Properties of Epoxy Systems with Clay Nanoparticles

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Summary: Low molecular epoxy resin was mixed with different concentrations of montmorillonite clay with alkylamine-modified surface. The presence of the clay nanoparticles influences the gel time of the amine cured resin as well as the mechanical properties. Toughness and modulus, both in the glass and the rubberlike region, increase with clay concentration. An increasing amount of lower mobility phase with increased clay concentration was observed.

Keywords: clay; epoxy resin; gelation; mechanical properties; nanocomposite

Introduction

Polymer – clay nanocomposites represent a new class of materials displaying improved mechanical and thermal properties, even at relatively low clay content, in comparison with conventional polymers and microcomposites. Montmorillonite based clay is modified before it is used as polymer filler. Clay interlayer cation (Na^+) exchange, e.g., with organic ammonium salts, is generally required in order to enhance the organophilic character of the clay to favour polymer insertion between the silicate sheets. The clays treated in this way are used for improving the properties of many thermoplastic and thermosetting polymers.[1-3] In the latter case, due to their chemical and physical structure, the presence of clays can complicate the curing process.

Experimental

Commercially produced epoxy resin based on Bisphenol A was mixed with various amounts of montmorillonite clay modified with alkyl amine. This system was cured by Jeffamine D 400 (amine-terminated polypropylene oxide) for 24h at room temperature and 16 h at 80 °C. The resulting samples with all clay concentrations remain fully transparent.

The gel time of the polymer-clay nanocomposite was followed at different temperatures and frequencies (multiwave mode) by means of DMA (Rheometric Scientific Ares). Dynamic

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mechanical properties were measured by means of the same device. The measuring frequency was 1Hz and heating rate 3 °C/min.

Results and Discussion

The influence of modified clay on gel time was studied on a system with 15 % filler. The results are shown in Fig. 1. The curing behaviour of the system without any filler and with a finite concentration of quartz sand was very similar. The time dependence of the loss tangent for both systems is practically identical and they are in accordance with Winter's criterion. The temperature plot of the gel time of neat epoxy resin with hardener and the same system with quartz sand can be described by an Arrhenius equation with identical values of activation energy and pre-exponential factor. In the case of presence of clay, both parameters of the Arrhenius equation differ (Fig. 1). The reason may be in various polymerization rates in intragallery and extragallery. These effects of the organically modified clays were discussed in the literature.[4]

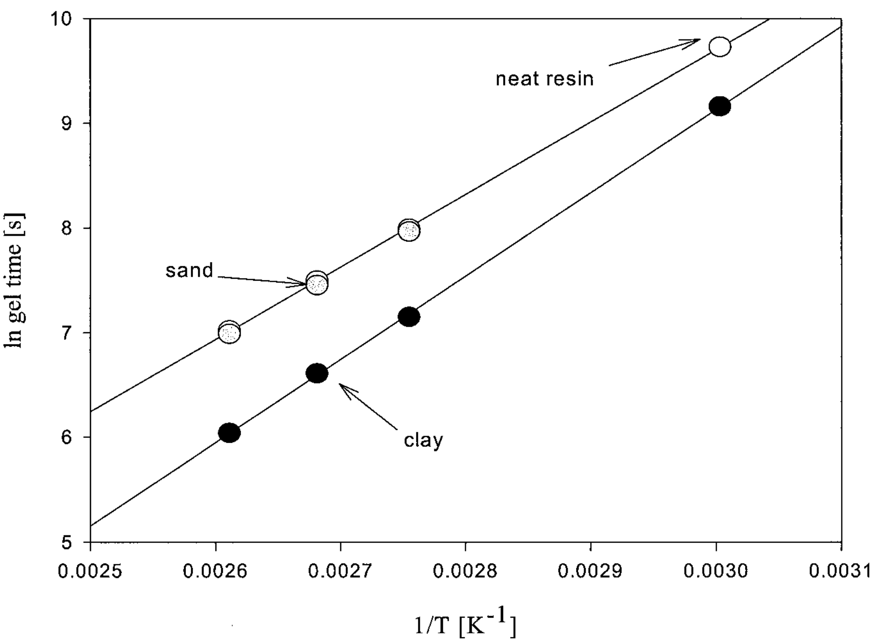

Fig. 1. Temperature dependence of gel time for systems filled with montmorillonite, quartz sand and neat polymer.

