VISCOSITY EFFECTS ON REACTION INDUCED PHASE SEPARATION AND RESULTING MORPHOLOGIES OF THERMOPLASTIC TOUGHENED EPOXY NETWORKS

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ABSTRACT

This research investigates how reaction induced phase separation (RIPS) of thermoplastic, which occurs during glassy polymer network cure, is determined by viscosity. Utilizing high T_g engineering thermoplastics in high viscosity thermoset systems, dissolution of multiple loading levels of thermoplastic and thermoset pre-polymer conversion will be achieved through use of a high shear continuous reactor. Samples will be cured using various isothermal curing profiles and characterized for morphology type and domain size as well as rheologically to determine minimum viscosity, time to gelation, time from phase separation to gelation, and average viscosity. The influence of cure conditions, thermoplastic loading levels, thermoplastic composition, and molecular weight on structural morphology will be resolved, establishing a well-defined rheological well during cure that leads to tunable and controllable phase separated morphologies, from dispersed droplet to co-continuous. By controlling viscosity of thermoplastic dispersed network pre-polymers through phase composition, cure schedule, molecular weight, directed phase separation will be achieved. Rheological profiles will be related to resulting network structure, which will lead to the ability to control and direct complex thermoplastic filled thermoset systems to targeted unique morphologies.

1. INTRODUCTION

1.1 Rheological Profiles during Cure

The glassy amorphous polymer networks utilized in advanced fiber reinforced composites offers unique environments for studying complex rheology profiles. The constantly changing chemical environment, and physical states changing from liquid to gel to vitrified solids, complicate the viscosity profile during cure. For prepreg applications where tack and drape are required, target viscosities are critical. In a thermoplastic filled epoxy thermoset, the viscosity is a dependent variable, which is a combination of solid loading levels, inert materials, thermoplastic content (ϕ), thermoplastic molecular weight, dispersion levels, cure prescription and thermoset conversion. This initial drop of viscosity during cure, and the building of viscosity during the chain extension reaction and the sharp increase of viscosity at gelation shape the rheological well, the viscosity profile during cure. At gelation, the reaction is hindered by high viscosity, but continues at a much slower rate. This complex rheological well has profound effects on morphologies of developing phase separated domains.

1.2 Reaction Induced Phase Separation

Reaction induced phase separation, RIPS, is well known within aerospace composite matrices and represents a complex chemical, morphological, and rheological changes that occur during the curing reaction. High performance thermoplastics including polyetherimide[1], PEI, polyetherketone[2], PEK, and polyethersulfone[3], PES, have been utilized to modify epoxies while maintaining thermomechanical properties. PEI has been shown to have characteristic micron-scale phase separation, which offers the ability to characterize the material well by means of optical and electron microscopy, in addition to rheologically as an increased viscosity during phase separation. With previous work showing that there is a critical viscosity for the reagglomeration of multi-walled carbon nanotubes (MWCNTs), the viscosity dependence on the development of phase separated domains will be explored utilizing isothermal cures.

1.3 Continuous Reactor

When compared to a batch process, the use of a high-shear continuous reactor to advance molecular weight of thermoset matrices, numerous advantages are realized, including reduced energy consumption, shorter reaction times, modular design, less variation in properties batch to batch. This reduced energy and time use lends itself to "green" manufacturing, with less energy and resources utilized to achieve the same product. Traditionally, the matrix chemistries (thermoset, thermoplastic toughenes, solid toughenes) are added into a batch mixer. The temperature is slowly increased while mixing occurs to slowly advance the molecular weight and achieve a target viscosity over several hours. This long heating cycle is followed by the cooling of the matrix to sub-ambient temperatures to quench the reaction, and a subsequent reheating prior to use for prepreg applications. The potential for on-demand production of a 'b-staged" epoxy prepolymer would offer significant energy savings over a batch process.

In the case of the high-shear continuous reactor, a twin screw extruder (TSE) is utilized to mix, disperse, and advance the prepolymer molecular weight in a continuous flow. The excellent modularity, heat transfer, insensitivity to viscosity changes, and devolatilization are very attractive for a number of applications.[4] Typically, the thermoplastic would be dissolved into the TGDDM at 150-160 °C, then the vessel cooled to 120 °C for the addition and solubilization of 44DDS. As shown in previous work, the simultaneous dissolution of high T_g thermoplastic and amine curative in TGDDM while driving the prepolymer conversion of the thermoset epoxy are possible with the high-shear continuous reactor.[5]

2. EXPERIMENTATION

2.1 Materials

The following materials were used as received: 4, 4'-diaminodiphenylsulphone (44DDS) (Royce International, Sarasota, FL, M_n = 248.3 g/mol, 4 μm particle size); tetraglycidyl -4,4'-diaminodiphenylmethane (TGDDM) (Royce International, Sarasota, FL, M_n = 422.5 g/mol); polyetherimide (PEI) (Ultem 1000P, SABIC Plastics, TX, USA, Mn = 39,000 g/mol, particle size 350 μm), and dichloromethane (DCM) (Acros, New Jersey, USA, HPLC Grade 99.9%)

