Dielectric In Situ Sensor Monitoring of Phase Separation and Changes in the State of Each Phase

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Summary: Frequency dependent dielectric measurements have been used to monitor and characterize the phase separation process and changes in state of each phase. The measurements are made in situ using a micro planar sensor. They can be made both in the laboratory as well as in an industrial production or use environment. Two examples are presented. The first is monitoring the onset of phase separation, the buildup in Tg and change in composition of each phase during "reactive processing" of a high performance thermoplastic (TP) PPI, thermoset precursors (TS) DGEBA-MCDEA intially homogeneous blend. The second example involves monitoring the stability, onset of phase separation, as a function of temperature on a mineral oil, stearyl alcohol, water, sufactant emulsion used in the cosmetic industry.

Keywords: blend, cure monitoring, dielectric, PEI; reactive processing, thermoset-thermosplastic

Introduction

Thermoset (TS)/Thermoplastic(TP) blends are materials resulting from the mixing of the TP polymer with the TS precursor (generally a diepoxy-diamine system).[1-8] Usually the mixture is initially homogeneous. With time and a temperature below the Tg of the TP, there is an increase in the molar mass of the TS precursor as the reaction advances. A liquid-liquid phase separation occurs at a given conversion. The phase separation process generally continues until the TP rich phase becomes rich enough to form a glass. The overall process is stopped when the TS is fully reacted or both phases have achieved the glassy state.

These TS/TP blends have two main applications 1) toughness improvement of TS networks with high performance ductile thermoplastics and 2) new processing routes which reduce the initial viscosity of otherwise intractable high temperature TP polymers such as polyphenylene ether and

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polyetherimides. The first application occurs at low concentrations (<20 wt %) of TP. The second application involves TP concentrations generally greater than 30 wt %. In this case phase inversion occurs resulting in a TP rich continuous (β) phase with occluded TS rich (α) phase particles.

Experimental

The TS precursor consisted of an epoxy prepolymer and diamine curing agent. The epoxy prepolymer used was a diglycidyl ether of bisphenol, a liquid at room temperature and with a low degree of polymerization, DGEBA $\bar{n} = 0.15$. (Ref. LY556 from Ciba Geigy). The curing agent was an aromatic diamine with a low reactivity, 4,4' methylene-bis (3-chloro-2,6-diethylaniline), MCDEA supplied by Lonza. The diamine was used at the stoichiometric ratio, epoxy to amine hydrogen groups equal to 1. The TP was Polyetherimide, PEI Ultem 1000 supplied by General Electric. The structures are shown in Figure 1. Blends with concentration higher than 30wt% of TP (33, 48 and 64 wt % of PEI) were prepared using a co-rotating twin screw extruder in a one stage process.

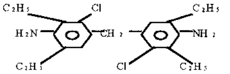
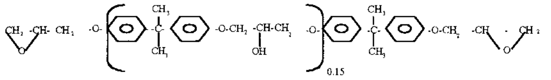
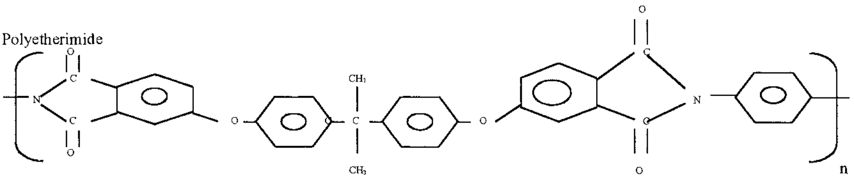
Name	**Formula**	**Source**
4,4'-methylene bis [3-chloro 2,6-diethylaniline] MCDEA		Lonza
Diglycidyl ether of Bisphenol A DGEBA		Ciba Geigy LY556
Polyetherimide PEI	 $\overline{Mn}$ = 26000 g/mol ; $\overline{Mw}$ = 50000g/mol Tg = 210°C	General Electric Ultem 1000

Fig. 1. Stuctures of MCDEA, DGEBA and PEI.

