Tailoring Assembly of Reduced Graphene Oxide Nanosheets to Control Gas Barrier Properties of Natural Rubber Nanocomposites

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S *Supporting Information*

ABSTRACT: Self-assembling of reduced graphene oxide platelets, as a tailored interconnected network within a natural rubber matrix, is proposed as a mean for obtaining nanocomposites with improved gas barrier, as compared to neat natural rubber. Interestingly, this nanocomposite structure results to be much more effective than homogeneous dispersion of graphene platelike particles, even at low graphene loadings. Such behavior is interpreted on the grounds of a theoretical model describing permeability of heterogeneous systems specifically accounting for self-segregated graphene morphology.

KEYWORDS: *nanocomposite, natural rubber, reduced graphene oxide, self-assembling, gas permeability, modelings*
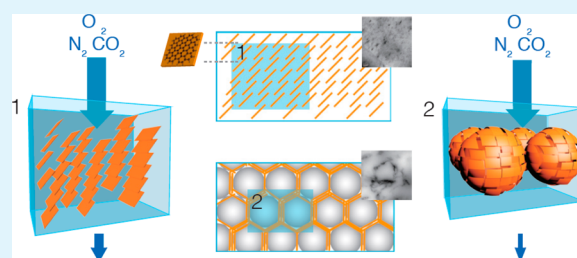
INTRODUCTION

Functional properties of natural rubber (NR)/reduced graphene oxide (RGO), such as electric conductivity or mass transport properties, can be properly controlled by tailoring the morphology of filler in the developed systems. Studies on systems in which graphene nanoparticles are used as functional filler for elastomers are available in the literature.[1] Their final properties are ruled by filler morphology and dispersion as well as by its interfacial interaction with the polymer. A satisfying uniform, homogeneous, and well-exfoliated graphene dispersion within an elastomeric material has been obtained by means of both a solution/suspension mixing of graphene oxide (GO) platelets followed by in situ reduction and by intercalating monomer/oligomers into interlayer spaces of GO, followed by in situ polymerization and chemical reduction.[2−4] On the contrary, a different spatial arrangements, in the form of an interconnected filler network within the natural rubber matrix, can be obtained by exploiting the self-assembly behavior of GO platelets. In fact, recently, JR Potts et al.[1] and some of the authors of the present contribution[5] have proposed, independently but almost simultaneously, an approach based on coagulation mixing of GO platelets with natural rubber latexes to prepare, by in situ reduction, a RGO nanocomposite masterbatch with a "segregated" three-dimensional network of RGOs. This structure originates from the confinement of platelets within the interstices of the coagulated latex particles, which act as a template for the network formation. The platelets are assembled on the latex particles giving rise to spheres with a core–shell structure with a partial or complete covering depending on graphene amount.[6] Moreover, a "not-

segregated" structure can be obtained by destroying this interconnected network processing the RGO nanocomposite masterbatch via twin-roll mixing. In this case, the graphene nanoparticles result exfoliated, uniformly oriented with respect to the sample surface and homogeneously dispersed within the rubber matrix.

In this contribution, the effect of both the segregated and not-segregated graphene morphology on the gas permeability of NR/RGO nanocomposites is addressed on the basis of the obtained experimental data and on their interpretation through theoretical models describing permeability of heterogeneous systems. It has been successfully proven that the obtainment of NR/RGO nanocomposites displaying a segregated network is a valuable tool to obtain a significant reduction of gas permeability with respect to the pristine rubber matrix. In fact, above a critical nanofiller content, latex spheres result completely coated by impervious RGO platelets forming a percolating and interconnected network that significantly increases the length of the diffusive path of low-molecular-weight molecules.

