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SOLVENT EFFECTS ON SILICA DOMAIN GROWTH IN SILICA/SILOXANE COMPOSITE MATERIALS

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ABSTRACT

The effect of solvent addition on the phase separation, mechanical properties and thermal stability of silica/siloxane composite materials prepared by *in situ* reinforcement was examined. The addition of a solvent enhances the miscibility of the reinforcement precursor, a partial hydrolyzate of tetraethoxysilane (TEOS-PH), with the polydimethylsiloxane (PDMS) polymer. As a result, the phase separation at the micron level, termed the large-scale structure, diminished in size. This decrease in particle size resulting from the addition of moderate amounts of solvent was accompanied by an improvement in the mechanical properties. However, solvent addition in the excess of 50 weight percent led to a decrease in mechanical properties even though the large-scale structure continued to diminish in size. Small Angle X-Ray Scattering (SAXS) was used to examine the ångstrom level or small-scale structure. This small-scale structure was only affected by the presence of solvent, not the amount. The silica/siloxane composite materials showed the same thermal transition temperatures as the original PDMS material.

KEY WORDS: Polymeric Materials/Composites, Siloxanes, Sol-Gel

1. INTRODUCTION

Polydimethylsiloxanes (PDMS) are inherently weak at room temperature due to their low glass transition and melting temperatures. However, blending in particulate fillers, such as pyrogenic silica, leads to a reinforced material with suitable properties for commercial applications (1-4). Unfortunately, the incorporation of reinforcing fillers requires significant amounts of time and energy and often the addition of processing aids. In the hopes of avoiding these disadvantages, a method of *in situ* reinforcement based on the generation of "silica" by sol-gel techniques has been developed for siloxane systems (5-9).

The generation of *in situ* sol-gel derived composite materials with tailored mechanical properties, requires a detailed understanding of process/structure/property relationships. One factor that seriously affects the phase separation in a system is the miscibility, both

initial and over the lifetime of the reaction. A study on the effect of changing the phase compatibility by adding a series of organic solvents was completed. The microstructure of the phase separation in these solvent containing systems has been analyzed using Scanning Electron Microscopy (SEM) and Small-Angle X-ray Scattering (SAXS). The effect of solvent addition on the mechanical properties of the resulting materials was determined by looking at the tensile strength, elongation, durometer and tear strength.

2. EXPERIMENTAL

2.1 Materials and Characterization Hydroxyl-terminated polydimethylsiloxane (M_n = 58,800) was provided by Dow Corning Corporation. Polydiethoxysiloxane (Silbond 40, a partial hydrolyzate of tetraethoxysilane, TEOS-PH) was obtained from Akzo Corporation and used without further purification. Dibutyltin dilaurate (DBTDL), $[CH_3(CH_2)_{10}CO_2]_2Sn[(CH_2)_3CH_3]_2$, was obtained from United Chemical Technologies and used without further purification. DBTDL came as a 25% solution in polydimethylsiloxane. Tetrahydrofuran (thf) and toluene (Reagent Grade) were obtained from Fisher Scientific and p-xylene (Reagent Grade) was obtained from Aldrich Chemical Company. All solvents were used as received.

Ultimate tensile strength and elongation values were obtained using an Instron Model 1122 Tester. Dogbone samples of dimensions 1 3/4 in (4.5 cm) long by 3/8 in (1 cm) wide were pulled to rupture at a speed of 500 mm/min using the procedure defined by ASTM Standard D412-87. Values reported are the average of five tensile samples. Die B tear values were obtained on a Model 1122 Instron Tester, according to ASTM Standard D624, using test pieces which were 4 1/4 in (11 cm) long and 1 in (2.5 cm) wide. Hardness values were obtained on a Type A Durometer according to ASTM Standard D2290. Sample pieces were stacked to a thickness of about 1 cm and hardness measurements were done at three different positions on each side of the sample. The reported values are the averages of six measurements.

Thermal gravimetric analyses were done on a DuPont Model 951 Thermal Gravimetric Analyzer. The temperature was ramped from 25 to 700 °C at 10 °C/min in a helium gas flow of 82 cc/min. About 15 mg of sample were used per run. Differential scanning calorimetry was done on a DuPont Model 910 Differential Scanning Calorimeter. The temperature was ramped from -150 °C to +150 °C at 10 °C/min in a helium gas flow of 100 cc/min.

