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Elastomer-Clay Nanocomposites: Effect of Elastomer Polarity

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Summary: Dynamic mechanical properties of non-polar and polar elastomer-based nanocomposites with Montmorillonite clay are studied in order to ascertain differences caused by elastomer's polarity. Natural as non-polar and polychloroprene as polar rubber are used to experimentally verify predictions based on different nature of elastomer-clay interactions in the two cases. The properties foretold and elucidated in terms of van der Waals interactions in the non-polar case and dipole-dipole interactions in the polar case agree well with experiment, concurrently sustaining general depiction of these unusual nanocomposites.

Keywords: clay; elastomers; nanocomposites; polarity; rheology

Introduction

In the past decade or so, chemically modified Montmorillonite clays, used as reinforcing nanofillers in elastomers, have proved to be excellent possible replacement for classical fillers like carbon black and silica.[1–3] The clay particles of nano-size thickness, micro-size other two dimensions and therefore large specific surface area emerge from elastomeric molecular intercalation into primary clay granules and their subsequent exfoliation, both processes occurring *in-situ*, say, during melt-mixing. Through their active surface these particles then interact with non-polar elastomer molecules by van der Waals attraction forces, forming multitude of intermolecular and multifunctional secondary linkages and so a secondary network. Despite essential impact of these networks on rheological properties of the so-formed nanocomposites, regardless of their being covalently crosslinked or not, the weak bonding causes them to be strongly sensitive to deformational and temperature changes. At low strains and/or temperatures they represent the skeleton of high stiffness, undergoing gradual breakdown, however, under severer conditions, which is rheologically detectable. Also involving energy dissipation, such breakdown, namely, can effectively be traced by dynamic mechanical functions of a nanocomposite, i.e. the storage and the loss moduli of elasticity, displaying simultaneously the states of resilience and energy loss.[4]

Apart from splendid reinforcement action of clay, recent dynamic mechanical studies of crosslinked non-polar elastomer/clay nanocomposites have also revealed an unusual, though practically beneficial, property of energy loss diminishing with increasing filler content and/or decreasing temperature. Such conduct has never been observed with carbon black or silica, demanding therefore an entirely novel explanation. Attempt has been made to elucidate the phenomenon in terms of relatively strong elastomer-clay interaction within van der Waals domain and subsequent partial restoration of energy released upon linkage rupture in form of molecular slingshot effect. Although not conclusive, such notion *does* explain the odd behaviour both phenomenologically and on molecular level.[5]

Elastomer/clay nanocomposites based on polar elastomers exhibit qualitatively similar comportment, but there are

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characteristic differences which are predictable in terms of the change in interactional nature and the notion of partial energy recuperation upon secondary network breakdown. The aim of this work is to present these differences and thus also substantiate the previous findings with non-polar elastomer-based nanocomposites. Owing to filler content - temperature superposition principle that has been found to exist for these systems,[5] the results for either of the effects alone would suffice to fulfill this aim. Therefore, since polarity–associated issues are treated here through the effects of filler content, the effects of temperature are plausibly omitted.

Experimental Part

For comparison purpose in the study, two structurally cognate elastomers were chosen: the polar polychloroprene rubber (CR - Baypren 110) and the non-polar natural rubber (NR - SMR 10). They were melt-mixed with 5, 10, 20 and 30 phr (parts by weight per 100 parts of rubber) of chemically modified Montmorillonite clay (Dellite 67G) in Banbury-type laboratory internal mixer (Pomini Banbury BR, head volume of 1.5 L, friction ratio of 1.16:1) in accordance with the standards ISO 2475 and ISO 1658, respectively. Admixed also were covalent crosslinking systems by component amounts conforming to the same standards. Crosslinking (vulcanization) of the so-obtained nanocomposite compounds was carried out by the instrument Rubber Process Analyser (RPA 2000 - Alpha Technologies). The same instrument was used to measure the nanocomposites' dynamic mechanical functions within the shear strain amplitude range of 0.01-10 and the temperature range of 40 °C – 100 °C at the constant frequency of 0.3 Hz which is low enough to allow for undisturbed molecular conformations during measurements.

Results and Discussion

Dynamic mechanical functions of NR- and CR-based nanocomposites with different contents of clay during strain-induced secondary network breakdown at constant temperature and frequency are demonstrated in Figures 1 and 2, respectively, the points representing the measured values. Denoting the shear strain amplitude by γ, the general picture is that the storage shear moduli $G'(\gamma)$, according to the theory of rubber elasticity proportional to corresponding linkage densities, monotonically decrease with increasing strain amplitude, whereas the loss moduli $G''(\gamma)$, proportional to the linkage density change, undergo maxima at strains of the strongest linkage density drop. The curves are calculated by expressions

