

RHEOLOGICAL IDIOSYNCRASIES OF ELASTOMER/CLAY NANOCOMPOSITES

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ABSTRACT:

Rheological properties of elastomeric nanocomposites with organically modified Montmorillonite clays, as possible replacements or supplements to classical active fillers, such as carbon black or silica, have been intensively studied in recent years. Possessing large specific surface areas acquired through the melt-mixing processes of elastomeric intercalation and subsequent filler exfoliation, the clay particles have indeed proved to be highly eligible reinforcing and thermally stabilizing ingredients for application in elastomers. In fact, their performance has shown to be in many respects superior to that of classical fillers, particularly owing to some unusual, though beneficial, exhibited properties. Namely, apart from uncommonly high surface activity, manifested by creation of a host of van der Waals type secondary linkages with elastomer molecules, the main curiosity of clay filler is its dissipative action. Using dynamic mechanical functions under different deformational and temperature conditions, as means for rheological characterization of nanocomposites, the foregoing nano-scale traits are clearly reflected in substantial stiffness at low strains and, unexpectedly, dwindling energy loss with increasing filler content and/or decreasing temperature. Besides, rheological analysis of this kind, together with appropriate theoretical grounds, has enabled elucidation of peculiar conduct, as well as macroscopic insight into the very nature of secondary interactions in elastomers.

ZUSAMMENFASSUNG:

Die rheologischen Eigenschaften von Elastomerkompositen mit den organisch modifizierten Montmorillonite-Clays, die als möglicher Ersatz oder Zutat für klassische Aktivfüller wie Ruß oder Siliziumdioxid dienen könnten, wurden in den letzten Jahren intensiv untersucht. Mit einer großen spezifischen Oberfläche, die im Schmelz-Mischprozess („melt-mixing“) durch Interkalierung der Elastomeren und folgende Exfolierung der Füller erworben wurde, haben sich die Clay-Teilchen wirklich als besonders versteifende und wärmebeständige Additive für die Anwendung in Elastomeren bewiesen. Tatsächlich haben sie sich in vieler Hinsichten besser als klassische Füller gezeigt, besonders weil sie einige ungewöhnliche doch vorteilhafte Eigenschaften aufweisen. Nämlich, neben der ungewöhnlich hohen Oberflächenaktivität, die sich durch Entstehung von zahlreichen van der Waals-artigen sekundären Verbindungen mit den Elastomermolekülen zeigt, liegt die Hauptmerkwürdigkeit der Clays in ihrer dissipativen Wirkung. Mittels dynamisch-mechanischer Funktionen in Abhängigkeit von verschiedenen Deformations- und Temperaturbedingungen wurden die Nanokompositen rheologisch charakterisiert; die vorangehend genannten Nanobereich-Merkmale wurden ganz klar in der bemerkenswerten Festigkeit bei niedrigeren Dehnungen und, unerwartet, im sinkenden Energieverlust bei steigendem Füllergehalt und/oder Temperaturabfall ausgedrückt. Außerdem hat derartige rheologische Analyse in Verbindung mit entsprechenden theoretischen Grundlagen das eigenartige Verhalten, sowie einen makroskopischen Einblick im Wesen der sekundären Wechselwirkungen in Elastomeren erläutert.

RÉSUMÉ:

Propriétés rhéologiques des nanocomposites en élastomères et argiles Montmorillonites, modifiées organiquement, comme remplacements ou suppléments possibles aux charges renforçantes, e.g. noir de carbone ou silice, étaient intensément étudiées pendant dernières années. Possédant large surface spécifique, obtenues par fondremélange procès d'intercalation élastomère et subséquente exfoliation de charge, les particules d'argile ont vraiment démontrés d'être très convenable ingrédients renforçants et équilibrants thermiques pour application aux élastomères. En effet, leur rendement se présentait sous divers respects supérieur au celui des charges classiques, particulièrement dû à certaines, inhabituelles, bien que bénéfiques, propriétés exposées. A savoir, à côté d'activité superficielle extraordinaire, manifestée par création de multitude de liaisons du van der Waals type avec les molécules élastomères, la curiosité principale de charge argile est son action dissipatrice. Utilisant des fonctions mécaniques dynamiques aux conditions de déformations et températures diverses, comme manière de caractérisation rhéologique de nanocomposites, les traits à nano échelle suscités sont clairement révélés par considérable rigidité aux déformations basses et, à l'improviste, par diminution de l'énergie perdue avec augmentation de charge contenue et/ou abaissement de température. En plus, analyse rhéologique de cette sorte, y compris fondement théorique approprié, a rendue possible élucidation du comportement curieux, ainsi que la pénétration macroscopique en nature même des interactions secondaires aux élastomères.