RESULTS AND DISCUSSION

The morphology of the segregated and not-segregated structures is shown in the Transmission Electron Microscopy (TEM) micrographs reported in Figure 1. Figure 1a, a′ illustrates the morphology of a segregated NR/RGO nano-
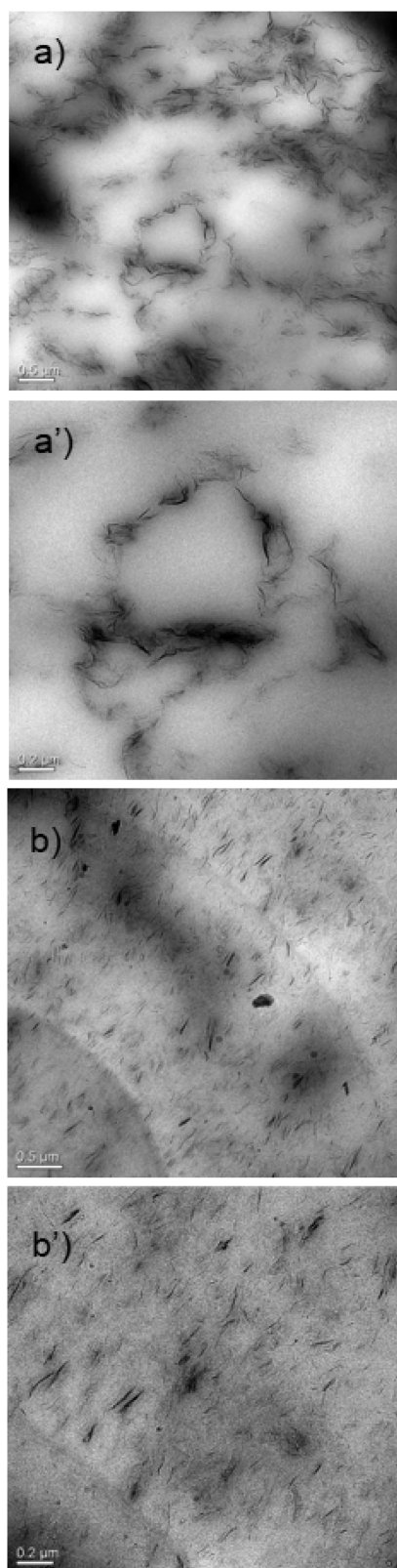
Figure 1. TEM of natural rubber/graphene composites with 3.38 vol % RGO prepared (a) by self-assembly in latex and static-hot pressing and (b) by self-assembly in latex and twin-roll mixing. (a′, b′) Magnified images of a and b, respectively.

composite with 3.38 vol % content of RGO, showing how platelets self-assemble on the surface of the NR latex particles, whereas micrographs reported in Figure 1b, b′ are related to

NR/RGO nanocomposites displaying the not-segregated morphology. Additional observations revealed that the structure of nanocomposites with both segregated and not-segregated morphology was somewhat homogeneous without micro- and macropores. An idealized schematic representation of the two different morphologies is reported in Figure 2. On the basis of
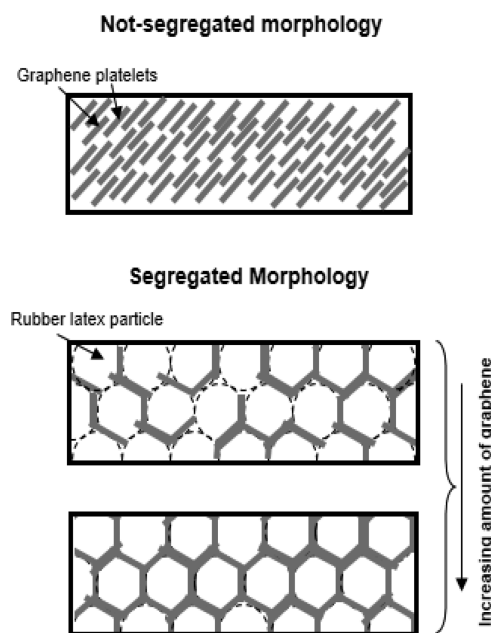

Figure 2. Schematic representation of the two different morphologies of natural rubber/graphene nanocomposites.

TEM micrographs, it is verified that the RGO nanoparticles display a thickness of ∼3 nm (i.e., two-three RGO platelets stack together) and that their aspect ratio is equal to 167. Furthermore for the "not-segregated" nanocomposite, a uniform orientation angle of the platelets comprised between 40 and 50° has been observed.