Small Angle X-ray Scattering (SAXS) measurements were taken on the 10-meter small angle x-ray camera at Oak Ridge National Laboratory. Data from different q ranges were matched by an arbitrary vertical shift factor. SEM data were obtained on Au/Pd coated samples using a JEOL 6400 scanning microscope.

2.2 General Procedure Polydiethoxysiloxane (TEOS-PH) and solvent were mixed together and then combined with hydroxyl-terminated polydimethylsiloxane (PDMS). The tin catalyst was then added to the mixture. The resulting solution of PDMS, TEOS-PH, solvent and catalyst was stirred until it became homogeneous, ca. 1 min. The mixture was then poured into a glass petri dish which had been treated with a mold release agent. The sample was degassed for 3 min and placed in a constant humidity cabinet and cured at 50% relative humidity (R_H) for 1 week. The amount of TEOS-PH was sufficient to both crosslink and fill the polymer matrix with silica at ca. 20 weight percent. The solvent was added in amounts sufficient to achieve a specific weight percent relative to the total sample weight.

3. RESULTS AND DISCUSSION

In order to investigate the effect of miscibility on phase separation, a series of samples were made in which varying amounts of an organic solvent were added to the formulation.

Samples were made which contained solvent from 0% to 90% by weight. Three different solvents with increasing dielectric strengths were investigated, namely xylene, toluene and tetrahydrofuran (thf).

3.1 Phase Separation SAXS was used to study the small-scale (ångstrom level) silica domain growth within these materials, while the large-scale (micron level) structure was examined using SEM. In general, the SAXS data indicates that there is a marked change in the small-scale structure with the addition of solvent to the system (Figure 1). The small-scale domain growth for the parent (no solvent) system is particulate in nature with distinct interfaces, as indicated by the -4.0 Porod slope (10-11). Upon changing the miscibility by adding a solvent, the small-scale structure changes to a network polymer phase separated system (Porod slope > -3.0). However, the SAXS data also indicates that the small-scale structure is minimally modified by varying the amount of solvent. Therefore, changes in properties which are associated with varying the amount of solvent are not likely due to structural changes at the ångstrom level.

Examination of the samples by SEM indicates that the addition of solvent decreases the size of the large-scale structure relative to the parent system. While the effect is observed with all three solvents, there is a slight difference in the degree of the effect. The size of the particles generated when using the three solvents vary in the order of increasing size as: xylene < toluene < thf. In addition to the initial decrease in large-scale particle size, the SEM data also indicates that the particle size is inversely proportional to the solvent concentration (Figure 2). The particle size decreased from approximately 10-20 µm to 1-2 µm as the solvent concentration increased from 10 to 90 weight percent.

3.2 Mechanical Properties Mechanical measurements indicate that increased miscibility leads to improved mechanical properties. All four properties evaluated (i.e., tensile strength, elongation, durometer and tear strength) improved with the addition of an organic solvent. The dielectric strength of the solvent was of far less importance than the actual presence of the solvent. While close examination of the mechanical data indicates that within the set of solvent samples thf leads to the highest mechanical properties and xylene to the lowest, in general all three systems had similar mechanical properties.

In order to determine the optimum amount of solvent, the mechanical properties were monitored as a function of weight percent solvent. The tensile strength and elongation values improve with increasing solvent, reaching a maximum at approximately 50%, and then decrease with further solvent addition (Figures 3 and 4). However, the durometer and tear strength only improve with increasing weight percent solvent (Figures 5 and 6).

3.3 Thermal Properties The thermal transitions and degradation temperature were determined to insure that the *in situ* reinforcement and solvent addition was not detrimental to the thermal stability of the resulting materials. Both the glass transition temperature (T_g), -111 to -120 °C, and the melt temperature (T_m), -42 to -44 °C, were unaffected by the addition of solvent. In addition, the 10% weight loss temperature (T_{10}) of 460-470 °C was undisturbed by the use of solvent during sample preparation.