2.2 Synthesis- continuous reactor (or with previous samples)

Syntheses of PEI filled epoxy matrix was conducted using a Prism TSE-16 as a continuous high-shear reactor, with 16mm screws and a 25:1 L/D. The screw design was used as previously described, and the temperature, screw speed, screw design, and throughput was kept constant.[5,6] TGDDM was preheated to 80 °C to facilitate pumping with a peristaltic pump into the reactor barrel, while a dry blend of 44DDS/PEI was conveyed into the barrel utilizing a Brabender solids feeder. All samples were formulated at 1:1 stoichiometric equivalents of epoxide to active amine hydrogens. The loading of PEI included 0%PEI, 5%PEI, and 10%PEI, and verified by TGA. Samples were collected and immediately stored in the freezer to arrest continued reaction until analyzed.

2.3 Thermal Analysis

Thermal gravimetric analysis (TGA) was performed using TA Instruments Q50 to determine degradation and confirm relative loading levels of PEI. Samples were heated from room temp at 10 °C/min to 700 °C.

2.4 Rheological Analysis

Rheological characterization was performed using the TA Ares G2 rheometer, using 25mm disposable aluminum parallel plates. Quenched prepolymer was thawed and loaded onto the parallel plates at 60 °C, the gap was set to 1.00 mm and allowed to equilibrate for 1 minute before a 20 °C/min ramp to the desired isotherm, and held at the specified temperature until gelation was reached. Isotherms of 120 °C, 140 °C, 160 °C, and 180 °C were studied, and a strain rate of 200% was used to minimize noise. Data collection was ended at gelation where the loss modulus and storage modulus were equivalent.

2.5 SEM Characterization

Samples were prepared for scanning electron microscopy by polishing the surface, then dissolving the PEI phase with DCM. The EMI Tech K550x was used to silver coat samples. Microscopy was taken using the Zeiss Zeus VP SEM.

3. RESULTS

Samples were prepared using the continuous reactor as previously discussed, and samples were cured at isotherms at 120 °C, 140 °C, 160 °C, and 180 °C to study rheological and morphological differences. Samples were prepared using the feed rates found in Table 1.

Table 1. Composition of TGDDM/44DDS/PEI matrices.

PEI Loading Level (%)	TGDDM (g/min)	44DDS (g/min)	PEI (g/min)
0	23.2	13.5	0
4.95	19.4	11.3	1.6
10.3	17.7	10.2	3.2

The degradation profile of the materials was found using TGA in figure 1. Increased loading levels of PEI did not alter the onset of degradation, and remaining weight agreed with expected loading levels.

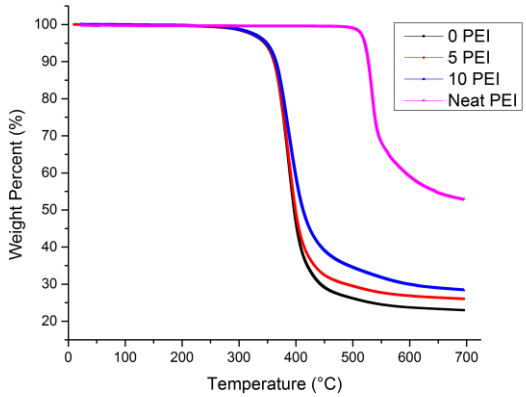

Figure 1. Thermal degradation profiles of TGDDM/44DDS/PEI.

3.1 Rheology

The examination of 0, 5, and 10% PEI samples yielded similar rheological profiles, with increased viscosity as loading level was increased at all temperatures, as seen in Figure 2. With addition of 10% PEI to TGDDM/44DDS, an increase of up to an order of magnitude in viscosity was noticed, as well as earlier increases in viscosity with an increased slope of the storage modulus.

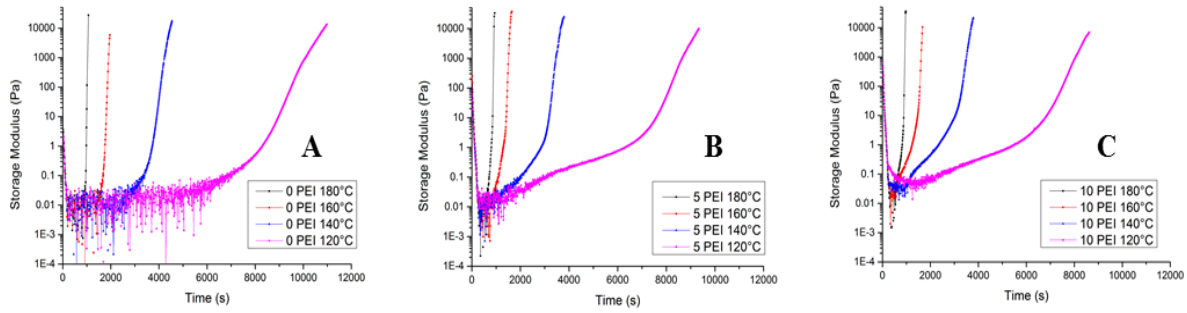

Figure 2. Storage modulus during isothermal cure at A) 0% PEI, B) 5% PEI, and C) 10% PEI.

