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POROUS EPOXY THERMOSETTING POLYMERS OBTAINED BY A PHASE SEPARATION PROCESS IN THE PRESENCE OF EMULSIFIERS

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SUMMARY: Macroporous epoxy thermosetting polymers, prepared by a polymerization – induced phase separation method and stabilized by emulsifiers were investigated. In such a method, phase separation and the resulting morphologies are controlled by the polymerization kinetics, the cloud point and the viscosity evolution. Epoxy-amine systems containing different concentrations of emulsifiers and water are prepared. The morphology is analyzed by Scanning Electron Microscopy and quantified by image analysis. It is shown that the emulsifier enhances the amount of water miscible in the matrix and greatly decreases the pore size and most all the pore size distribution of porosities.

Introduction

Currently, there are many of synthesis to obtain porous polymer structures, but phase separation can be one of the most versatile . This method of synthesis separates an initially miscible solvent from i-mers as polymerization takes place. Application field of micro or macro-porous (depending on the pore size [**1**]) is enormous (membranes, filters, chromatrography, dielectrics etc.). Our study aims at generating porous thermosetting polymers with controlled porosities which exhibit either closed-cell structures or co-continuous structures of micron and sub-micron sizes. Such materials have already been suggested for high permitivity films in microelectronics but could also serve as matrices to host a second phase with functional properties e.g. conductive, electro-optical. Our systems are obtained by a phase separation process in the course of a polymerization. The morphology of our systems results from the polymerization-induced phase separation of an inert solvent initially miscible in an epoxy precursor. The porous structure is provided when the solvent is extracted from the polymer matrix. So far such systems have been thoroughly studied by Kiefer and al. [**2,3,4**] using high T_g thermosets (epoxies or cyanurates) and organic solvents (hexane, cyclohexane).

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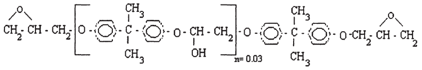
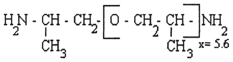
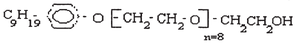
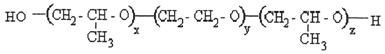
Here we present new epoxy-amine / water systems processed in the presence of emulsifiers and sometimes a catalyst. The emulsifiers are chosen to « compatibilize » the polymer and water phases : a polyethylene glycol 4–nonylphenol emulsifier and Poly(propylene oxide)-block-poly(ethylene oxide)-block- Poly(propylene oxide) were also tested. The use of such amphiphilic molecules is likely to modify several parameters in the formation of the porous materials : volume fraction of initially miscible water, polymerization kinetics, cloud point conversions, and the size distribution of porosities. As a consequence, our study will first present a kinetic study to determine the polymerization conversions and the gel points, then a phase separation study (cloud points).

Experimental

All the compounds used are listed in Table 1.

Table 1. Formula of compounds used

Name	Source	Formula	Mn (g/mol)
DER 332	Dow Chemicals		348.5
D400	Huntsman	 $H_2N-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-\left[O-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-\right]_{x=5.6}NH_2$	400
polyethylene glycol 4–nonylphenol Antharox	Rhône Poulenc		616
Poly(propylene glycol) – block – poly(ethylene glycol) – block – poly(propylene glycol) (PPO-PEO-PPO)	Aldrich	 $HO-\left(CH_2-\underset{CH_3}{\underset{\mid}{CH}}-O\right)_x-\left(CH_2-CH_2-O\right)_y-\left(CH_2-\underset{CH_3}{\underset{\mid}{CH}}-O\right)_z-H$ X+z = 16.9 y=22.73 X+z= 50.9 y= 7.5	2000 3300