The emulsion, used in the cosmetics industry and supplied by ICI Wolrdwide Industries, was a non reactive mixture of a mineral oil, stearyl alcohol and two commercial surfactants Brij 721 and Brij 72 in water.

Background

Frequency dependent measurements of the dielectric impedance of a material as characterized by its equivalent capacitance, *C*, and conductance, *G*, are used to calculate the complex permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, where $\omega = 2\pi f$, f is the measurement frequency and C_o is the equivalent air replacement capacitance of the sensor.[9,10]

$$\begin{aligned} \varepsilon'(\omega) &= \frac{C(\omega)\ \text{material}}{C_o} \\ \varepsilon''(\omega) &= \frac{G(\omega)\ \text{material}}{\omega\, C_o} \end{aligned} \qquad (1)$$

This calculation is possible when using the planar sensor with interdigitated gold electrodes.[9,10] Thereby it's geometry is invariant over all measurement conditions. Both the real and the imaginary parts of ε^* can have dipolar (d) and ionic (i) charge components.

$$\begin{aligned} \varepsilon' &= \varepsilon'_d + \varepsilon'_i \\ \varepsilon'' &= \varepsilon''_d + \varepsilon''_i \end{aligned} \qquad (2)$$

Plots of the product of frequency (ω) multiplied by the imaginary component of the complex permittivity $\varepsilon''(\omega)$ make it relatively easy to visually determine when the low frequency magnitude of ε'' dominated by the mobility of ions and when at higher frequencies the rotational mobility of bound charge dominates ε''. Generally, the magnitude of the low frequency overlapping values of $\omega\varepsilon''(\omega)$can be used to measure the change with time of the ionic mobility through the parameter σ where

$$\sigma\,(\text{ohm}^{-1}\text{cm}^{-1}) = \varepsilon_o \omega \varepsilon''_i\,(\omega) \qquad (3)$$

$$\varepsilon_o = 8.854 \times 10^{-14}\ C^2\ J^{-1}\ \text{cm}^{-1}$$

The changing value of the ionic mobility is a molecular probe which can be correlated with viscosity in simultaneous laboratory experiments. In turn this calibration of σ with viscosity can be used to monitor changes in the viscosity by measuring $\sigma(t)$ during cure.

The dipolar component of the loss at higher frequencies can the be determined by subtracting the ionic component. The peaks in ε" dipolar (which are usually close to the peaks in ε") can be used to determine the time or point in the cure process when the "mean" dipolar relaxation time has attained a specific value $\tau = 1/\omega$. The dipolar mobility, as measured by the mean relaxation time τ, is monitoring the α–relaxation process associated with vitrification and it can be used as a molecular probe of the buildup in T_g. For example, the time of occurrence of a given dipolar α- relaxation time as measured by a peak in a particular high frequency value of ε"(ω) can be quantitatively related to the attainment of a specific value of the glass transition temperature.

Interfacial polarization processes which occur in heterogeneous dielectrics will be present at the onset of phase separation, that is beginning at the onset of the transition from a homogeneous to a heterogeneous two phase system.[11-13]. These effects arise at the interface of two media having differing permittivities and conductivities. These interfacial effects can be quite strong sometimes creating increases in ε' by factors of 10 and a charge polarization relaxation time. The effect is dependent on the magnitude of the conductivity difference (σ_2-σ_1) between the occluded phase σ_2, and the continuous phase, σ_1.