Interestingly, the 10% PEI sample at the 120 °C cure reached gelation the earliest, while in the higher temperature cures gelation occurred the soonest in the 5% PEI samples, Figure 3A.

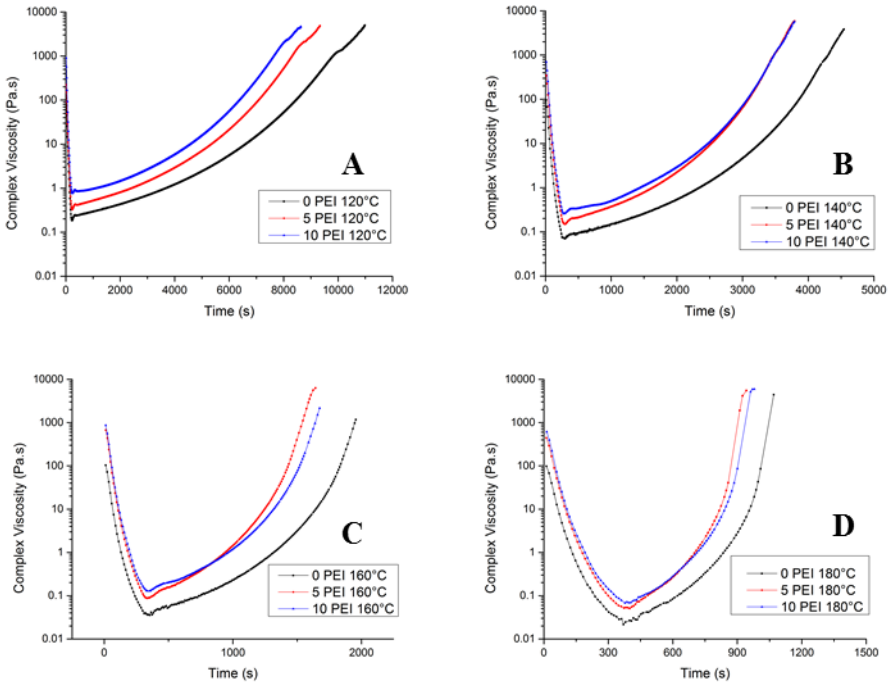

Figure 3. Rheological viscosity well during cure of TGDDM/44DDS/PEI matrices at isotherms of A) 120 °C, B) 140 °C, C) 160 °C, D) 180 °C.

With increased thermoplastic loading, the networks are physically gelling earlier. The effects of the loading level on cure kinetics are being explored to determine if the earlier crossover is gelation due to thermoplastic loading level or if equivalent degrees of cure have been achieved.

3.2 Scanning Electron Microscopy

With the differences in viscosity, network development of phase separated domains did not show significant differences between examined loading levels. At higher viscosities, either through loading level or low temperature cure, minor differences can be observed in figures 4-8, but further experimentation into higher loadings and lower temperature cures will determine the extent of these effects. In figure 4 B, no phase separation could be seen, and in 4C, incomplete phase separation when compared to the rest of the SEM microscopy is observed.

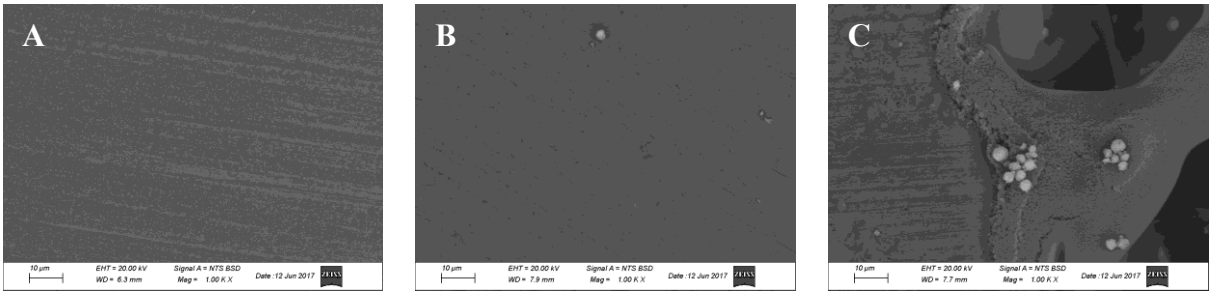

Figure 4. SEM microscopy of 120 °C cure for A) 0% PEI, B) 5% PEI, and C) 10% PEI.

