



*Dedicated to the memory of
Professor Eugen Segal (1933-2013)*

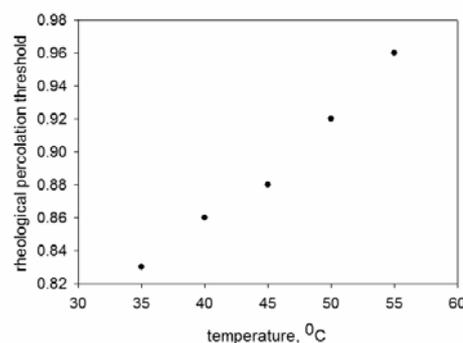
TEMPERATURE IMPLICATIONS ON THE RHEOLOGICAL PERCOLATION THRESHOLD IN POLY(4-VINYLPYRIDINE)/BARIUM TITANATE NANOCOMPOSITES

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Novel polymer nanocomposites were prepared by introduction of barium titanate nanopowder into poly(4-vinylpyridine). The technique employed in the preparation of the samples consists in solution shearing combined with ultrasonication. The formation of nanoparticle networks in polymer matrix leads to changes in the sample's microstructure. These modifications are reflected in the shear viscosity dependence on shear rate, observed as a thinning domain at low shearing (under 1 s^{-1}). This flow behavior becomes more pronounced as the reinforcement is higher. The sudden changes noticed in the low-frequency storage modulus ($> 1 \text{ wt}\%$ BaTiO₃) are indicative of the transition from viscoelastic liquid- to solid-like flow. The result reflects the enhancement of the interactions occurring among the nanoparticles. The percolation threshold is affected by temperature, which causes more movement of the polymer chains and disrupts the nanofiller network.



INTRODUCTION

Polymers containing nanoinclusions provide several advantages over micron-filled polymers since they exhibit better resistance to degradation¹ and improvement in thermo-mechanical and dielectric properties². The enhancement of the physical properties might be caused by several factors,³⁻⁵ including the large interaction area of nanoparticles, changes in the space charge distribution and in the polymer morphology. The surface area-to volume ratio is higher comparatively with microcomposites, resulting that a significant volume fraction of polymer surrounding the particle is influenced by the

particle surface and has properties different from the bulk polymer.

The final characteristics of the polymer nanocomposite are dependent on nanofiller nature, size and the state of dispersion. There are some applications where a perfectly homogeneous dispersion is required, but in other cases a controlled aggregation of the nanofiller is desired.^{6,7} Many investigation methods⁸ have been used to evaluate the dispersion degree of nanoparticles in various systems. Among them, rheology is one of the most fast and sensitive methods to the changes in the reinforced polymer microstructure. Rheological properties of polymer nanocomposites in solution or the molten state are

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important for designing and/or optimizing their preparation and shaping processes. For this reason, it is essential to determine the percolation threshold because the rheological behavior of reinforced polymers is generally very different before and after the percolation threshold.

In this work, a new system of polymer nanocomposites based on barium titanate (BaTiO_3) and poly(4-vinylpyridine) (P4VP) is prepared by solution shearing combined with ultrasonication. The rheological behavior of P4VP/ BaTiO_3 is examined in light of interactions between the nanofiller and polymer chains or between barium titanate nanoparticles at different temperatures.

RESULTS AND DISCUSSION

The rheological properties of the P4VP/ BaTiO_3 nanocomposites are investigated with a stress rheometer under steady state flow. Fig. 1 shows the

dependence of shear viscosity as a function of shear rate for neat polymer and the corresponding nanocomposite solutions.

The P4VP matrix presents a Newtonian behavior in the entire range of shearing, while the corresponding P4VP/ BaTiO_3 nanocomposites exhibit an increase in shear viscosity and significantly depends on shear rate at low shearing. The Newtonian regime is reduced as the BaTiO_3 amount increases, while the thinning behavior becomes more pronounced. The viscosity of the samples containing 10, 20, and 30 wt% nanofiller is decreasing probably due to the disruption of nanoparticle network formed in P4VP as the shear rate increases.

