



Time and shear dependent rheology of maleated polyethylene and its nanocomposites

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Abstract

Dipole–dipole and/or hydrogen-bonding interactions between the pendant functional groups within maleated high-density polyethylene (PE-g-MAN) establish a physical polymer network, whose formation kinetics and shear-sensitivity are revealed by dynamic oscillatory testing. The pronounced time and shear dependent viscoelastic properties of PE-g-MAN were not observed for a corresponding imide derivative, PE-g-imide, presumably due to weakened functional group associations in the latter material.

The melt compounding of PE-g-MAN with onium-ion exchanged montmorillonite clay (NR_4^+ -MM) resulted in a partially exfoliated hybrid nanocomposite structure, whose viscoelastic behaviour differed significantly from that of the unfilled polymer. The presence of dispersed clay platelets altered the extent of functional group associations, thereby changing the dynamics of network formation.

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1. Introduction

The rheological behaviour of polymer-clay nanocomposites has attracted considerable attention, because it relates to their microstructure and governs their processing characteristics. Through studies of dynamic oscillatory [1–8] and steady-shear rheology [6–8], it has been shown that polymer-nanoclay composites display enhanced viscoelastic properties compared to the matrix polymers, and exhibit time and shear dependent responses [1–7]. Several researchers have attributed these phenomena to the formation of a percolated network structure by clay platelets or tactoids [4–7].

Clay intercalation or exfoliation within a polyolefin matrix is accomplished by introducing pendant anhydride groups, which improve the strength of physical interactions at the polyolefin-filler interface [1,4,7,9]. Since the incorporation of associating groups within polyolefins influences their rheological properties in the melt state, especially when hydrogen-bonding is predominant [10–12],

rheological studies of polyolefin nanocomposites should consider the behaviour of the unfilled maleated polyolefin.

In this report, we present oscillation time sweep experiments that demonstrate the time and shear dependent rheological behaviour of maleated polyethylene (PE-g-MAN). The nature of the functional group interactions is analyzed through comparative studies with an imide derivative (PE-g-imide), and discussed in the context of available literature. Changes in the melt rheology of PE-g-MAN brought on by the introduction of exfoliated montmorillonite clay and other additives are also examined.

2. Experimental

2.1. Materials

Montmorillonite clays were used as supplied (Cloisite® Na^+ (Na^+ -MM), Southern Clay Products Inc., Gonzales, Texas; unexchanged and Nanomer® I.44PA (NR_4^+ -MM), Nanocor Inc., Arlington Heights, IL; ion-exchanged with dimethyldialkylammonium halide (70% C_{18} , 26% C_{16} and 4% C_{14})). 2,6-Di-*tert*-butyl-4-methylphenol (BHT, 99+ %),

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dimethyldioctadecylammonium bromide (98%) and 1-hexadecylamine (90%) were used as received from Sigma-Aldrich.

Poly(ethylene-graft-maleic anhydride) containing approximately 1 wt% of pendant succinic anhydride groups was obtained from DuPont Canada (PE-g-MAn, Fusabond® M611-25, MFI=9.6). An imide derivative of this resin was prepared by reaction of PE-g-MAn (40 g) with 1-hexadecylamine (0.9849 g, 0.1020 mmol) at 190 °C for 6 min using a Haake PolyLab torque rheometer, connected to a Rheomix 610p mixing chamber equipped with roller rotors. (Scheme 1). Analysis of a thin film of the derivative by FT-IR (Nicolet Avatar 360 E.S.P. spectrometer) revealed the 1709 cm^{-1} and 1790 cm^{-1} resonances characteristic of the desired imide product (PE-g-imide), while a complete loss of resonances derived from the succinic anhydride and succinic acid (1786 and 1708 cm^{-1} , respectively) verified that a near quantitative conversion was achieved [13].

2.2. Composite preparation

Mixtures of the desired polymer (40 g), BHT (0.02 g, 0.09076 mmol) and the required amount of NR_4^+ -MM clay were prepared by dry blending in a tumble mixer. These were introduced to the Haake batch mixer at 190 °C and 60 rpm, using a fill factor of 70%, and mixed for 7 min. Pure PE-g-MAn was processed under identical conditions, to ensure consistent processing history. All materials used in this study were stabilized with BHT in order to limit oxidative degradation of PE-g-MAn, which would result in crosslinking.