4. CONCLUSIONS

The addition of organic solvents during the *in situ* generation of silica reinforcement in siloxane matrices leads to improved mechanical properties. This change in properties is accompanied by changes in the phase separation within the system. There is an initial change in the small-scale structure and a continuous change in the large-scale structure. Therefore, the initial improvement in the mechanical properties may be due to the phase separation at both levels. However, further improvements are most likely linked to changes in the large-scale structure.

These results indicate another tool which can be utilized to target mechanical properties for specific applications. Clearly, changing the miscibility of the system by solvent addition controls the nature of the phase separation and allows engineering of the inorganic phase.

5. ACKNOWLEDGMENTS

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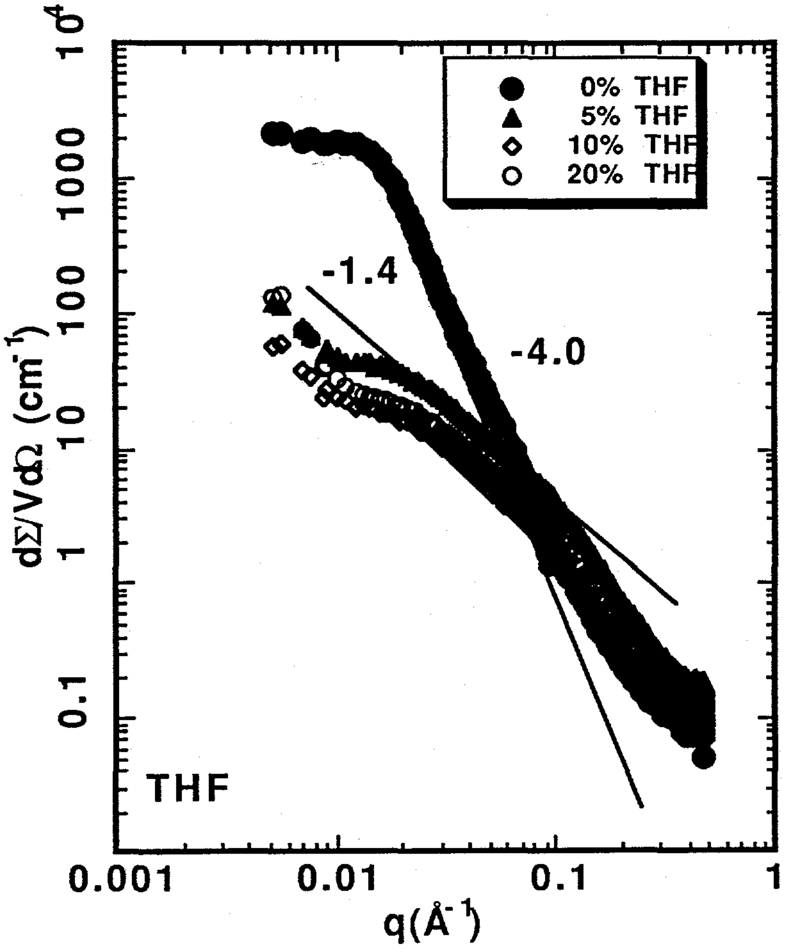

Figure 1. SAXS data for 0-20 weight percent thf.