The most well known theoretical model of this effect is the Maxwell-Wagner-Sillars model.[11-13] Using the Maxwell-Wagner-Sillars model, the complex dielectric permittivity of the mixture ε*(ω), of orientated occluded ellipsoids with complex dielectric constant, ε^*_2 (ω), at a volume fraction ν_2 dispersed in a continuous matrix (ν_1) with a complex dielectric constant, $e^*_1(\omega)$, can be calculated from the following equation:

$$\varepsilon^* = \varepsilon^*_1 \frac{\varepsilon_1^*(1-\nu_2)(1-A)+\varepsilon_2^*[\nu_2+A(1-\nu_2)]}{\varepsilon'_1+A(1-\nu_2)(\varepsilon_2^*-\varepsilon_1^*)} \qquad (4)$$

where A(0≤A≤1), is the depolarization factor of the ellipsoidal filler particles. It depends on the shape of the particles (length of the long a to b short axis ratio for spheroids) and of the orientation of the field relative to the particle.

Discussion

Figure 2a shows for 33% PEI blend the changing value of ε′ during the 135°C cure over the frequency range of .005, .05, .125, .5, 5, 25, 50, and 250 KHz. The lowest frequency is the top line. The value of ε′ shows a sharp rise at 128 minutes indicating the onset of phase separation.

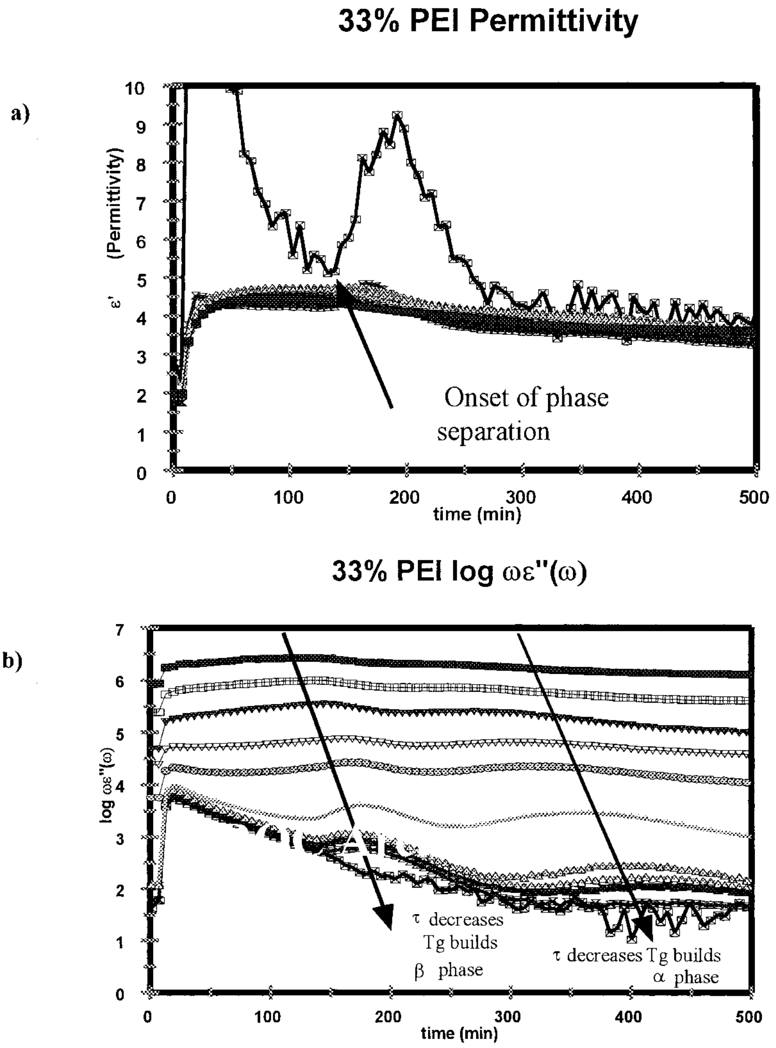


Fig. 2. a) Dielectric Sensor output during cure at 135°C; b) Dielectric sensor output during cure at 135°C, highest frequency is top line.