The changes observed in the samples' microstructure during reinforcement are also reflected in the rheological moduli. The dependence of storage modulus G' on the nanoparticle content content at 1 rad/s and 35°C is presented in Fig. 2.

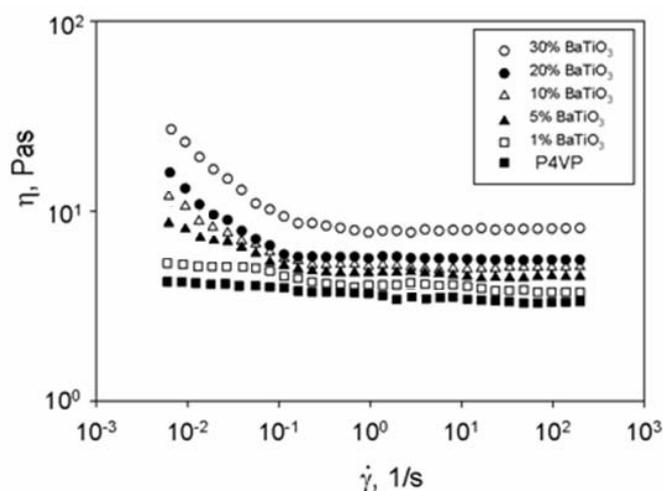


Fig. 1 – Shear viscosity as a function of shear rate for studied P4VP/ BaTiO_3 nanocomposite solutions in DMAc at 35 °C.

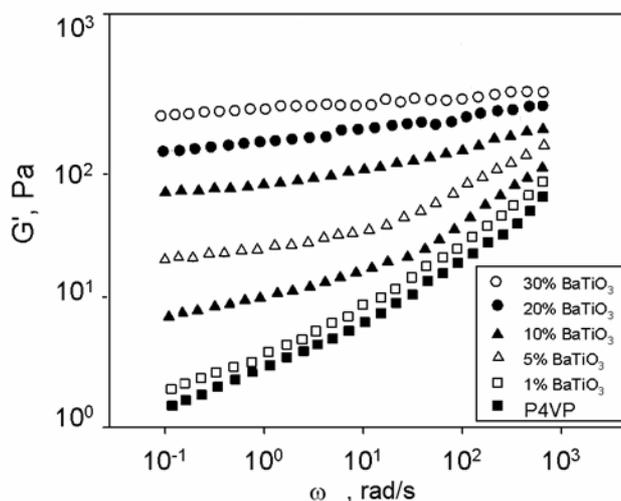


Fig. 2 – Storage modulus dependence on angular frequency for the studied P4VP/ BaTiO_3 nanocomposite solutions at 35 °C.

The pure P4VP exhibits terminal behavior similar to linear polymers with scaling properties of approximately $G' \propto \omega^2$ and $G'' \propto \omega^1$.⁹ The power law dependence of both shear moduli on angular frequency, ω , weakens monotonically with increasing BaTiO₃ amount. The effect of nanofiller on the viscoelastic properties of the nanocomposites is strong particularly at low ω values.

The observed nonterminal behavior reveals that the nanoparticles determine the restriction of P4VP chain relaxation, and also influences the local motion of polymer chains in the solution. In other words, the significant jumps remarked in the low-frequency storage modulus, starting with 1 wt% BaTiO₃, are indicative of the transition from viscoelastic liquid- to solid-like flow. This is caused by the enhancement of the interactions occurring among the nanoparticles, leading to formation of a percolation network. Comparatively with the viscous G'' modulus, the elastic G' one is found to be more sensitive to the dispersion quality of nanofiller, which is a result of the interfacial energy.¹⁰

For a deeper analysis of the data derived from the oscillatory tests the curves $G' = G'(\omega)$ are fitted to the power law described by equation (1):

$$G'(\omega) = A \cdot \omega^t \quad (1)$$

where A is a constant and t is the relaxation exponent.

The variation of the relaxation exponent with the nanofiller content for the studied P4VP/BaTiO₃ nanocomposite solutions. For the pure Newtonian systems this parameter is equal with 2, whereas for polymers with low reinforcement this value

changes. Literature indicates lower values than 2 for polymer melts with broad molecular weight distribution.⁸ For the investigated nanocomposites the relaxation exponent ranges between 0.33-1.24, as shown in Fig. 3.

