by means of dynamic mechanical analysis and dielectric relaxation spectroscopy.

There are some reports, which refer to the characterization and analysis of the electrical and dynamic mechanical properties of the *in situ* synthesized silica. For example, Liu et al. reported silica synthesis from tetraethoxysilane and 3-aminopropyltrimethoxysilane in polyimide via sol–gel process and proved that such composites in comparison to the one prepared by blending

demonstrated higher dielectric constant, dependent on the silica content and temperature [49]. Polyimide/silica nanocomposites properties were also studied by Fragiadakis et al. [50], Tsai et al. [51] and Wahab et al. [52]. Wang and Hsieh demonstrated the silica nanoparticles synthesized in UV-curable co-polyacrylate resin restricted the motion of functional groups in the matrix that the nanocomposite with satisfactory dielectric properties could be obtained [53]. Bandyopadhyay et al. investigated dynamic mechanical and thermal properties of the acrylic rubber/silica hybrid nanocomposites, in which silica was synthesized from TEOS. He showed that polymer–filler interactions could be illustrated by the loss tangent characteristic since the amplitude of the relaxation reflects the chain flexibility of the polymer molecules. Additionally, it is influenced by the silica particles size [54]. Since mechanical and dielectric properties of the hybrids of carboxylated acrylonitrile-butadiene rubber and sol–gel synthesized silica have not been extensively investigated and described in the literature, we decided to study this system in detail.

2. Experimental

2.1. Materials

Silica fillers were synthesized *in situ* from *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DAMS, Unisil) in a carboxylated acrylonitrile-butadiene rubber, containing 6.4% of carboxyl groups and 26.3% of acrylonitrile mers (XNBR, Krynac X 7.5, kindly donated by Bayer) randomly distributed along polymer chains. The silane was added during the preparation of rubber mixes and was also the cross-linking agent. Alternatively, a free radical initiator, dicumyl peroxide (DCP, Aldrich), was used as the cross-linking substance when no silica filler precursor was added. The composition of rubber blends was as follows: XNBR 100, DCP 0 or 1 phr (parts per hundred rubber), DAMS 0, 5, 10, or 20 phr, see Table 1.

A schematic structure of cross-linking nodes is shown in Scheme 1. The character of cross-linking bonds depends on the cross-linking agent. It is ionic in nature, when an aminosilane is added or it is a covalent C–C bond, when a free radical initiator is used.

2.2. Preparation of rubber mixes and vulcanizates

Rubber mixes were prepared at the temperature of about 35 °C with a laboratory two-roll mill, with roll dimensions of $D = 200$ mm and $L = 450$ mm. The rotational speed of the front roll was $V_p = 2$ s⁻¹ with friction coefficient $f = 1.1$. The duration in time for plasticizing the rubber was 4 min. After this period the other components

Table 1
Composition of rubber blends.

XNBR [g]	100	100	100	100
DCP [phr]	1	–	–	–
DAMS [phr]	–	5	10	20

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