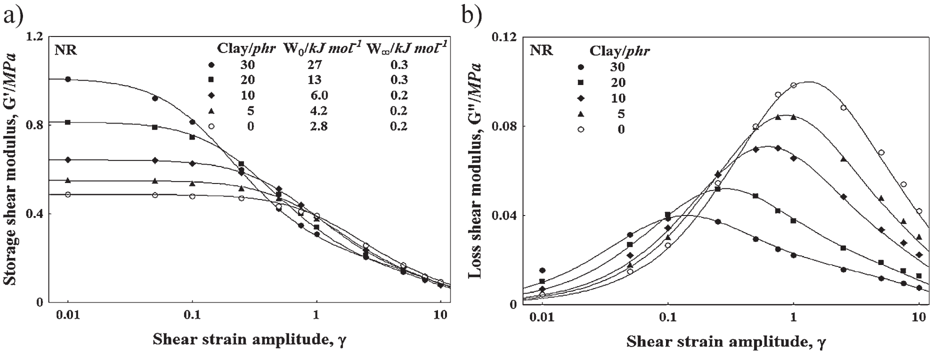

Figure 1.
Strain dependence of *a*) storage moduli of elasticity and *b*) loss moduli of NR-based nanocomposites with different contents of clay at 40 °C and 0.3 Hz

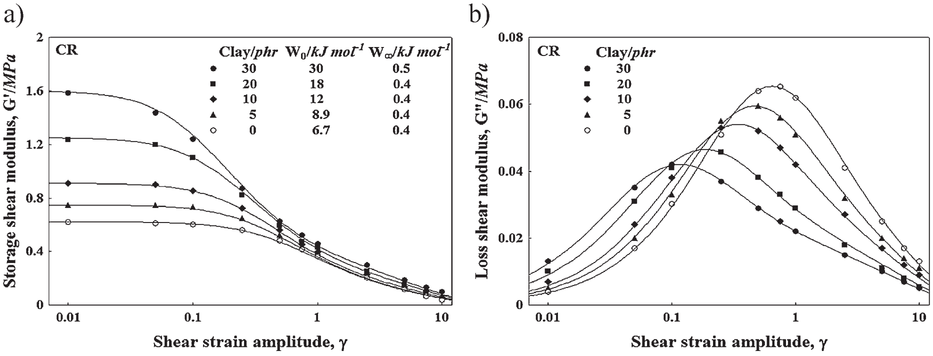

Figure 2.

Strain dependence of *a*) storage moduli of elasticity and *b*) loss moduli of CR-based nanocomposites with different contents of clay at 40 °C and 0.3 Hz

stemming from a statistical mechanics-based model of a secondary network breakdown, vis.:[4,5]

$$G'(\gamma) = G'_0(1 + W\gamma/kT)\exp(-W\gamma/kT), \qquad (1)$$

$$G''(\gamma) = G''_{\max}(W\gamma/kT)\exp(1 - W\gamma/kT) \qquad (2)$$

where G'_0 and $G''_{\max}$ are the initial storage modulus (at $\gamma = 0$) and the maximum loss modulus (at $\gamma = \gamma_{max}$), respectively, k the Boltzmann constant, T the temperature and W the secondary linkage rupture, or dissociation, energy. This energy generally depends on strain: $W(\gamma) = W_\infty + [1/(W_0 - W_\infty) + \gamma/3kT]^{-1}$ where W_0 and W_∞ ($W_0 >> W_\infty$) are low- and high-strain boundary energies, respectively, depending on filler content and temperature. As can be seen, agreement of the model with experience is rather good in all the cases, which also enhances confidence in determined values of the energies W_0 and W_∞ given (per mol) in Figures 1*a* and 2*a*. The model further predicts the strain γ_{max} to be determined by their reciprocal difference: $\gamma_{max} \approx 3kT/2(W_0 - W_\infty)$, the correctness of which can easily be verified by the data and diagrams in the figures.

If the filler content is given in terms of its volume fraction Φ_V, it can be shown that G'_0 and $G''_{\max}$ depend on it exponentially as:[5]

$$G'_0(\Phi_V) = G'_0(0)\exp(\kappa'\Phi_V), \qquad (3)$$

$$G''_{\max}(\Phi_V) = G''_{\max}(0)\exp(-\kappa''\Phi_V) \qquad (4)$$

where $G'_0(0)$ and $G''_{\max}(0)$ are the functions of elastomers alone, with κ' and κ'' being constants. Vindication of these equations is given in Figures 3*a* and 3*b*.

Filler content dependence of the linkage rupture energy, or, more specifically, of the boundary energies W_0 and W_∞ displays an explicit and directly verifiable difference between non-polar and polar elastomer-based nanocomposites. In fact, only that of W_0 really matters because W_∞ is almost independent of filler content. At high strains, namely, the secondary networks are thoroughly destroyed regardless of filler loading and W_∞ therefore accounts for breakdown of sporadic molecular entanglements and eventual other molecular associations, such as those of dipole-dipole nature in the case of CR, possessing superior strength. Comparison of these values in Figures 1*a* and 2*a* confirms this assertion. The energy W_0, on the other hand, strongly depends on the filler volume fraction Φ_V. By considering effective volume V_0 of an elastomer-clay secondary linkage, comprising the distance r of an interacting elastomer's molecular segment from the clay particle's surface, as shown in Figure 4, it has been ascertained that the initial linkage density, say, n_0, and V_0 are related as $n_0V_0 = const.$[5] Assuming the filler particle dimensions to be constant on the average, n_0 is then proportional to the reciprocal volume of the dashed cylinder (which could as well be some other upright