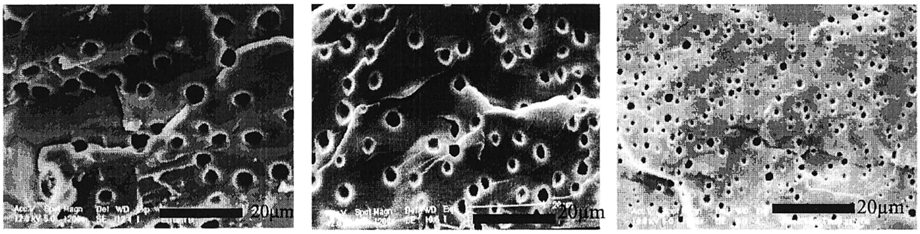
The monomers and the additives were stirred together in the following order: 3.485 g epoxy and a given percentage of emulsifier and water, then 2g diamine to provide the steochimetric ratio equal to one, this clear solution was collected into a 10 mm diameter sealed glass tube. Then the polymerization was carried out in an oven at 30°C or 50°C. The solid mixture was heated up to 70°C for 24 hours in order to evaporate the water. The volume fraction of initially miscible emulsifier and water in the mixture was characterized by a cloud point method. SEC is used to measure the reaction conversion, tetrahydrofuran is used as the eluent at a flow rate of 1 ml.min^{-1}. Assuming the equireactivity of the epoxy groups, the conversion was calculated using the relationship: $\mathbf{x = 1 - (A_t / A_0)^{1/2}}$ where A_t is the peak area of DGEBA monomer at time t and A_0 is the peak area of DGEBA monomer at t=0. The morphology was investigated by scanning electron microscopy (Phillips XL20, 12 Kv), the fractured surfaces were sputtered with gold. The results of image analysis are obtained on an average of at least 100 pores, for each sample three SEM micrographs were analyzed.

Results and Discussion

The morphologies (type and size) mainly depend on a competition between the polymerization and phase separation kinetics. Therefore, finding a method to control the morphologies requires measurement of the reaction kinetics, the behavior of the systems towards demixing upon polymerization and the role of an emulsifier. First we have to select an effective surfactant by considering its miscibility with monomers, its influence on the reaction kinetics and its influence on the solvent droplet size. Among the three surfactants tested, Table 2 shows that the volume of Antharox miscible is much higher than for the other polymeric surfactants and shows also that the mixture of DGEBA/D400/ANTHAROX remains homogenous after polymerization until 35% of Antharox. Figure 1 shows that systems with surfactants PPO-PEO-PPO exhibit closed porosities eight times larger than those with Antharox. Therefore Antharox has been chosen.

Table 2.

System (wt% with respect to the total mixture)	**Before (20°) polymerization**	**After(50°) polymerization**
DGEBA + D400 + **35%** ANTHAROX	**Clear**	**Clear**
DGEBA + D400 + **14%** PPO-PEO-PPO Mn = 2000	Cloudy	Cloudy
DGEBA + D400 + **9%** PPO-PEO-PPO Mn = 3300	Cloudy	Cloudy
DGEBA + D400 + 10% WATER	Cloudy	Cloudy
DGEBA + D400 + **15%** WATER + 2% ANTHAROX	**Clear**	Cloudy
DGEBA + D400 + **12%** WATER + 2% PPO-PEO-PPO Mn = 2000	Clear	Cloudy
DGEBA + D400 + **12%** WATER + 2% PPO-PEO-PPO Mn = 3300	Clear	Cloudy