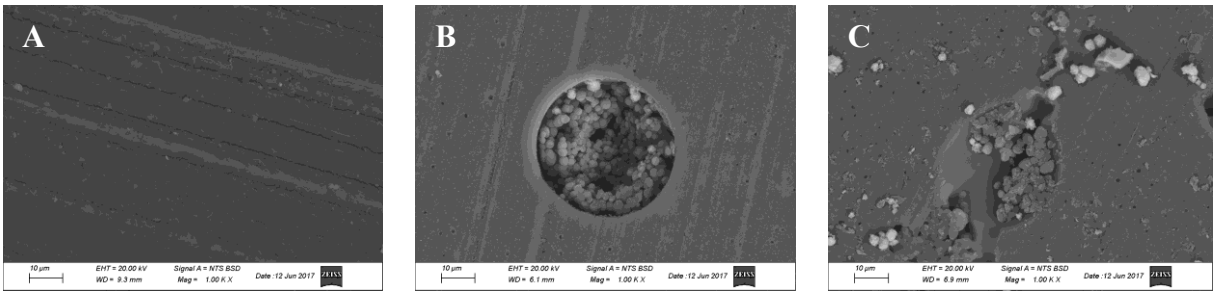

Figure 5. SEM microscopy of 140 °C cure for A) 0% PEI, B) 5% PEI, and C) 10% PEI.

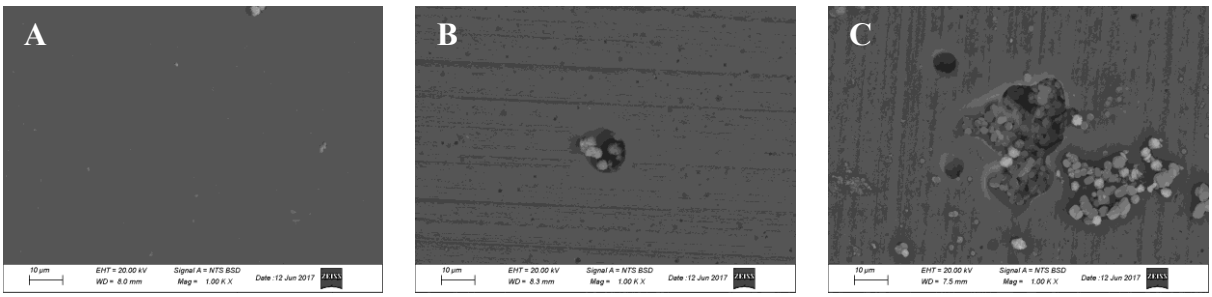

Figure 6. SEM microscopy of 160 °C cure for A) 0% PEI, B) 5% PEI, and C) 10% PEI.

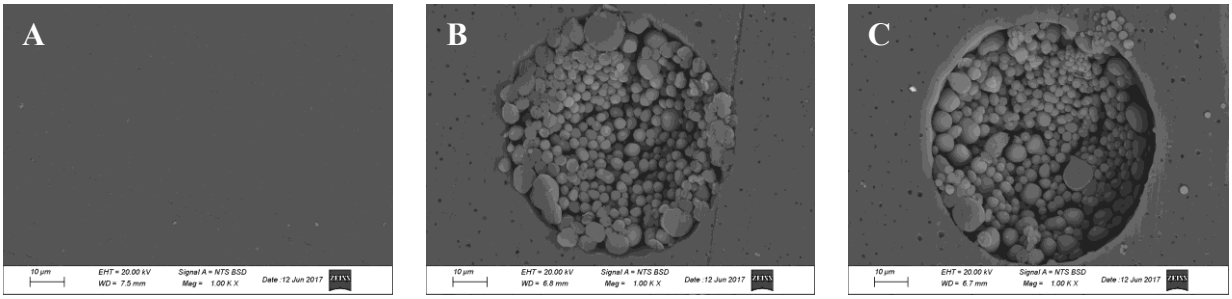

Figure 7. SEM microscopy of 180 °C cure for A) 0% PEI, B) 5% PEI, and C) 10% PEI.

4. CONCLUSIONS

This work provides a basis for further analysis of the thermoset/thermoplastic reaction induced phase separation behaviors. At higher loading levels and low temperature, viscosity limited cures the beginnings of limited phase separated domains can be observed. At low loading levels and high viscosities, RIPS was visually limited in the SEM microscopy. Future work will examine higher loading levels of thermoplastics, various molecular weights of thermoplastics, different thermoplastic chemistries, as well as nanoparticle loading levels to provide further insight into RIPS behaviors for high performance materials.

5. REFERENCES

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