It has been proven that the two different morphologies display markedly dissimilar behavior in terms of relative permeability of gases (i.e., the ratio of nanocomposite permeability to the permeability of neat rubber matrix) as a function of RGO volumetric fraction. In Figure 3 it is reported, as an example, the case of oxygen permeability at 38 °C: for both morphologies, the relative permeability decreases as the
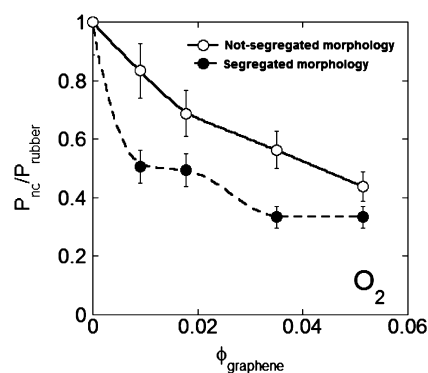

Figure 3. Oxygen relative permeabilities at 38 °C for the samples with not-segregated and segregated morphologies as a function of the volumetric fraction of graphene. Lines are only guides for the eye.

RGO content increases. Identical results have been obtained for all the investigated gases (i.e., oxygen, carbon dioxide, and nitrogen) at all the investigated temperatures (30, 38, and 48 °C) (see the Supporting Information). However, for all the investigated gases and at each volumetric fraction of RGO particles, samples with a segregated morphology display a permeability significantly lower than that of not-segregated specimens. Moreover, in the case of segregated specimens there is evidence of a double step decrease of the permeability, whereas, in the case of the not-segregated morphology, the permeability decreases steadily, with an initial slope markedly lower than that observed for the segregated morphology. This is to be ascribed to both the different orientation of the nanoparticles (iso-oriented at 40−50° in the "not-segregated" case and quasi-randomly oriented in the case of "segregated" ones) and the different topological arrangement of the nanofiller. However, we anticipate here that it is not possible to rationalize the observed differences in permeability only by invoking the different orientation of the particles. In fact, a NR/RGO nanocomposite characterized by randomly oriented particles, but not displaying the geometrical arrangement induced by the presence of latex spheres, would still be predicted to have a relative permeability higher than in the case of the "segregated" samples. Finally, it is worth noting that the cross-linking density of natural rubber depends on the nanocomposite preparation procedure, i.e., hot pressing or twin roll-mixing procedure. In particular, through preliminary chemical and structural analysis (i.e., NMR and SAXS analysis), it has been proved that the nanocomposites with segregated morphology have a rubber network characterized by cross-linking density lower than the one of samples with not-segregated morphology. This evidence further strengthens the finding that the segregated morphology is more effective in increasing the gas barrier properties of the samples.

To properly model the permeability results, it is worth accounting the effect of the presence of filler on the mass transport properties. Permeability of a penetrant within a neat polymeric film is determined by the combination of a kinetic factor, i.e., the diffusivity of penetrant molecules, and a thermodynamic factor, i.e. the penetrant solubility. A decrease of permeability can result from a decrease of diffusivity and/or solubility. It is well-known that the addition of impermeable filler particles, such as RGO particles, to a pure polymer film promotes a decrease in the penetrant permeability as a consequence of a 2-fold "geometric" effect: the decrease in the area available to the penetrant flux and the increase in the diffusive path.[7−12] Another nongeometric effect of the presence of impervious particles is the reduction of the volume available for the penetrant sorption, resulting in a decrease of the penetrant solubility. This effect, in ideal cases, can be simply accounted for by rescaling the solubility of the pure polymer, by the volume fraction of the matrix in the hypothesis that particles do not provide any contribution to solubility.

To interpret the experimental steady state gas permeability data, we have used, respectively for "not-segregated" and "segregated" nanocomposite morphologies, a model assuming a uniform dispersion of oriented platelike filler and a model addressing the case of an ordered assembly of coated spheres, as core−shell spheres, embedded in a surrounding matrix (see the Supporting Information for full details of models). In both cases, a macroscopic one-dimensional geometry is considered, where the driving force, in terms of difference in the chemical potential of the penetrant, is established between the two

surfaces of a nanocomposite sheet thus promoting a macroscopic net flux of penetrant normal to the plane of the sheet itself.