The decrease of the parameter t is connected with an entanglement transition where the nanofiller form an interconnected network in the suspension. At high content of BaTiO₃ the sample presents a decreased low-frequency power-law indicating a solid-like rheological behaviour. The reduction of the relaxation exponent occurs in a broader filler content regime. This observation might be explained in terms of a less robust BaTiO₃ network formed when reaching the critical filler amount for mechanical interlocking of nanoparticles.

In other words, the studied nanocomposites undergo a rheological transition after the critical filler content required for the formation of an entangled and mechanical rigid network. The most sensitive to these agglomerate networks is the elastic storage modulus G' in the terminal region. The G' data collected at 1 rad/s are plotted as a function of the filler content for the P4VP/ BaTiO₃ suspensions, resulting a rheological percolation diagram – see Fig. 4.

In order to perform a deeper analysis on the rheological percolation, the data of the samples are fitted by the statistical percolation theory¹¹ in analogy to the fitting performed for the electrical conductivity of the cured systems:

$$G' \propto (\phi - \phi_{percol})^\beta \quad (2)$$

where ϕ is the filler content, ϕ_{percol} is the percolation threshold and β is the critical exponent.

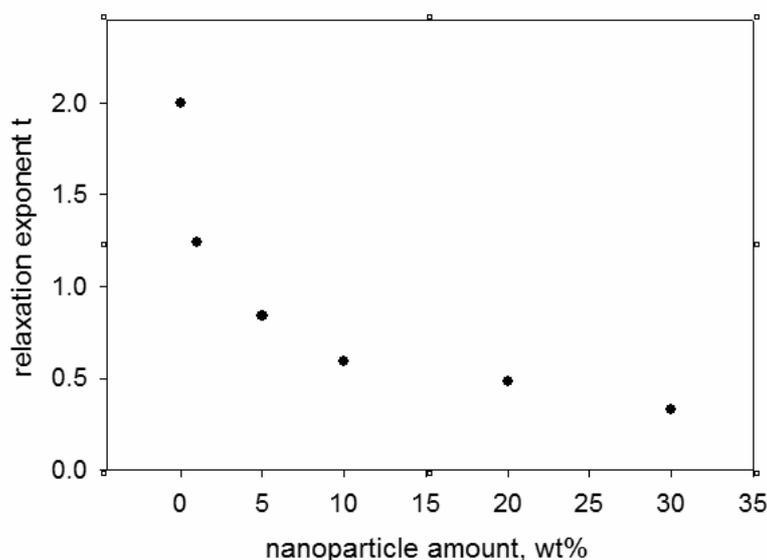


Fig. 3 – Relaxation exponent dependence on nanoparticle amount for the P4VP/BaTiO₃ samples at 35°C.

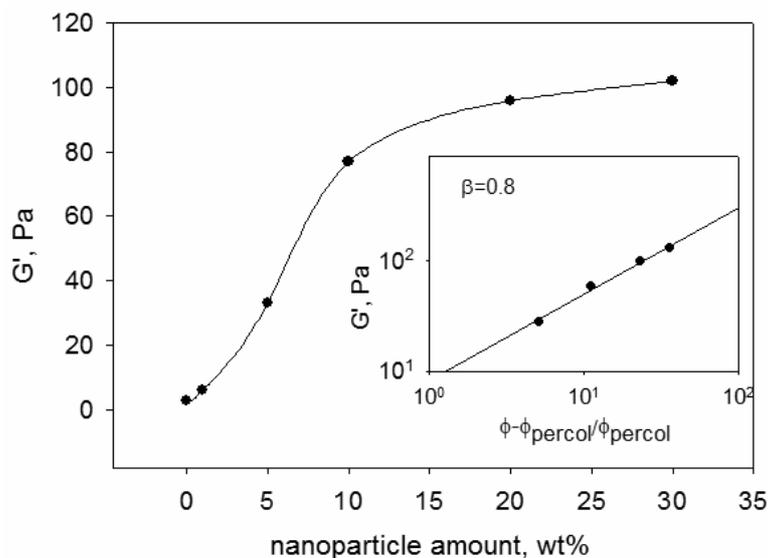


Fig. 4 – The dependence of the storage modulus on nanoparticle amount for the P4VP/BaTiO₃ samples at 35 °C. The inset graph represents the storage modulus plotted against the reduced mass of the system.