2.3. Rheological characterization

Rheological measurements were performed under a nitrogen atmosphere using a Reologica ViscoTech controlled stress rheometer equipped with 20 mm diameter parallel plates. The instrument was operated at 150 ± 0.1 °C with a gap of 1.5 mm. Measurements of the elastic modulus (G'), viscous modulus (G'') and complex viscosity (η^*) were

recorded in the oscillatory mode as a function of time. The amplitude of the stress oscillations was 10 Pa and the frequency 0.01 Hz, unless otherwise noted. Stress sweeps verified that data were acquired within the linear viscoelastic regime. Samples were presheared at a shear stress of 10,000 Pa for 300 s to ensure that each material possessed a consistent shear history.

2.4. X-ray diffraction

The structure of the composites was examined by X-ray diffraction (XRD) using a Scintag XDS 2000 diffractometer (Cu $K\alpha$ radiation $\lambda = 1.5406$ Å, generator voltage = 45 kV, current = 40 mA). Samples were pressed films approximately 400 μm thick and were scanned in 2θ ranges from 1 to 40° at a rate of 1°/min. Measurements were recorded every 0.03°. For comparative purposes, the XRD patterns were normalized using the intensity of the strongest reflection.

2.5. Transmission electron microscopy

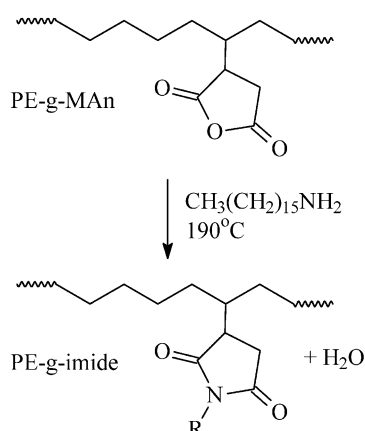
A FEI Tecnai 20 transmission electron microscope (TEM) operated at 200 kV was used to characterize the structure of the composites. Sections approximately 70 nm thick were prepared at -100 °C using a Leica ultracut cryo-ultramicrotome equipped with a diamond knife and placed on formvar coated copper grids.

3. Results and discussion

3.1. Time and shear dependent rheological properties of PE-g-MAn

Oscillation time sweep measurements revealed a pronounced time dependence of G' and G'' of PE-g-MAn, as shown in Fig. 1(a). This behaviour is typical of polymer crosslinking processes, where the intersection of G' and G'' denotes the point of gelation [14]. However, our test samples contained an excess of antioxidant and were completely soluble in xylene after rheological analysis. There was no evidence of gelation when unmaledated high-density polyethylene was analyzed under identical conditions, indicating that radical-mediated crosslinking was not the origin of the effects shown in Fig. 1(a).

We propose that intermolecular associations of succinic anhydride and succinic acid functionalities are responsible for the rheological behaviour reported herein. Due to the susceptibility of anhydrides to hydrolysis, maleated polyolefins contain both succinic anhydride and succinic acid functionalities in proportions that are dependent upon humidity and temperature [15]. FT-IR analysis of PE-g-MAn samples subjected to rheological testing revealed that the succinic anhydride form dominated the population of functional groups in our system. However, small amounts of



Scheme 1.

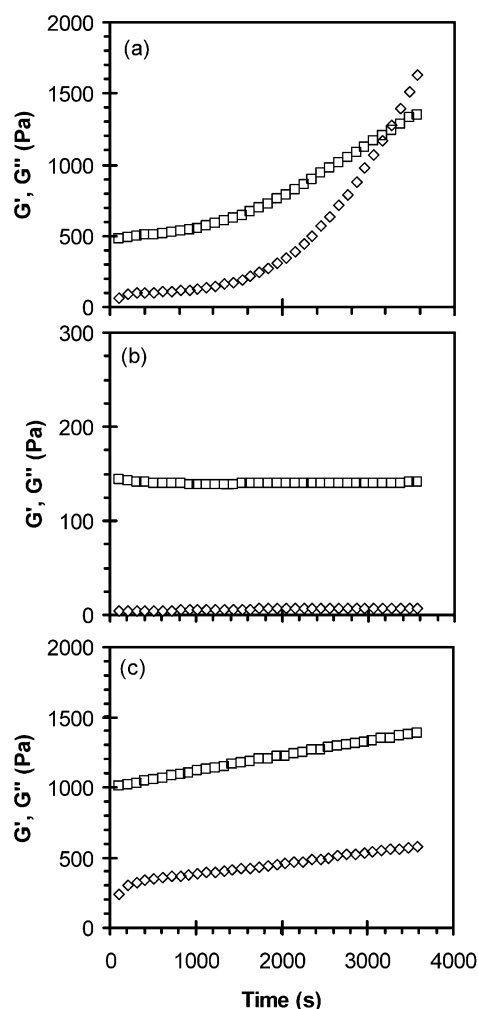


Fig. 1. G' and G'' as a function of time at 150 °C for (a) PE-g-MAN, (b) PE-g-imide, (c) 5 wt% NR₄⁺-MM/PE-g-MAN where, \diamond G' and \square G'' .

the hydrogen-bonding succinic acid functionality persisted in all cases.