In particular, to interpret the results for the not-segregated morphology, it has been used an expression for the relative permeability provided by the theory developed by Bharadwaj,[13] which accounts for the orientation of impermeable disk platelike particles dispersed in a matrix

$$P_R = P_{nc}/P_m = \frac{1 - \phi}{1 + (L/2W)(2/3)\phi(s + 0.5)} \quad (1)$$

where P_{nc} and P_m represent, respectively, the permeability of the nanocomposite and that of the neat matrix, ϕ represents the volumetric fraction of the filler, and L/W represents the aspect ratio of the plate-like filler, L being the main dimension of the particles and W their thickness. The order parameter, s, accounts for the orientation of the particles with respect to the normal to the surfaces of the nanocomposite sheet (see Supporting Information for further details) and it is used as the only fitting parameter of the model. This parameter ranges from $-1/2$, in the case of nanoplatelets uniformly oriented normally to the plane of the sample film, to 1, in the case of nanoplatelets uniformly oriented parallel to the plane of the film. In the case of randomly oriented filler particles, s is equal to zero.

For the case of segregated morphology, permeability data have been interpreted by properly modifying a model proposed by Moosavi et al.[14] to predict the thermal conductivity of a composite material. In the original Moosavi model, it is considered a homogeneous matrix displaying a constant thermal conductivity, filled with an array of multicoated spherical inclusions in which each coating layer is characterized by a different constant thermal conductivity. This approach has been here extended to mass transport under the following hypothesis: (i) spheres are coated by a single layer of RGO particles and (ii) simple ideal Fickian constitutive expression for mass flux holds. It can be demonstrated that a perfect parallelism exists between the steady-state mass balance and the steady-state thermal energy balance, with permeability playing the role of thermal conductivity and pressure playing the role of temperature (see the Supporting Information). In this case, it is assumed that the composite material consists of a rubber matrix embedding rubber spheres partially or fully coated by the RGO platelike particles. As the overall concentration of RGO increases, a wider part of the spheres surface is covered thus decreasing the 'effective' permeability of each coated sphere. For modeling purposes, the equally sized coated spheres are considered as being formed by a rubber core coated by a uniform shell with a thickness equal to d, which is the thickness of the platelets (∼3 nm) and a permeability that is a decreasing function of the overall RGO concentration. Furthermore, as the overall RGO concentration increases, the shell permeability, calculated by a proper averaging procedure, decreases from the initial value of the pure polymer to a zero value attained when RGO concentration is above a threshold value, $\phi^*_{graphene}$. This volume fraction represents the minimum value of RGO concentration for which the polymeric spheres are expected to be totally covered by the graphene nanoparticles. In this condition the shell is virtually impermeable and, consequently, the coated latex spheres act as impermeable spheres embedded in a permeable matrix. In particular, the following explicit expression has been determined for the relative permeability of a segregated nanocomposite

$$P_R = P_{nc}/P_m = 1 - 3F/\delta \qquad (2)$$

where P_R represents the relative permeability, F represents volumetric fraction of coated spheres, and δ is a summation term that depends on the effective permeability of the shell, on the spatial arrangement of the coated spheres and on the order of approximation. It is worth of notice that, in the present context, the model is used in a totally predictive fashion (i.e., with no fitting parameters). Full details on this modeling procedure are provided in the Supporting Information.

In Figures 4a,b are collectively reported relative permeability data determined at all the temperatures and for all the gases,
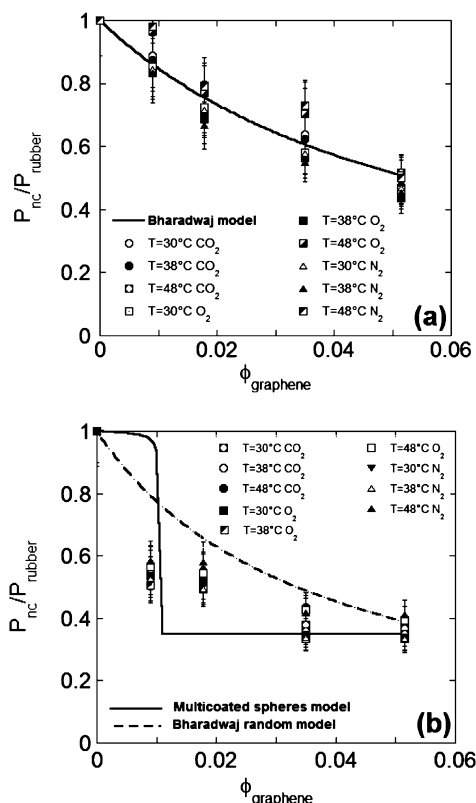

