

# RHEOLOGICAL BEHAVIOR OF EPOXY-AMINE SYSTEMS MODIFIED BY SEPIOLITE.

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## Introduction

Among the thermosetting polymers, epoxy resins are the most important and widely employed due to their inherent properties such as high modulus, excellent chemical and corrosion resistance and good dimensional stability [1]. In order to improve toughness it has commonly incorporated a rubbery phase or a rigid thermoplastic that form a second phase during the cure. [2,3]

In the last years, nanocomposites based on organically modified silicates in a polymeric matrix represent an area of research which has shown explosive growth.[4] This has been due in large part to the potential to achieve property enhancements significantly greater than that using conventional fillers, thermoplastics or rubbers.

In this work, sepiolite has been employed as inorganic nanofiller for epoxy resins. Sepiolite consists of fibrous talc-like layers stacked in long ribbons with micro-channels and grooves parallel to the fibre axis. The micropores and channels are responsible for the high surface area and sorptive capacity of the mineral.

The aim of this paper has been to study the gelification and vitrification processes by oscillatory rheology of the epoxy resin in presence of natural and organically modified sepiolite. Two curing agents: an aliphatic and an aromatic diamine have been used to build up the epoxy network. The influence of the modification of sepiolite, concentration and curing agent has been determined.

## Experimental

### *Materials*

The epoxy resin used was Araldite<sup>®</sup> GY250, a commercial diglycidyl ether of bisphenol-A kindly provided by Vantico Spain. The curing agents were a diamine terminated polypropylene oxide Jeffamine D230 (D230) kindly supplied by Huntsman Corporation and an aromatic diamine 4,4'-methylene-bis-(2,6 diethyl) aniline (MDEA) supplied by Lonza Cure. The unmodified sepiolite Pangel S9 and the organically modified sepiolite Pangel B5 from Tolsa (Spain) were used as nanofillers. The dimensions of a single sepiolite fibre vary between 0.2 and 3  $\mu\text{m}$  in length, 10-30 nm in width and 5-10 nm in thickness [5].

### *Sample preparation*

Sepiolite dispersions in the epoxy pre-polymer were obtained by using a high-speed mixer Dispermat<sup>®</sup> CN20 (VMA-Getzmann GMBH, Germany) at 7200 rpm with a 5 cm diameter disk for 25 min. The sepiolite loading expressed as grams of sepiolite per hundred grams of resin (phr) were as follows: 0, 2.5, 5.0 and 7 phr. The curing agent (Jeffamine D230 or MDEA) was added to the sepiolite/pre-polymer dispersions at a stoichiometric ratio epoxy/amine,  $[E]/[H]=1$ .

### *Rheological measurements*

Rheological oscillatory measurements were performed on a controlled stress rheometer TA Instruments AR1000N, using the parallel plate (25 mm diameter) shear mode to

measure the storage modulus,  $G'$ , the loss modulus,  $G''$  and the loss tangent,  $\tan \delta$ . The thickness of the samples was about 1.0 mm. The rheological study of the curing process was performed at 75 °C for the Jeffamine D230 system and at 130 °C for the MDEA system. Time sweeps were carried out in a multifrequency experiment (frequencies between 5 and 50 rad/s).

## Results and Discussion

Gel times were determined from multifrequency rheological experiments as the time for the  $\tan \delta$  to be frequency independent. Table 1 shows gel times as a function of sepiolite concentration and hardener. Addition of sepiolite decreases gel time. In presence of the organically modified sepiolite,  $G' > G''$  for higher sepiolite concentrations and gel time cannot be determined by this method.

Table 1 Gelation times for epoxy/amine/sepiolite systems at different sepiolite concentrations.

Hardener	sepiolite	phr	$t_{gel}$ (min)
D-230 $T_C=75\text{ }^\circ\text{C}$	S9	0.0	54.2
		2.5	51.1
		5.0	46.7
		7.5	42.0
	B5	2.5	52.4
		5.0	44.1
		7.5	$G' > G''$
MDEA $T_C=130\text{ }^\circ\text{C}$	S9	0.0	102.0
		2.5	91.0
		5.0	80.3
		7.5	75.2
	B5	2.5	97.0
		5.0	$G' > G''$
		7.5	$G' > G''$

Vitrification times as a function of sepiolite are summarized in Table 2 and slight dependence on sepiolite concentration is detected.

Table 3 Vitrification times for epoxy/amine/sepiolite systems as a function of sepiolite concentration.

Hardener	sepiolite	phr	$t_{vit}$ (min)
D-230 $T_C=75\text{ }^\circ\text{C}$	S9	0.0	140.7
		2.5	137.0
		5.0	141.9
		7.5	134.9
	B5	2.5	135.9
		5.0	140.6
		7.5	156.7
MDEA $T_C=130\text{ }^\circ\text{C}$	S9	0.0	209.4
		2.5	187.2
		5.0	174.4
		7.5	190.2
	B5	2.5	200.0
		5.0	184.8
		7.5	172.3

## Conclusions

The curing behaviour of epoxy/amine systems in presence of unmodified and organically modified sepiolite as nanofiller has been investigated by oscillatory rheology. Gelation times decrease as the concentration of sepiolite increases due to a catalytic effect of the nanofiller. Vitrification times depend on the frequency and are nearly independent of the concentration of sepiolite.

## References

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