Thermoreversible Gels of Polymers in Recycled Motor Oil

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SUMMARY: A study of the dynamic viscoelastic properties of gels of Ethylene Vinyl Acetate (EVA) and Styrene-Butadiene-Styrene (SBS) copolymers in recycled motor oil is presented. Both systems form gels with enhanced elastic moduli, with respect to SBS/aromatic oil gels which have been used to develop synthetic binders. Although the procedure described by Winter is conveniently applied to obtain gel-sol transition of EVA/oil gels, it is not suitable for SBS/oil gels which do not give rise to a homogeneous liquid when they melt. For EVA/oil gels the relaxation exponent at the gel point is $\Delta=0.5$, which according to Muthukumar's model corresponds to a fractal dimension $d_f=2$. The variation of the elastic modulus with polymer concentration follows the scaling law G_e-c^n, with n=2.8 for EVA/oil and n=1.3 for SBS/oil. In the case of EVA/oil gels the validity of theoretical models relating fractal dimension to n exponent is discussed.

Introduction

The use of recycled motor oil to obtain products of a certain utility is a subject of both industrial and environmental interest. One potential application is the preparation of synthetic binders and bitumen modifiers based on polymer/motor oil gels of adequate viscoelastic response. This requires a methodical study of these systems within the framework of the theoretical and experimental research on thermoreversible gels, a subject which deserves great attention among scientist. Notwithstanding there are several works which report on the respective abilities of Ethylene Vinyl Acetate (EVA) and Styrene-Butadiene-Styrene (SBS) copolymers to form gels in different solvents [1-3)], including aromatic oil for SBS[4)], the use of recycled motor oil as solvent of these copolymers to obtain physical gels has not been reported in the literature. In this paper we analyse the dynamic viscoelastic results of these novel gels, considering the gel-sol transition and the dependence of the elastic modulus on concentration.

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Experimental

Gels were prepared solving , respectively, the copolymers ethylene-co-vinyl acetate (PA-410 supplied by Repsol Chemical Company, EVA: vinyl acetate content 18% *Mw=66.000, Mn=23.000*) and styrene-butadiene-styrene (Kraton D-1101 CS supplied by Shell Chemical Company, SBS: styrene content 31% *Mw=146.000, Mn=105.000*) in recycled motor oil and cooling to the appropriate temperatures. The range of polymer concentration was (3-50 wt.%) for EVA/oil and (5-40wt%) for SBS/oil.

Dynamic viscoelastic functions (G′, G′′ and tan δ) were determined in a Physica Rheolab MC 100 (Couette geometry) and in a Carri Med CSL 100 (parallel plates geometry) rheometer. Linear viscoelastic conditions were obtained from strain amplitude sweeps.

Results and Discussion

Storage modulus and loss tangent, as a function of frequency, of both EVA/oil and SBS/oil systems at different temperatures are shown, respectively, in Figures 1 and 2.

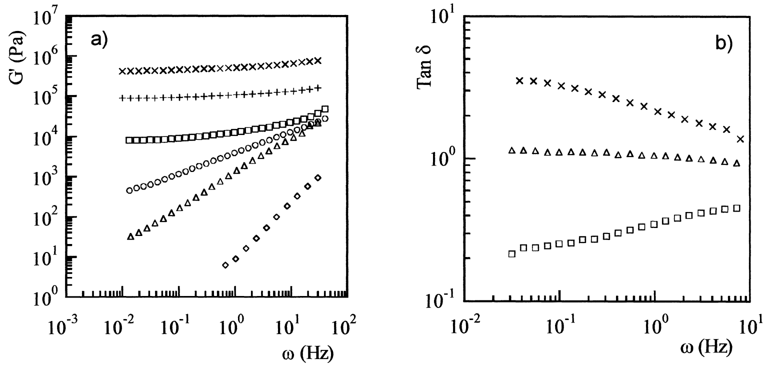

Fig. 1 a) Storage modulus as a function of frequency at various temperatures (◊)85°C,(Δ)75°C, (O)73°C, (□)70°C, (+)65°C, (x)25°C for EVA/oil 50wt.% b) Loss tangent as a function of frequency at three temperatures (□)70°C, (Δ)73°C, (x)75°C selected to show gel-sol transition for EVA gels (see text).

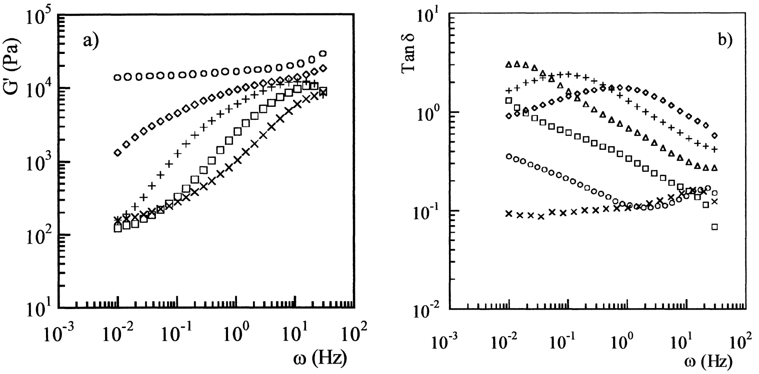

Fig. 2 a) Storage modulus as a function of frequency at various temperatures (x) 99°C, (□)90°C, (+)80°C, (◊)70°C, (O)25°C for SBS/oil 10wt.% b) Loss tangent as a function of frequency at various temperatures (x)25°C, (O)40°C, (□)70°C, (Δ)80°C, (+)90°C, (◊)99°C for SBS gels.