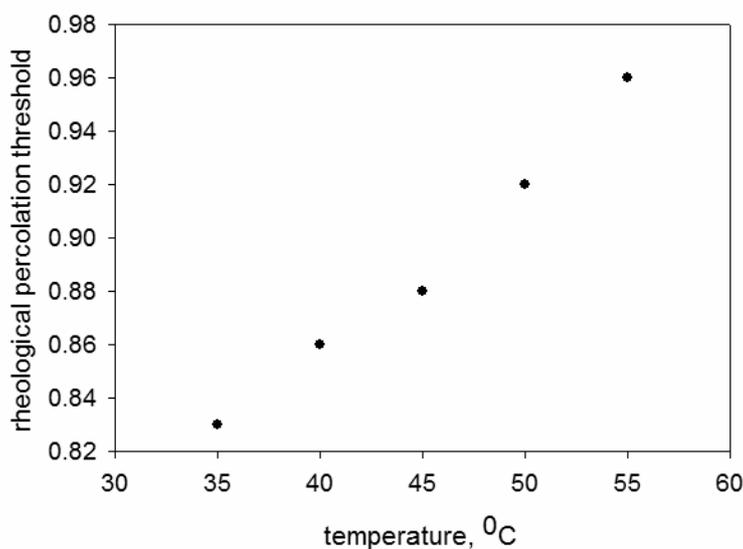


Fig. 5 – The variation of the rheological percolation threshold with temperature for the P4VP/BaTiO₃ samples.

The percolation threshold in the fitting was incrementally changed ($\Delta\phi = 0.01$ wt%) in order to get a best fit of the rheological data. Also, the temperature influences the rheological percolation threshold. According to Fig. 5 the temperature induces higher movement of the polymer chains and disrupts the nanofiller network and thus the threshold slightly increases.

EXPERIMENTAL

Materials. P4VP with average molecular weight $M_w = 60000$ g/mol, the solvent *N,N*-dimethylacetamide (DMAc, 99.5% purity) and the BaTiO₃ nanopowder (< 100 nm particle size) are purchased from Sigma-Aldrich.

Preparation of the P4VP/DMAc solutions. Several concentrated 35% P4VP solutions in DMAc are prepared. The BaTiO₃ dispersion is obtained by mixing different amounts of nanopowder with 2 mL of DMAc in a flask and then ultrasonication of the resulting mixture for 1 h. The polymer is then mixed with an appropriate amount of BaTiO₃/DMAc, to obtain 1, 5, 10, 20, and 30 wt% BaTiO₃. The nanocomposite solutions are homogenized by vigorously shearing during 30 min.

Rheological measurements. The rheological analysis of the nanocomposite solutions is performed on a stress-controlled instrument with cone-plate configuration. Shear viscosities are recorded over the 0.01–300 s⁻¹ shear rates, at several temperatures (35–55°C). Oscillatory shear tests were carried out within the linear viscoelastic regime of the samples. For this reason, a shear stress of 2 Pa was selected for the frequency sweep tests.

CONCLUSIONS

This paper is focused on the preparation of some new nanocomposites using P4VP as matrix in which are introduced different percents of barium titanate nanoparticles. The synthesis procedure is a traditional one, consisting in solution shearing of the matrix with the nanofiller suspension, stabilized by ultrasonication. The sudden changes recorded in the shear viscosity reflect a good dispersion of then nanofiller in the polymer. Also, the response of storage modulus at low angular frequencies reflects the formation of a percolated structure inside the P4VP matrix. When the temperature increases from 35°C to 55 °C the thermo-dynamical movement of the polymer chains affects the nanoparticle network leading to a small increase of the rheological percolation threshold. This type of polymer nanocomposites are useful in fabrication of embedded capacitors.

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