Figure 2b displays for the 33% PEI blend the loss component ε″ of the permittivity scaled by frequency with time during isothermal cure at 135°C. Two sets of peaks in ε″ occur. The first set occurs both before and after phase separation. They occur at the higher frequencies before phase separation and at the lower frequencies after phase separation. A second set of peaks starting at the higher frequencies occur only after phase separation. These peaks can be used to determine the achievement of a relaxation time τ where $\tau = (2\pi f)^{-1}$ at the time of a peak in ε″(ω) at that frequency, f. The imaginary loss, component ε″ shows overlapping values at the lower frequencies. These values of ε″ can be used to determine a frequency independent conductivity using equation 3. In the following discussion these two dielectric quantities (τ, σ) and the viscosity (η) will be measured and analyzed along with the previously reported values of extent of reaction x and the values of T_g to characterize the phase separation behavior of the reactive TP/TS blend. The relations can be used to build a fundamental basis from which the transformations of the reactive TP/TS blend can be monitored in situ during polymerization-fabrication using dielectric measurements.

Before phase separation. The TP/TS blend is a homogeneous mixture in which one observes, at different levels of TS precursor dilution, the changing conductivity of the epoxy-amine i-mers as the viscosity and the extent of reaction increases. Equation 3 was used to calculate the conductivity from the dielectric data. In Figure 3, the values of log(σ(t)) are plotted versus the log of viscosity, reported previously.[6,7] This correlation in figure 3 permits the sensor monitored value of σ(t) before phase separation to be used as a means to monitor the changing values of viscosity prior to phase separation. Examples of the relationship between the changing σ(t) versus x(t) and viscosity are reported in Table 1.

Table 1. Slopes, conductivity, viscosity and extent of reaction.

% PEI	Slopes		
	log (σ) vs x	log (η) vs x	log (σ) vs log (η)
0	-1.6	3.2	-0.7
33	-4.9	4.8	-1.3
48	-6.9	3.9	-1.8

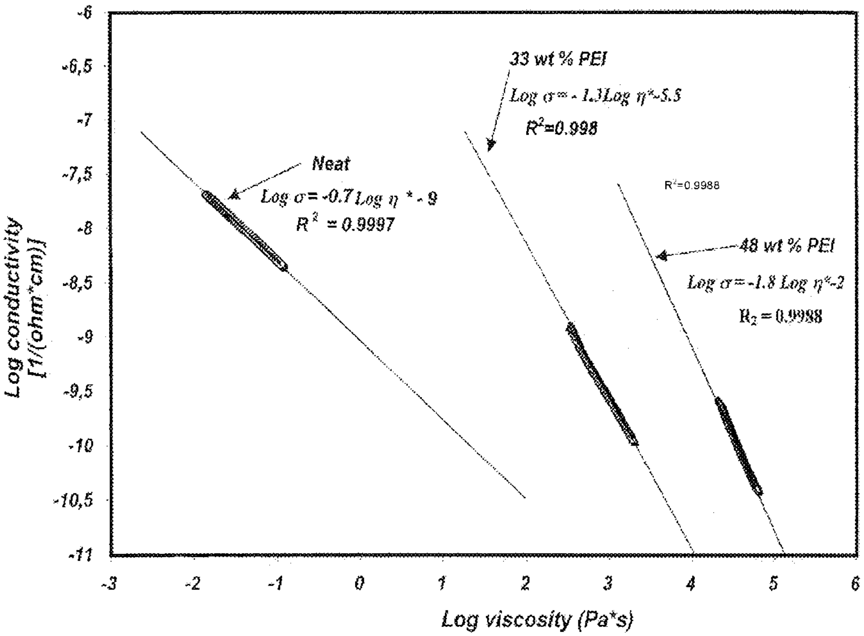


Fig. 3. Log(conductivity) versus log(viscosity).