KEY WORDS: Rheological properties, elastomers, Montmorillonite clay, peculiarities

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Figure 7 (left): Clay content dependence of zero-strain storage shear modulus, $G'_o(\phi_v)$, maximum loss shear modulus, $G''_{max}(\phi_v)$, and zero-strain network breaking energy, $W_o(\phi_v)$, for EPDM-based nanocomposites at temperatures of 40 and 100°C and frequency of 0.3 Hz.

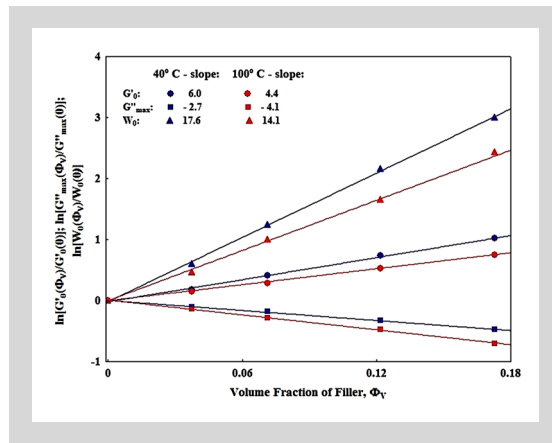
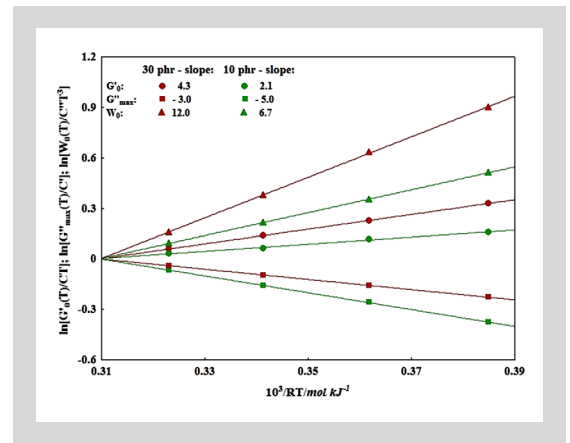


Figure 8: Temperature dependence of zero-strain storage shear modulus, $G'_o(T)$, maximum loss shear modulus, $G''_{max}(T)$, and zero-strain network breaking energy, $W_o(T)$, for EPDM-based nanocomposites of 10 phr and 30 phr clay content and frequency of 0.3 Hz



ferences in $G'(\gamma)$ and corresponding values of W_o due to variation of temperature are distinctly smaller than those obtained for variations in filler level, whereas W_∞ slightly increases with temperature, as predicted. Similarly as in the case of decreasing filler content in Figure 3, slight overshooting of maximum slope strains with increasing temperature can be observed, tentatively pointing to a form of filler-temperature superposition principle in these composites. Equivalent here would be high filler - low temperature states and vice versa.

This is substantiated in Figure 6 by the exhibited increase in G''_{max} with increasing temperature, which is completely contrary to experience with classical fillers. If a high filler content and low temperature conditions are taken as hypothetically analogous, at least from the viewpoint of energy dissipation, then the explanation of such conduct is the same as in the filler content case. Intensified thermal motion at elevated temperatures impedes restoring of the breakdown-released energy, resulting in stronger dissipation and subsequently in higher maximum loss moduli. Although the differences are not great, they are sufficient enough to indicate entirely different mechanisms taking place in elastomer/clay nanocomposites. It should be noted in the end that low strain deviations from the theory, occurring due to internal friction, which is not accounted for in the model, have nothing to do with the foregoing behavioural reasoning.