Based on the time dependency of the elastic and loss moduli, coupled with the existence of a cross-over point, it is postulated that intermolecular dipole–dipole and hydrogen-bonding associations between functional groups yield a physical network within PE-g-MAN. It is well documented that functional groups generate reversible networks, which, unlike covalently-bonded networks, are labile [11,12,16,17]. Network effects are particularly intense within ionomers, wherein poorly solvated ion-pairs aggregate extensively to yield materials of greatly enhanced modulus and heat distortion temperatures [16,17]. Although hydrogen-bonding interactions are much weaker, their role in the formation of temporary crosslinks in ethylene-acrylic acid copolymers [11] and thermoreversible elastomeric networks in urazole-substituted polybutadienes [12] has been documented.

Reaction of PE-g-MAN with 1-hexadecylamine to form PE-g-imide (Scheme 1) reduces the succinic acid content of the resin and introduces a long-chain alkyl substituent to the

pendant functional group. By reducing the intensity of intermolecular associations, the viscoelastic moduli were decreased relative to the parent material. Furthermore, there is no evidence of network formation, since G' and G'' remained stable throughout the time period examined (Fig. 1(b)).

Samples were subjected to varying amplitudes of stress oscillation, equal to 10 Pa and 10,000 Pa, as well as annealing conditions, where samples were not subjected to oscillation in the intervals between measurements. The application of a high shear stress inhibited the growth of G' , as demonstrated in Fig. 2, suggesting that the extent of functional group association in PE-g-MAN can be restricted by the action of shear forces. The shear sensitivity of these samples is evidence of the relative weakness of functional group associations in the PE-g-MAN system.

The shear-labile nature of the physical network is further demonstrated by Fig. 3, which shows three complete cycles of network formation and network decomposition under the action of two different modes of deformation. Network growth was monitored through an hour-long oscillation time sweep experiment, which was followed by a period of steady-shear at 23,000 Pa, which resulted in almost complete network breakdown. In each cycle, network collapse was immediate upon the application of a continuous high shear stress, indicating that the polymer physical network is formed and eradicated in a completely reversible manner. This confirms that the observed increases in the G' of PE-g-MAN are not due to chemical crosslinking, but rather originate from physical associations between functional groups.

The potential for the network structure to persist in a semi-crystalline sample of PE-g-MAN was also explored. Fig. 4 shows the G' of PE-g-MAN at 150 °C as a function of time. Periodic cooling to 50 °C for 300 s at the intervals noted in the figure resulted in the material being solidified inside the rheometer. After crystallizing, the sample was

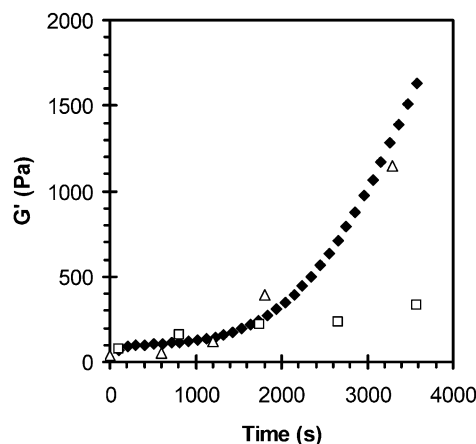


Fig. 2. G' as a function of time under different shear stresses at 150 °C and 0.01 Hz for PE-g-MAN where amplitude of imposed stress oscillation is, \blacklozenge 10 Pa, \square 10,000 Pa. \triangle Denotes annealing conditions between measurements, where no oscillation is applied.