The onset of phase separation is characterized by the creation of an interface between forming phases. From the point of view of dielectric behavior, the initial onset of the phase separation process has the potential to generate a large change in the permittivity ε' since interfacial surfaces with charge separated by molecular distances represent a large increase in capacitance i.e., $C_0 \approx$ area/distance. Furthermore, once the phase separation process has generated an occluded phase of conductive epoxy rich i-mers, the % phase, surrounded by a PEI rich nonconducting continuous phase, there is the potential as previously described for a Maxwell-Wagner-Sillars relaxation effects. Figure 2a (33 wt% PEI) clearly shows a large sudden increase in the value of ε' at 128 minutes. Another sample showed this rise at 105 minutes. The cloud point was observed at 118 minutes. For the 48% PEI blend the sharp rise in ε' occurred at 211 and 202 minutes in two separate runs. For the 48% PEI system the cloud point was observed at

235 minutes. Rheological measurements showed the phase separation transition at 113 minutes for 33% PEI and 216 minutes for 48% PEI [6,7]. Clearly as summarized in Table 2 the onset of the dielectric interfacial polarization, as seen by a sharp rise in ε', is a good instrumental means to monitor in situ with a capacitance sensor the onset of the phase separation process.

Table 2. Comparison of detected times (min)of phase separation for PEI / TS blends.

	33 wt. %	48 wt. %
Dielectric	115	205
cloud point	118	235
DSC (Ref 8)	118	235
Rheology	113	216

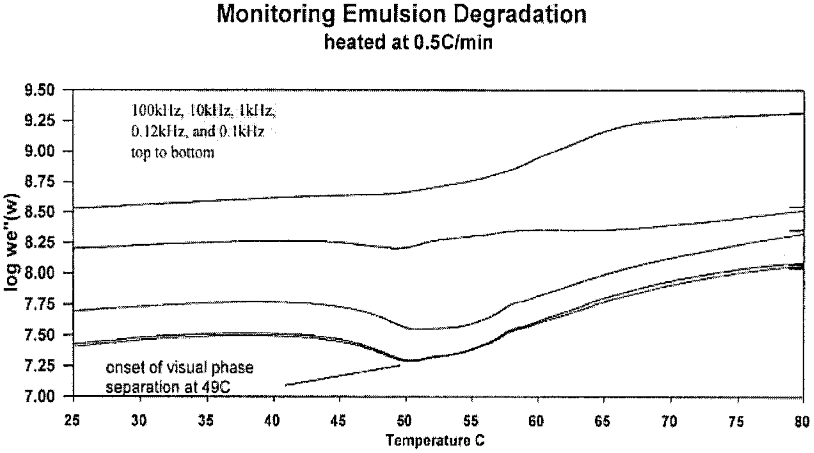
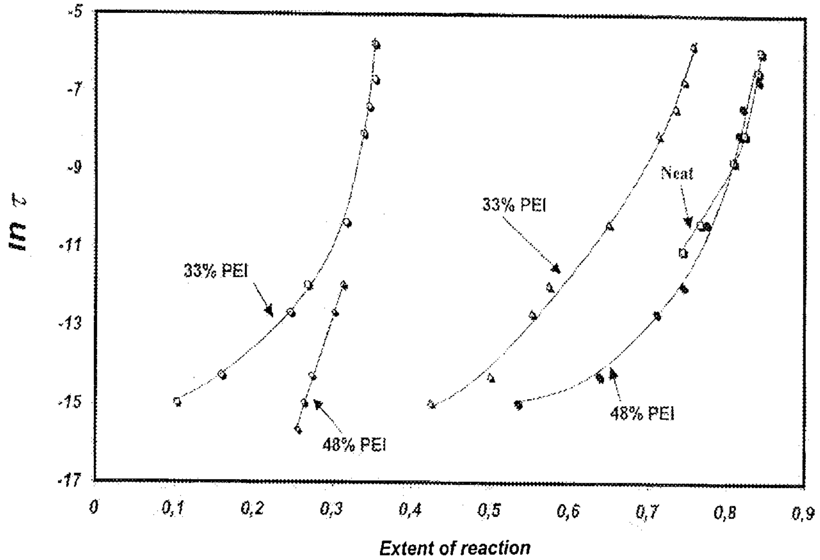


Fig. 4. Monitoring Emulsion Degradation.