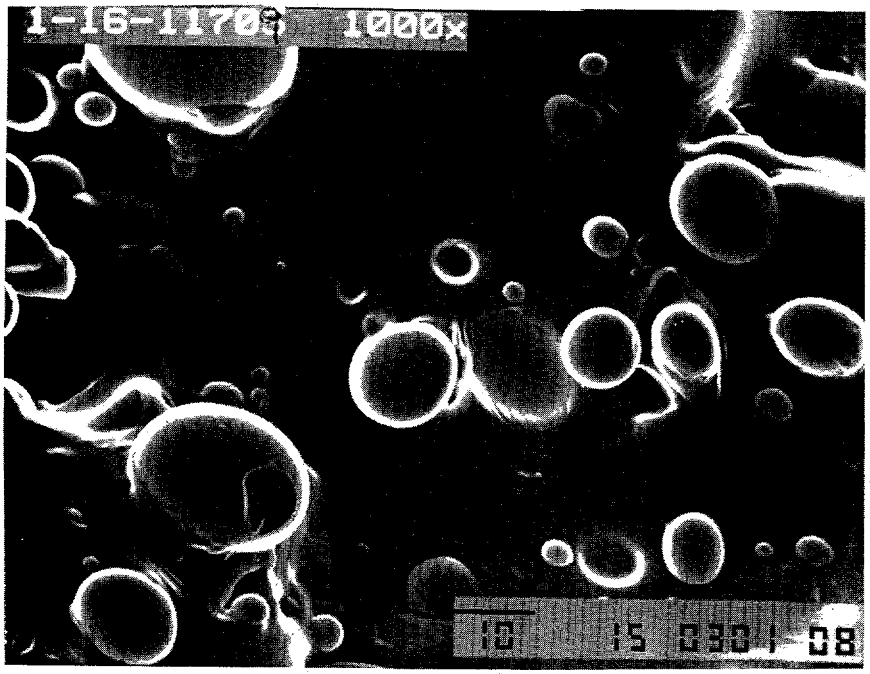

Figure 2a. SEM of sample prepared with 10 weight percent toluene (scale = 10 μm).

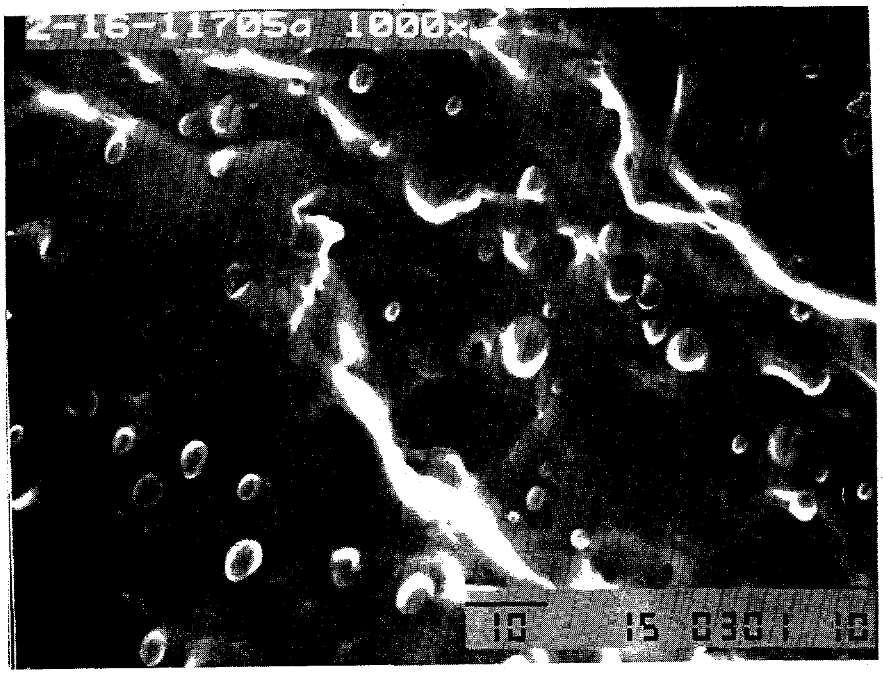

Figure 2b. SEM of sample prepared with 20 weight percent toluene (scale = 10 μm).