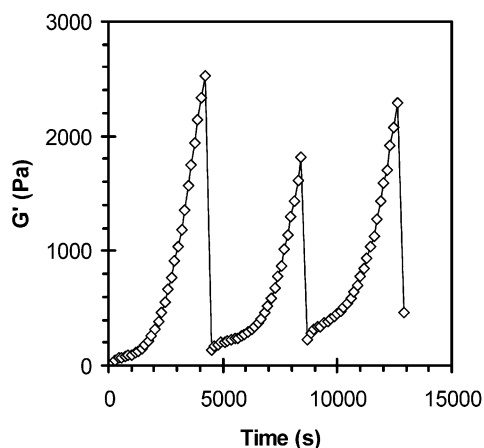


Fig. 3. Reversible behaviour of G' at 150 °C, 3.764 Pa and 0.007 Hz for PE-g-MAN.

reheated to 150 °C and the monitoring of G' was resumed. When G' measurements are translated in time, such that the crystallization periods are not shown, a continuous G' versus time profile is observed. It is apparent that the rate and extent of G' growth was largely unaffected by repeated crystallization. This suggests that the polymer network established is not destroyed by solidifying the polymer, since the methylene sequences in proximity to functional groups are not crystallizable. We further note that increasing the shear stress from 10 to 23,000 Pa at the end of the study reduced G' to its initial value.

3.2. Effect of functional groups on the structure of polymer/clay composites

In agreement with previous findings [1], the melt compounding of PE-g-MAN with onium-ion exchanged montmorillonite clay (NR_4^+ -MM) produced composites whose (001) diffraction peak was greatly diminished (Fig. 5(a)). Since this peak is derived from the interlayer spacing of the clay, its reduction is evidence of significant clay

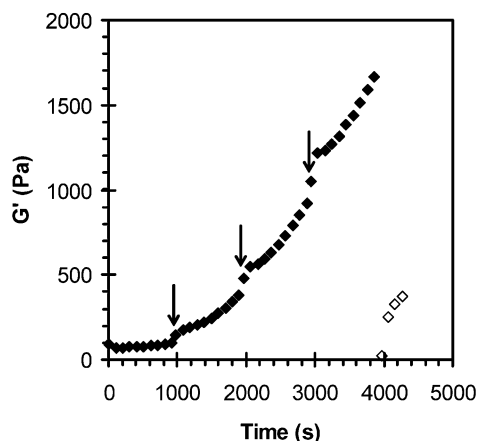


Fig. 4. Effect of crystallization on G' at 150 °C for PE-g-MAN (\rightarrow indicates cycle of cooling to 50 °C, holding for 300 s and reheating to 150 °C; \diamond represents G' after shearing at 23,000 Pa for 300 s).

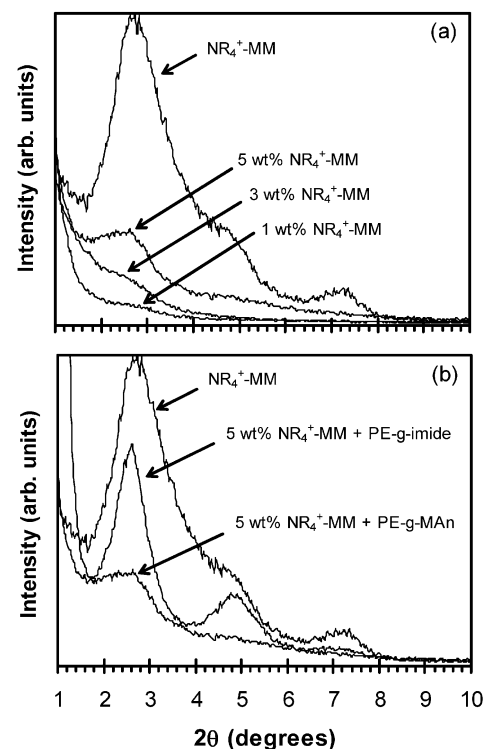


Fig. 5. (a) XRD diffraction patterns of NR_4^+ -MM and its nanocomposites with PE-g-MAN as a function of clay content. (b) XRD diffraction patterns of NR_4^+ -MM and its composites with PE-g-MAN and PE-g-imide.

exfoliation and dispersion within the polymer matrix, resulting in a hybrid nanocomposite structure. TEM microscopy confirmed that substantial amounts of exfoliated clay were dispersed throughout the polymer matrix. (Fig. 6).