Figure 4. (a) Experimental relative permeability of investigated gases for nanocomposite with not-segregated morphology along with fitting by Bharadwaj model. (b) Experimental relative permeability of investigated gases for nanocomposite with segregated morphology and prediction of modified Moosavi model.

along with modeling outcomes, respectively for the case of samples with not-segregated and segregated morphology. The experimental data for the not-segregated specimens compare well with the Bharadwaj model[13] using an aspect ratio value equal to 167. The value of the order parameter s has been determined by fitting the relative permeability data, obtaining an averaged value for the orientation angle of the normal to the platelets equal to 63°. This value is rather close to the one estimated by TEM analysis, which is comprised between 40 and 50°.

The behavior of the samples displaying segregated morphology are compared, instead, with the predictions of the ad hoc modified version of the multicoated model proposed by Moosavi et al.[14] The model supplies a quite good qualitative and quantitative estimate for relative permeability. It is worth mentioning that both the models discussed above do not account for possible interactions between penetrant molecules

and nanofillers but only for the geometrical effects related to the presence of impermeable particles. Although data do not collapse onto a single "master" curve, as should be expected if only geometric effects had come into play, this mismatch is considered to be within the range of a reasonable experimental error and the effect of interactions has then been neglected. In Figure 4b is also reported, for comparison purposes, the relative permeability as predicted by the Bharadwaj model in the case of a random orientation of RGO filler. Interestingly, the relative permeability values obtained for the sample with segregated morphology stay well below those attainable in the case of a random orientation of the nanoparticles, attaining a relative permeability equal to 0.5 at a volumetric fraction of RGO equal to around 0.01. On the contrary, the same value of relative permeability is instead predicted to be attained, in the case of randomly oriented particles, at a RGO volumetric fraction higher than 0.03.

■ CONCLUSION

It has been shown that tailoring the structure of NR/RGO nanocomposite by suitable processing procedures to obtain an assembly of platelets as an interconnected network within NR matrix can be exploited effectively to improve their gas barrier properties. The features of this graphene-segregated structure have been compared with those of a rubber/graphene nanocomposite where platelets are homogeneously dispersed in a not-segregated morphology. Significant qualitative and quantitative differences in the dependence of the relative permeability on the volume fraction of filler have been found for the two morphologies. Samples with uniformly oriented platelets show a smooth decrease of gas permeability with volume fraction of graphene, successfully modeled using the approach proposed by Bharadwaj. Conversely, samples characterized by a "segregated" morphology display a steeper decrease of permeability at low graphene concentration; the filler arrangement being more effective in decreasing the overall permeability of the sample due to confinement of graphene on the surface of the rubber latex spheres. Above a threshold graphene concentration, in our case approximately equal to 3.38 vol %, the nanocomposite behavior emulates that of a matrix filled by impermeable spheres. A modified version of the Moosavi model, proposed to analyze the experimental results, has supplied a reasonable physical interpretation of the mass transport behavior of samples with segregated morphology.

■ EXPERIMENTAL SECTION

Preparation of Graphene/Natural Rubber Composites. Graphene oxide (GO) aqueous solution, obtained through oxidation of natural graphite flake, was mixed with natural rubber latex. Afterward the GO platelets were in situ reduced by using hydrazine hydrated and the formed RGO platelets self-assembled on the surface of latex particles. Other additives, including cross-linking sulfur, were added in the dispersion and the system was allowed to coagulate. The obtained NR/RGO solid was then hot pressed under static pressure and in situ vulcanized at 150 °C to form the graphene segregated network structure. Moreover, the NR/RGO solid was also treated with a twin-roll mixing, giving rise to a not-segregated graphene structure in which the reduced graphene oxide platelets are homogeneously dispersed in the rubber matrix. More details about the preparation and compositions of

graphene natural rubber composites are reported in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Chemicals and sample preparation procedures, supplementary TEM micrographs, description of the experimental method for determination of permeability, complete set of data for permeability and relative permeability, and details on the theoretical models. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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■ ACKNOWLEDGMENTS

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