Determination of the stability of emulsions is an important property for a wide variety of industries, particularly for cosmetics. Often the temperature or aging time at which the emulsion phase separates is determined visually. Dielectric sensing is an automated instrumental method which can also detect the maximum stable temperature zone for a particular surfactant system. Figure 4 displays the changing value of $\log[\omega * \varepsilon''(\omega)]$ versus temperature at .1, .12, 1, 10, and 100 kHz. A distinct drop in the otherwise expected increase in ε'' occurs at 45°C. In the 45°C to 50°C region the emulsion is phase separating, initially into a continuous phase with a lower dielectric loss, but which experiences a larger temperature dependence during the 0.5°C / minute temperature ramp. The phase separation process was detected visually in the 50 to 53 degree temperature range. Dielectric sensing detects changes on molecular level and when the A/d ratio of the interface is large such as at the earliest stages of phase separation. For these reasons changes in ε'' are detected before phase separation is observed visually.

Relaxation peaks. They are observed in Figure 2b both before, during and after the onset of phase separation. The focus of this discussion is an analysis of these dipolar peaks and their basis as a consequence of the phase separation MWS process, the buildup in T_g of the PEI rich continuous β-phase and the buildup in T_g of the epoxy rich occluded α-phase. From the beginning, before, during and after the onset of phase separation, the epoxy groups in the homogeneous, and in both the α and β phases continue to react. With increasing extent of reaction more epoxy i-mers become insoluble in the PEI and diffuse in to the α, occluded epoxy rich phase. As the TS i-mers diffuse out of the β-phase, the β-phase becomes richer in PEI. As a result the T_g of the continuous β–phase increases. Since T_g of the neat PEI is well above the 135°C cure temperature, a point in time is reached where the increase in weight percent of PEI in the β-phase causes the T_g of the β-phase to approach 135°C. At this time, the β-phase enters into the glassy state and the epoxy-amine oligomer diffusion process into the α-phase is quenched. Throughout this time and continuing after achievement of the glassy state in the β-phase, the TS i-mers in the occluded α–phase continues to react. As in the β-phase, but due to reaction advancement, the Tg of the α-phase increases until its T_g also reaches 135°C. Again once this buildup in T_g in the α-phase has occurred, the α-phase reaction is quenched by formation of a glass. Post cure at a higher temperature can of course increase T_g of both phases up to completion of the epoxy reaction in both the α and β-phases.

The relationship between the time of occurrence of peaks in $\varepsilon''(\omega)$ and the corresponding relaxation time τ, and the extent of reaction x(t) in the TP/TS blend before phase separation and after phase separation in the TS rich occluded phase is shown in Figure 5.



Monitoring extent of reaction from τ

Fig. 5. Monitoring correlation of extent of reaction with τ for PEI / TS blends at 135°C.

Conclusions

Frequency dependent dielectric measurements are an excellent technique for monitoring the complex chemical, composition and morphological changes occurring during cure of high temperature TP/TS blends. The T_g alpha-relaxation peaks can be used to monitor the buildup in T_g and thereby reaction advancement in the homogeneous phase before phase separation and in the occluded phase after phase separation.

The onset of phase separation is readily detected by a sharp MWS charge polarization rise in ε'. The dielectric detected time is in close agreement with mechanical and cloud point techniques. The conductivity in these blends does not follow the generally expected inverse viscosity power dependence and decreases much more rapidly then expected based on the concentration of thermoplastic and the change in viscosity. The results support a hydrogen bond exchange mechanism which is strongly affected by the concentration-proximity of the proton exchange groups.

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