From G' and G'' versus frequency plots we infer that at 25°C both systems yield a gel, since moduli are practically frequency independent (Figures 1a and 2a show this for G') with a higher elastic than viscous response ($\tan \delta < 1$). Typical gel viscoleastic behaviour disappears when temperature is increased, disclosing the response of a viscous solution (for which G' is proportional to ω^2 and G'' to ω) in the case of EVA/oil system, but not in the case of SBS/oil system that shows a more complex gel-liquid transition. Considering literature results with similar systems2), we assume that the origin of EVA/oil gels lies in PE crystallites which act as thermoreversible crosslinks of the network. In this system the gel-sol transition temperature is obtained from plots like those shown in Figure 1b, following the procedure described by Winter et al.5-6) which establishes that the transition corresponds to the temperature associated to a frequency independent loss factor. The results are shown in Table 1.

Table 1 Gel-sol transition temperatures of EVA/oil gels. Due to limitations in the measuring system, the transition has not been determined for 15% and below.

C (wt.%) EVA	T_{gs} (° C)
20	67.5
25	68.0
30	70.0
40	70.5
50	73.0

On the other hand, as has been pointed out by Chambon and Winter$^{7)}$, the phase angle δ (independent of frequency at the gel point) is proportional to the relaxation exponent Δ:

$$\delta_c=\Delta\,\pi/2 \quad \text{or} \quad \tan\delta_c=G''/G'=\tan(\Delta\,\pi/2) \qquad (1)$$

which suggests that the gel-sol transition is described by the scaling relation:

$$G'(\omega)\text{-}\ G''(\omega)\text{-}\omega^{\Delta} \qquad (2)$$

From plots like those shown in Figure 1 we deduce that for all of our EVA/oil gels (3 to 50 wt.% polymer concentration) the relaxation exponent at the transition temperature is Δ=0.5. Such exponent has been found in stoichiometrically balanced network polymers and networks with excess cross-linker$^{5)}$, but also in physical gelatin gels$^{8)}$. A theoretical model developed by Muthukumar$^{9\text{-}10)}$ relates the value of the relaxation exponent to the fractal dimension d_f at the gel point:

$$d_f= 2\Delta/(1-\Delta) \qquad (3)$$

This relation gives a fractal dimension d_f=2 for our EVA/OIL gels. The correlation of the fractal dimension with the elastic modulus is contemplated in the final part of the paper.

Viscoelastic results of SBS/ oil system (such as those shown in Figure 2) reflect the same complex feature described several years ago by Watanabe et al. for SBS/n-tetradecane systems$^{3)}$. At low temperatures the polystyrene solid domains act as cross-links for the interconnecting polybutadiene chains: the system behaves like a gel. However to the difference of EVA/oil gels, increasing the temperature up to 100°C does not yield a homogeneous solution, but a microphase-separated structure which is rheologically noticed by the trend to constant G' at low frequencies and the swallow maximum in tan δ. This result is compatible with the viscoplastic behaviour detected by Watanabe et al. when, allegedly, the polystyrene blocks are demixed from polybutadiene matrix and go to other polystyrene domains. The complexity of the system reverts also in the analysis of the gel-sol transition, since, as can be seen in Figure 2b, tan δ does not become frequency independent and therefore the transition temperature can not be determined in this case. This result suggests that the procedure proposed by Winter[5-6)] is reliable when a transition from a gel to a homogeneous liquid takes place (as is the case of our EVA/oil gels), but becomes unapproachable when an intermediate state, like a liquid with a microphase-separated structure, is present. Figure 1 and 2 show that at low temperatures an equilibrium elastic modulus, G_e, of the gels can be defined as the value of the storage modulus when frequency tends to zero. The variation of G_e with polymer concentration is represented in Figure 3 which shows that both gel systems follow the scaling law $G_e \propto c^n$, with n=2.8 for EVA/oil and n=1.3 for SBS/oil. From a practical point of view we remark that our gels posses enhanced elastic moduli, with respect to SBS/aromatic oil gels which are used to develop synthetic binders[4)].

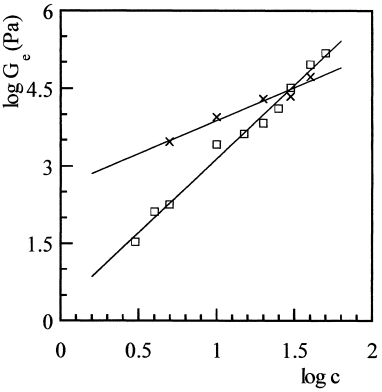

Fig. 3 Variation of the equilibrium elastic modulus, G_e, with polymer concentration for (□)EVA/oil and (x) SBS/oil gels.

We have not found in the literature experimental studies which correlate the elastic modulus of the gel with its fractal dimension, but theoretical models like mean field theory[11)] and percolation theory[12)] (Rouse limit) predict, respectively, n=3 for d_f=4 and n=2.67 for d_f=2.5. These predictions do not agree with the values n=2.8 and d_f=2 obtained experimentally for EVA/oil gels. Better agreement is obtained applying the theory of Jones and Marques[13)] for a freely hinged network of rigid chains, which gives an exponent n=3 for a fractal dimension d_f=2.

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