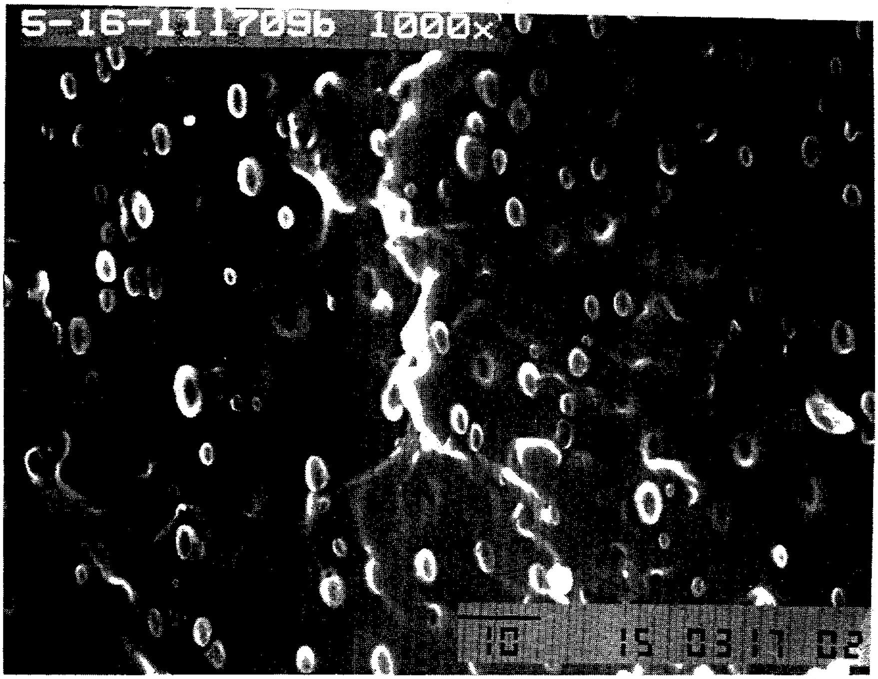

Figure 2c. SEM of sample prepared with 50 weight percent toluene (scale = 10 μm).

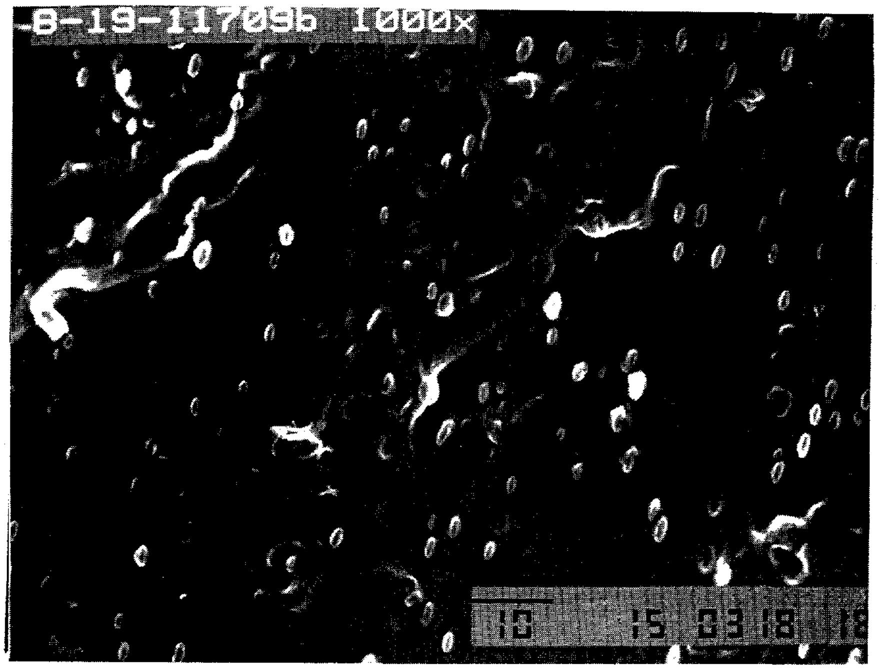

Figure 2d. SEM of sample prepared with 80 weight percent toluene (scale = 10 μm).