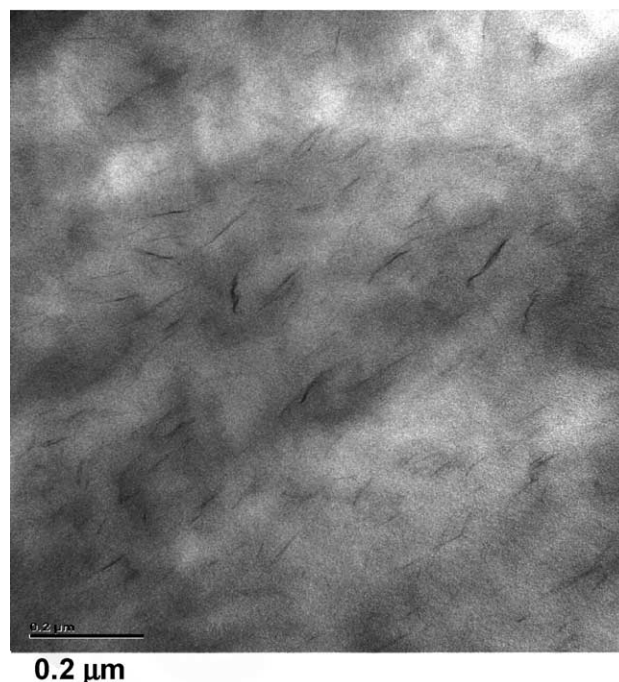


Fig. 6. TEM image of 5 wt% NR_4^+ -MM/PE-g-MAN nanocomposite.

In contrast, the intense (001) diffraction peak observed in Fig. 5(b) for the NR_4^+ -MM/PE-g-imide sample is indicative of an unexfoliated, conventional polymer composite. It is clear that the pendant imide functionality does not provide the intensity of interactions at the polymer-filler interface that are necessary to exfoliate the clay. Therefore, the cohesive forces between clay layers cannot be overcome during melt compounding and delamination is not observed. The reduced activity of an imide functional group is consistent with the rheological response of the PE-g-imide sample discussed above, where no evidence of functional group associations was seen.

3.3. Influence of clay on the rheology of PE-g-MAN

The presence of 5 wt% of exfoliated NR_4^+ -MM is known to enhance the viscoelastic properties of PE-g-MAN substantially [1], as shown in Fig. 1(c). Of greater interest is the effect of clay on the dynamics and extent of PE-g-MAN network formation. The G' of the nanocomposite increased at a much lower rate than the unfilled polymer, and no crossover point between G' and G'' was observed.

We suggest that the intensity of intermolecular functional group associations that establish a physical polymer network within PE-g-MAN is reduced by the presence of exfoliated clay platelets. That is, functional group associations may be affected by interactions between filler and pendant succinic anhydride/succinic acid grafts. The rheological response of the composite is then governed by both polymer–polymer and polymer–clay interactions. Furthermore, the nanocomposite exhibited shear-dependent behaviour similar to that observed for the unfilled system (Fig. 7).

It is noted that the incorporation of 5 wt% unexfoliated unexchanged sodium montmorillonite (Na^+ -MM) clay also affected the evolution of G' and G'' with time in a similar manner. These results indicate that while functional group interactions within PE-g-MAN affect its rheological behaviour at low shear stresses, a range of additives, including

the montmorillonite-based fillers of current interest, can disrupt these labile associations.

Based on these results, we suggest that time-dependent rheological properties commonly reported for clay-filled functionalized polyolefins cannot be attributed solely to the evolution of a network between clay platelets and/or tactoids. Rather, the properties of the functionalized matrix must be considered, in light of the observed rheological effects caused by functional group associations. While it is clear that exfoliated clay influences how the rheological properties vary with time, further work is required to determine whether functional group associations are simply inhibited in the presence of clay, or whether polymer/clay interactions are established, resulting in entirely new network structures in nanocomposite materials.

4. Conclusions

PE-g-MAN exhibits time and shear dependent rheological properties in the melt state, whose origins lie with dipole–dipole and/or hydrogen-bonding interactions between pendant functional groups. The resulting polymer network is highly sensitive to applied shear stresses and the presence of montmorillonite clay fillers.

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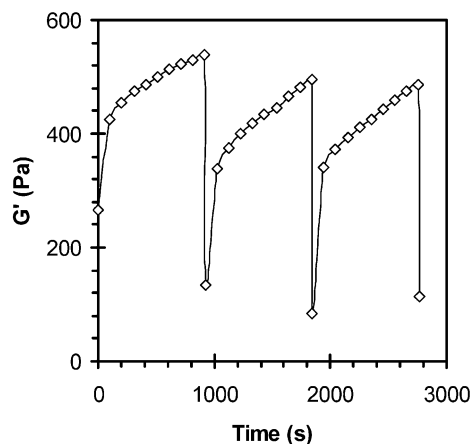


Fig. 7. Reversible behaviour of G' at 150 °C for 5 wt% NR_4^+ -MM/PE-g-MAN nanocomposite.

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