a) Matrix + 8wt%water + 2wt% PP-PE-PP 3300

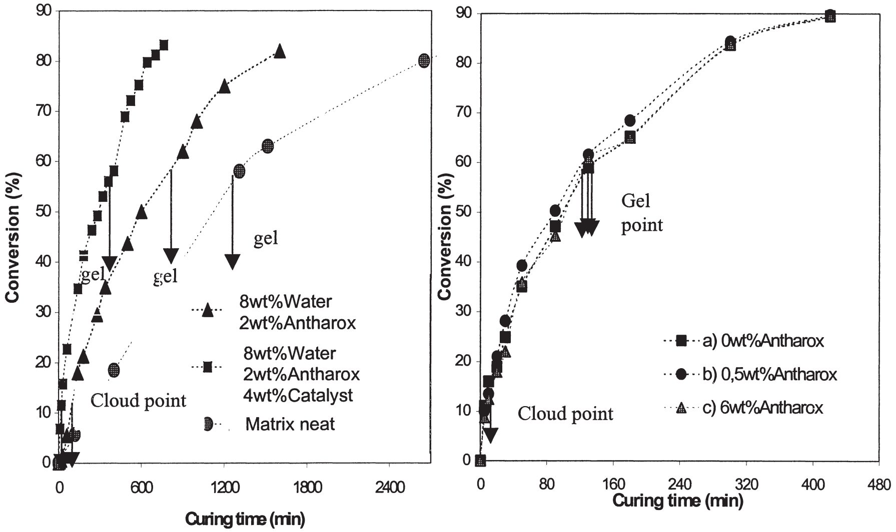
b) Matrix + 8wt%water + 2wt% PP-PE-PP 2000

c) Matrix + 8wt%water + 2wt% Antharox

Figure 1. Comparison of morphologies obtained with different emulsifiers

Reaction kinetics

Figure 2a shows the influence of water and a catalyst (CIBA, XB3130) on the time evolution of polymerization – conversion. These experiments show that the reaction rate is significantly raised by using 8wt% water and even more with the catalyst. It is well know that the hydroxyl groups catalyze the epoxy – amine reaction [**5**]. On the other hand, the concentration of catalyst and water does not significantly change the gel point and the 'cloud point'. Figure 2b shows that the addition of an emulsifier (Antharox) does not change the reaction rate neither the gel point. Also the 'cloud point' conversion observed during polymerization is not changed by the presence of Antharox, but the final morphology is greatly modified (Fig.3) .



a) **b)**

Figure 2. Conversion versus time during isothermal curing : a)30°C, influence of water and catalyst on the kinetics, b) 50°C, influence of the Antharox emulsifier on the kinetics (system Dgeba/D400/8wt% water/Antharox)

Therefore, the emulsifier allows to keep the same polymerization kinetics and the same cloud points, thus the difference in morphology is provided by the fact that the emulsifier prevents coalescence of growing water droplets. However, the role of the emulsifier and its influence on the phase separation mechanism can be more complex: at the concentrations used, it may form micelles before the cloud point which are swollen (or inflated) by the separating water ; or else it may be dissolved in the reacting system and migrate to the droplet interface after the cloud point.

Morphology

Figure 3 shows that the mean diameter not only decreases but also attains a more uniform distribution when Antharox is increased. The mean diameter is seen to attain an asymptote at about 0.5wt% (of emulsifier) while the distribution of droplets is still narrower upon adding the emulsifier. Indeed the percent cumulative are very broad for the sample which do not contain Antharox. This distribution becomes significantly narrower when Antharox is added. Figure 3d represents the morphology in the presence of both emulsifier and catalyst, we found that the polymerization at 30°C with a catalyst allows further decrease in the mean diameter.