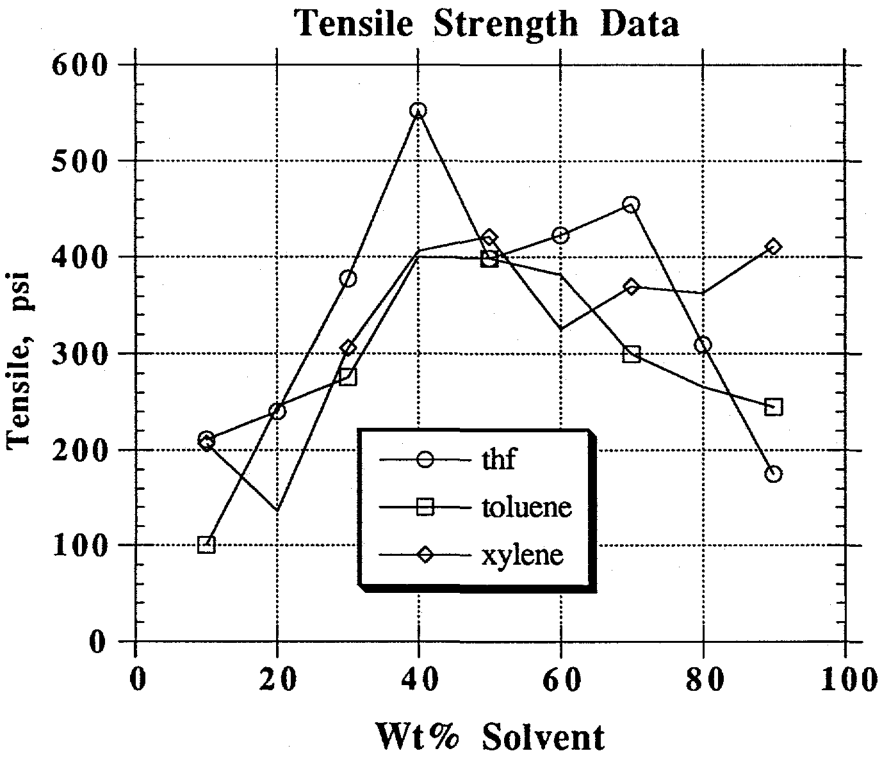

Figure 3. Plot of tensile strength (psi) versus weight percent solvent.

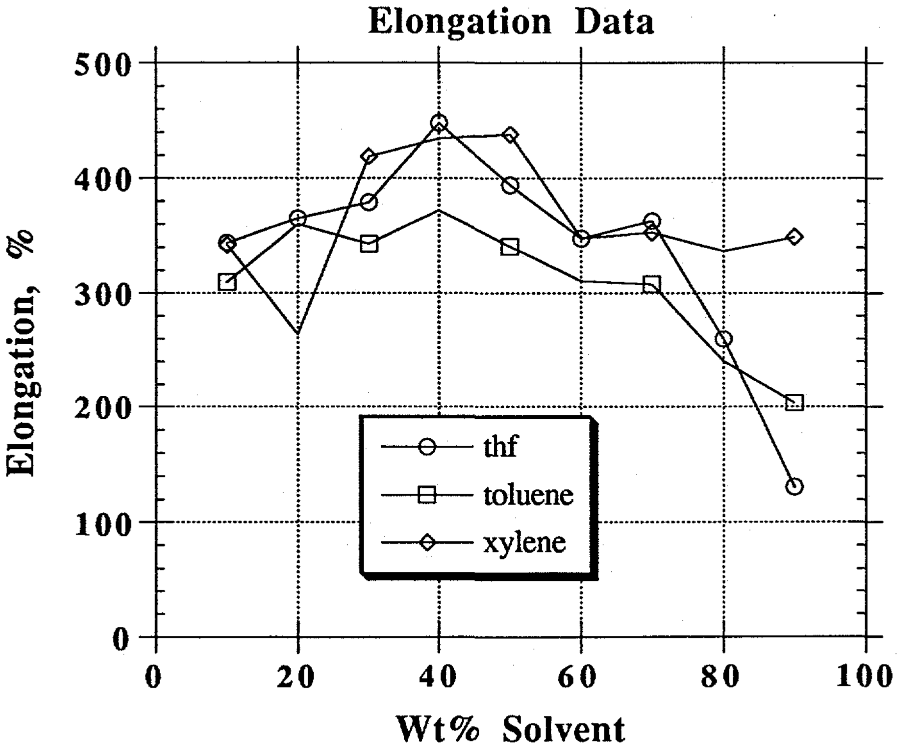

Figure 4. Plot of elongation (%) versus weight percent solvent.