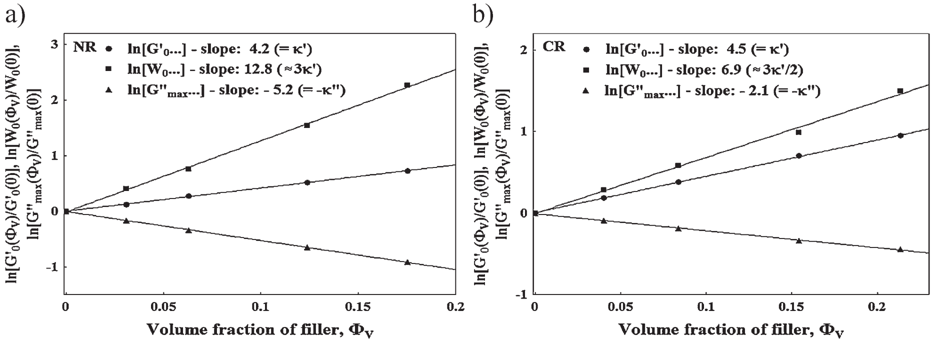

Figure 3.
Clay content dependence of initial storage moduli, initial linkage rupture energies and maximum loss moduli of a) NR-based and b) CR-based nanocomposites at 40 °C and 0.3 Hz

body of equal, parallel base surfaces and constant height) in Figure 4 and subsequently to r^{-2}. Now, if interaction is of induced-dipole, or van der Waals, nature,[6] as in the case of non-polar NR, then W_0 should be proportional to r^{-6} and therefore to ${n_0}^3$. In the case of CR, conversely, its polar molecules interact with polar clay particle surfaces in a dipole-dipole manner, where the energy W_0 is proportional to r^{-3}, or thus to ${n_0}^{3/2}$. Considering Eq. (3) and the proportionality of G'_0 and n_0, the $W_0(\Phi_V)$ forms should then read:

$$W_0(\Phi_V) = W_0(0)\exp(3\kappa'\Phi_V), \tag{5}$$

$$W_0(\Phi_V) = W_0(0)\exp(3\kappa'\Phi_V/2), \tag{6}$$

for non-polar and polar elastomer-based nanocomposites, respectively, with $W_0(0)$ pertaining to pure elastomers, i.e. to entanglement structure in the case of NR and dipole-dipole association structure in the case of CR. Verification of Eqs. (5) and (6) for NR- and CR-based nanocomposites is also presented in Figures 3*a* and 3*b*, respectively.

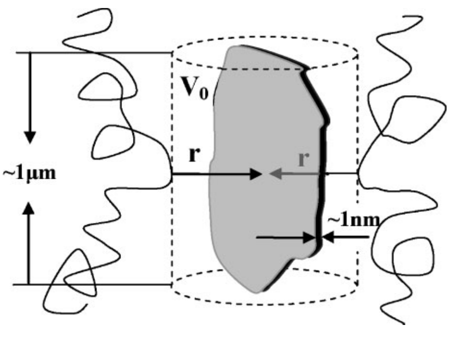

Figure 4.
Interactional detail and effective linkage volume

There are, of course, other manifestations of differences in elastomers' polarity. An immediate issue is the substantially stronger low-strain filler reinforcement of CR, which is discernible from corresponding storage moduli in Figures 1*a* and 2*a*. Although to a certain extent this could be due to CR's own dipole-dipole associations, the main reason is in more eased and efficient intercalation and exfoliation processes of clay nanoparticle formation by the polar molecules. This results in greater secondary linkage density and consequently in superior moduli. Additionally, the energies W_0 are somewhat higher and less filler content-sensitive for CR-based nanocomposites, a consequence of which being more closely packed strains of the highest network breakdown rate, $\gamma_{\max}$, or the maxima in loss moduli on the strain scale, as demonstrated in Figures 1*b* and 2*b*. For this reason, CR-based nanocomposites do not exhibit progressive overshooting of $\gamma_{\max}$ with decreasing filler content (Figure 2a), which the nanocomposites based on non-polar elastomers, such as NR, regularly and characteristically do (Figure 1a).

Conclusion

The work shows that elastomer/Montmorillonite clay nanocomposites are qualitatively almost unaffected by elastomer's state of polarity. There are, however, distinct quantitative differences in rheological properties of non-polar and polar elastomer-based nanocomposites, which can be predicted and explained in terms of different nature of elastomer-clay interaction in the two cases. That is demonstrated by dynamic mechanical functions of their typical representatives, though of comparable molecular structure: the non-polar NR-based and the polar CR-based nanocomposites. Whereas the non-polar case is dominated by induced-dipole, or van der Waals, elastomer-clay interactions, exhibiting lower storage and higher loss moduli, prevailing in the polar case are longer-range and somewhat stronger dipole-dipole interactions, resulting in superior stiffness and lesser energy dissipation. As good agreement of the modeled conduct is obtained with experience, this is another example in polymer physics of how macroscopic, rheological comportment of material can provide insight into molecular-level features and vice-versa.

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