The presence of clay has no influence on the reaction stoichiometry. The excess of amine (15 % wt.) in polymer clay nanocomposites brings about a 10 °C drop in the glass transition. The shear modulus in the rubber-like region is reduced with increased excess of epoxy groups in the polymer extragallery. These effects of the organically modified clays have been discussed in the literature[4] clay nanocomposite (Table 1).

Table 1. The influence of the excess of epoxy groups.

Excess of epoxy groups	Tg	G_e
[%]	[°C]	[MPa]
0 %	52	12.7
10%	50	9.1
20%	50	5.72

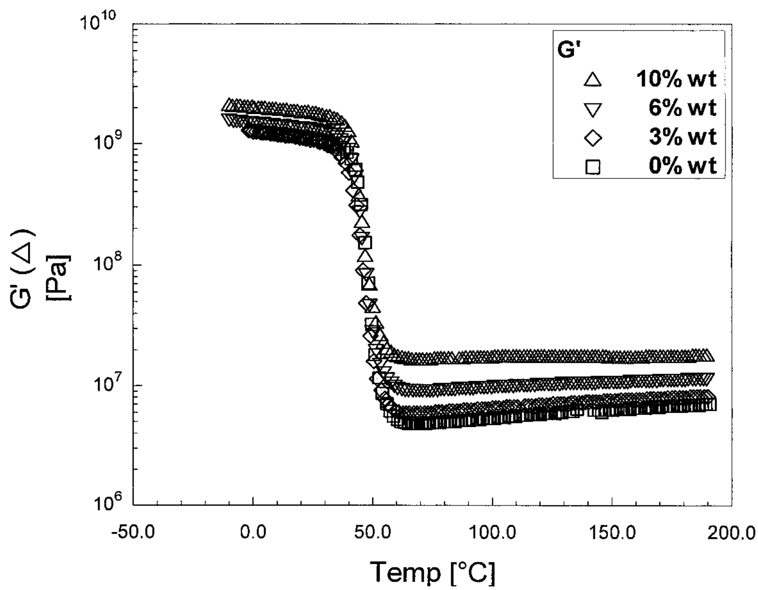

Fig. 2. Temperature dependence of storage shear modulus for systems with different clay concentrations.

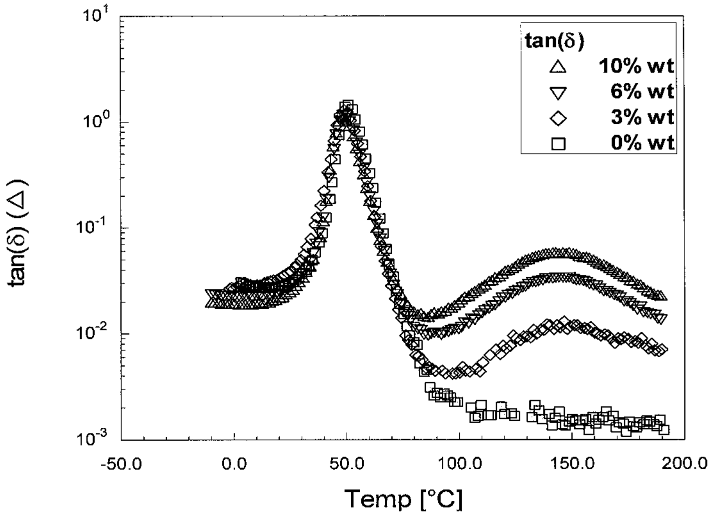

Fig. 3. Temperature dependence of loss tangent for system with different clay concentrations.