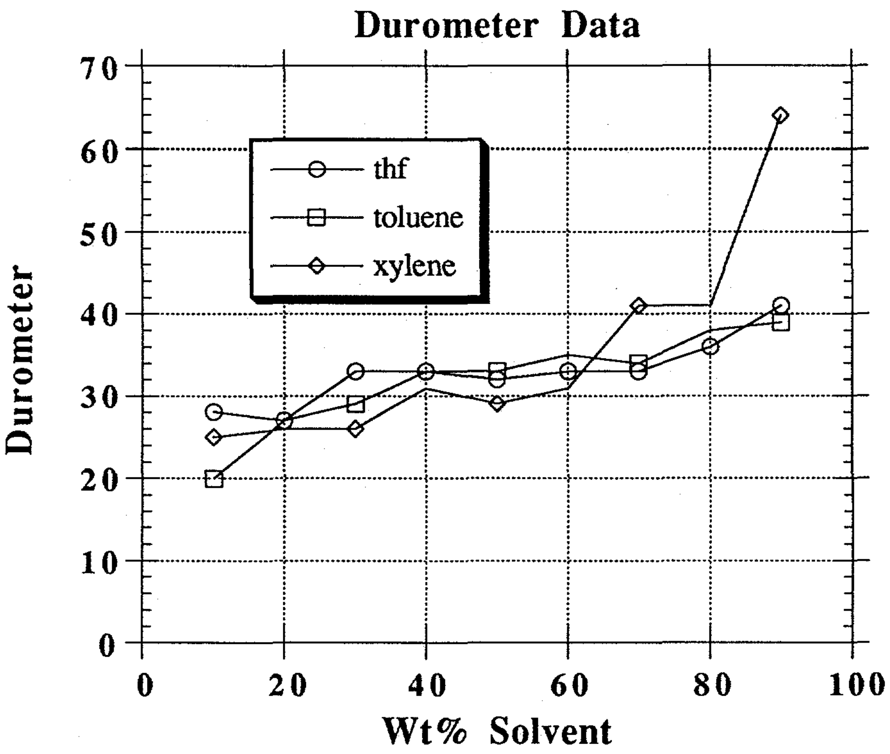

Figure 5. Plot of durometer versus weight percent solvent.

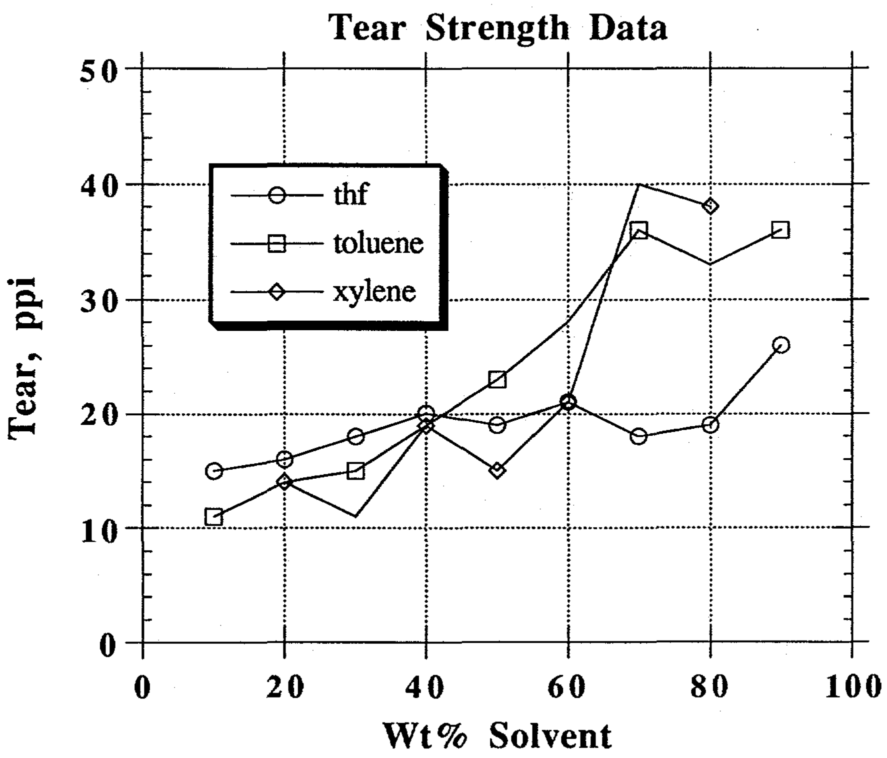

Figure 6. Plot of tear strength (ppi) versus weight percent solvent.