4.2 EFFECT OF FILLER CONTENT

Although the effect of filler content is evident from Figures 3 and 4, it is explicitly given by Eqs. 4-8, their verification being demonstrated in Figure 7 for two temperatures. As can be seen, the displayed logarithmic plots of G'_o , G''_{max} and W_o versus volume fraction of filler are linear. The corresponding slopes are higher for the lower temperature, which is to be expected, considering the general pattern of G'_o , G''_{max} and W_o dependence on temperature. These results, including

the obtained values of the constants κ and κ' , are in good agreement with theoretical predictions and so consistent with explanation of the phenomena in terms of merely partial loss of generated energy upon secondary network breakdown. Additional work, however, will be needed to clarify and resolve this idiosyncrasy more thoroughly.

From the results given in Figure 7 it is further discernible that at both temperatures the logarithmic slope of $W_o(\phi_v)$ is close to three times that of $G'_o(\phi_v)$, denoting that W_o is proportional to the cube of the linkage density, n^3 . Regarding assumptions of the model, this in turn means that the network breaking energy is proportional to r^6 , which is characteristic of van der Waals interaction between molecules of the mutual distance r . This result is interesting in itself, since it shows direct relation between fundamental, molecular-level effects and rheological properties without any structural details of interacting objects.

4.3 EFFECT OF TEMPERATURE

The effect of temperature is already shown in Figures 5 and 6, but Figure 8 presents explicit verifications of Eqs. 9–12 for two different filler loadings. It is evident that the equations are highly correlated with experience, the corresponding activation energies possessing magnitudes characteristic of secondary interactions. Despite lying within appropriate range, these energies are in general considerably lower than those of mechanical network breakdown. The reason is that the energy barrier to be surpassed in order to break a secondary linkage is significantly lowered by covalent crosslinks, making the secondary network less susceptible to temperature changes.

In the case of G'_o , the activation energy E expectedly decreases with decreasing amount of filler, to vanish almost completely for pure elastomer. The course in the case of G''_{max} is quite the opposite, with the activation energy E' increasing. The sum of the two energies seems to be

roughly constant, which has proved to be the case also for other filler loadings, not shown here. As in the filler case, this is in favour of the possible elucidation of peculiar dissipative mechanisms by partial recovery of the energy lost in the network breaking process. But, as mentioned, further experimental and theoretical work will be needed in the physics of elastomeric nanocomposites in order to be certain of such explanation.

From Figure 8 it is as well evident that, regarding the effect of temperature, the network breakdown energy is proportional to the third power of the storage modulus, too, vindicating Eq. 12 and so authenticating the origin of elastomer-filler interaction. This is another example of macroscopically enabled insight into nanoscale performance.

5 CONCLUSIONS

Rheological approach to mechanically characterize elastomeric nanocomposites with organo-modified Montmorillonite clay has proved eligible in that it has, among the standard issues, clearly revealed certain curious properties, never met in composites with classical active fillers, such as carbon black and silica. On one hand, high surface activity of nanofiller and corresponding storage moduli may well be expected, if molecular intercalation and clay exfoliation are properly achieved during mixing. On the other, however, lowering of energy dissipation with increasing filler content and decreasing temperature is absolutely unusual, but could be highly beneficial for some practical purposes. Both phenomena stem from great efficiency of nanofiller, offering a plausible, although yet not conclusive explanation.

The foregoing analogous actions of filler and temperature indicate an otherwise usual superposition of the two effects by high filler loadings corresponding to low temperatures and vice versa. But in the case of energy dissipation this superposition, while still in power, implies equivalent states completely opposite to those obtained in elastomeric composites with classical fillers. Yielding low loss moduli at high contents of filler and low temperatures is a unique display among active fillers in elastomers.

Apart from surprising, but remarkable properties, the approach has disclosed another noteworthy finding with respect to these nanocom-

posites: a possibility of pursuing nanoscale phenomena by macroscopic methods. Namely, a theoretical model devised to describe strain and thermally induced breakdown of elastomer-filler secondary network, together with rheological measurements yields not only the energies of elastomer-filler interactions, but also the insight into their very van der Waals nature.

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