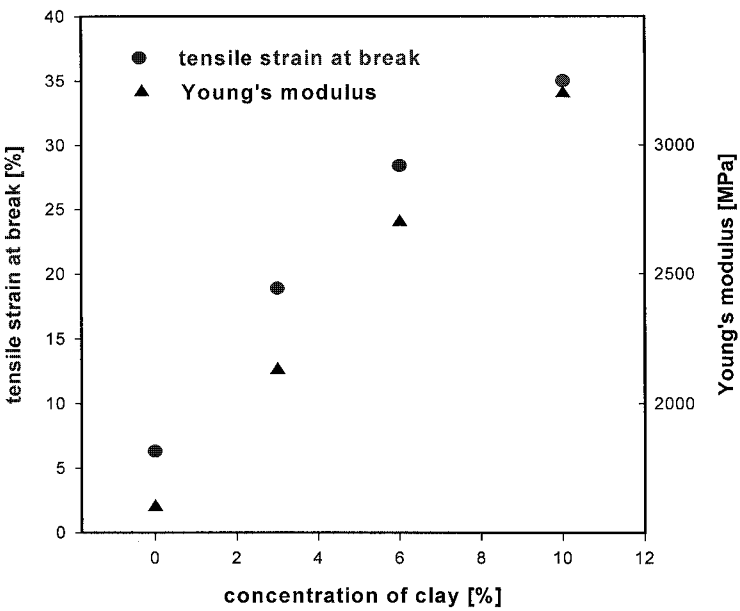

Fig. 4. Plot of tensile strain at break and Young's modulus vs. clay concentration.

The value of the storage modulus in the glassy state and in the rubber-like region increases with clay concentration in the system. The position of the main transition region does not depend on the concentration of clay. The loss tangent (Fig.3) shows two maxima in presence of clay. The shape and position of the main (first) loss tangent peak (50 °C – 52 °C) is the same for all clay concentrations and is connected with the behaviour of the epoxy network. The second loss tangent maximum at 150 °C is strongly influenced by the clay concentration. The loss tangent peak at high temperature is supposed to be connected with the lower mobility phase of epoxy network cast on the clay particle surface.

The tensile properties of systems with different clay concentrations were followed as well. A plot of tensile strain at break and Young's modulus vs. clay concentration is shown Fig. 4. It is a very unusual simultaneous improvement of modulus, toughness and strain at break. Measured tension properties for all clay concentrations are compared in Figure 5.

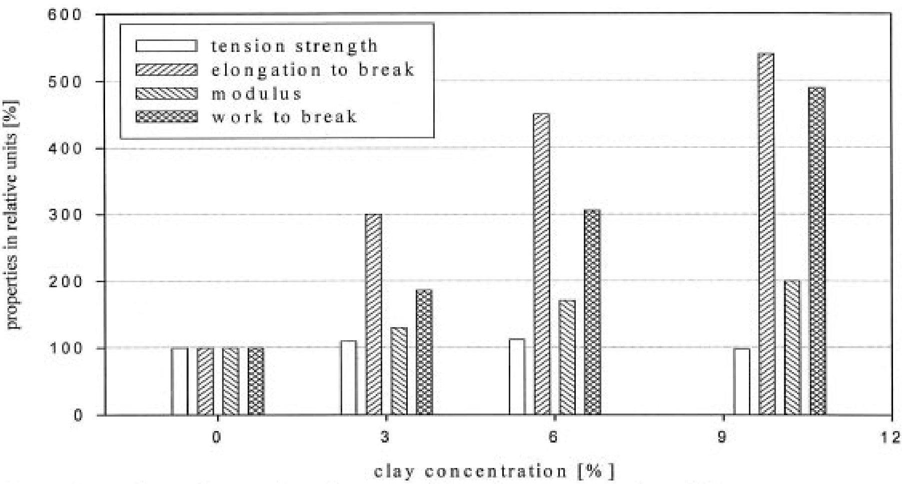

Fig. 5. Comparison of properties of systems with various concentrations of clay.

The addition of clay to epoxy networks influences positively ultimate properties in tension. The elongation to break rises more than five times in the clay concentration range 0 % - 10 %. Simultaneously, Young's modulus is doubled and the toughness of the polymer-clay nanocomposite is improved substantially as well. According to Pinnavaia[5] the improved elasticity can be connected with the plasticizing effect of clay surface modification and the conformational effects on the polymer at the clay-matrix interface. However, we observed an increasing amount of lower mobility phase with increased clay concentration.

Conclusions

The addition of modified clay to epoxy – amine hardener system influences the rate of curing reaction. The presence of clay increases the values of the modulus both in the glassy state and the rubber region. The position of the glass transition does not seem to be influenced. The clay brings about the development of a secondary maximum at higher temperatures. The origin of this maximum might be in the formation of a polymer phase with limited mobility on the surface of clay particles or among them. The clay substantially improves the tension mechanical properties.

Acknowledgement

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