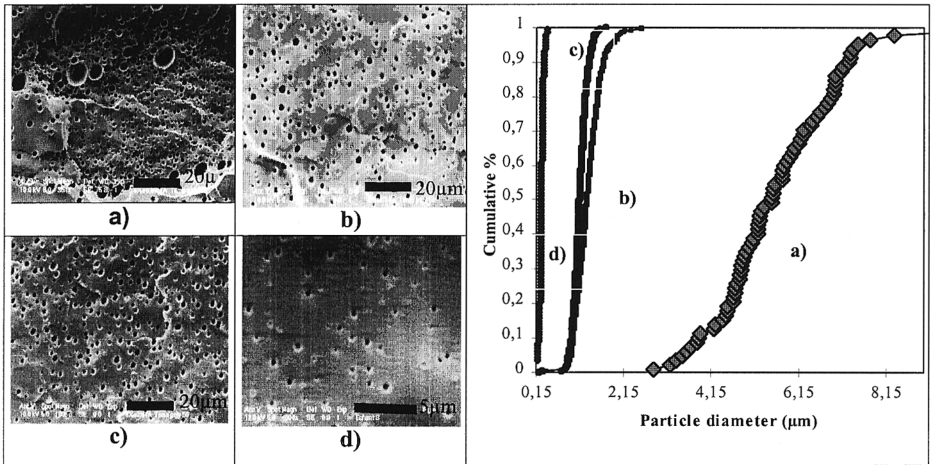
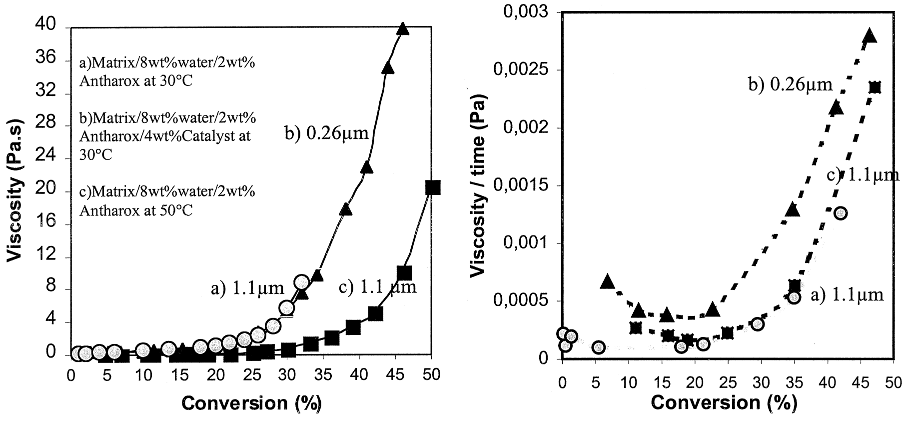


Figure3. Cumulative (linear) distribution of the particle size measured for: **a)** Dgeba/ D400/ 8wt%Water at 50°C, **b)** Dgeba/ D400/ 8wt%Water/ 0.5wt%Antharox at 50°C, **c)** Dgeba/ D400/ 8wt%Water/ 6wt%Antharox at 50°C and **d)** Dgeba/ D400 / 8wt%Water / 6wt%Antharox / 4wt%Catalyst at 30°C.

Viscosity evolution and consequences on morphology

Rheological measurements were performed in order to understand the fact that the mean diameter do not change with temperature while the kinetics rise. First we plot the conventional representation of viscosity versus conversion (fig 4a), it is obvious that the viscosity depends only on the polymerization temperature and not on the catalyst; this kind of representation does not allow to see the effect of viscosity on the morphology because systems with very different mean diameters, a)1.1 µm and b)0.26µm, have the same viscosity tendency. Then we calculated the ratio of the viscosity to time as a function of the polymerization conversion (fig 4b); with this new representation we can see that systems a) and c) at two different temperatures have the same evolution of viscosity to time ratio therefore the same final mean diameter. This ratio can therefore be used to take into account the effect of viscosity, temperature and the polymerization kinetics. This mathematical ratio does not have a physical meaning but allows to relate the influence of the viscosity on the mean diameter.



a) **b)**

Figure4. Reological measures a) Evolution of the complex viscosity versus conversion b) Ration viscosity/time versus conversion

Conclusion

Porous epoxy-amine thermosets were prepared via the phase separation of water in the course of polymerization of the epoxy-amine monomers. The morphology can be controlled by the polymerization kinetics, the position of the cloud point during polymerization and the addition of an emulsifier. A polyethylene glycol 4–nonylphenol emulsifier was found to give the best performance. This emulsifier was shown not to modify the polymerization kinetics and the cloud points, but it allows a very significant decrease in pore diameter and pore size distribution. Finally a viscosity to time ratio was introduced and calculated along the polymerization time to account for the diameter evolution.

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