SUSPENSION OF SIC POWDERS IN ALLYLHYDRIDOPOLYCARBOSILANE (AHPCS): CONTROL OF RHEOLOGY

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ABSTRACT

Inert particulate fillers can be blended with preceramic polymers prior to infiltration of composite preforms to increase pyrolysis yield and decrease shrinkage, thus reducing the number of infiltration/ pyrolysis cycles required for densification. However, particulate filler loadings and concentration of added dispersants necessary to maintain low viscosity (< 0.50 N·s /m^2) slurries vary with the characteristics of the particular AHPCS polymer batch. These batch to batch variations occur with alterations in the synthesis process and method of allyl substitution, which in turn alter polymer structure and molecular weight distribution. A number of different polymer batches were characterized by NMR, GPC and thermal analysis, and the influence of polymer structure on rheology of filled systems determined. When the high molecular weight fraction increased to too great a level, suitably fluid slurries could no longer be attained.

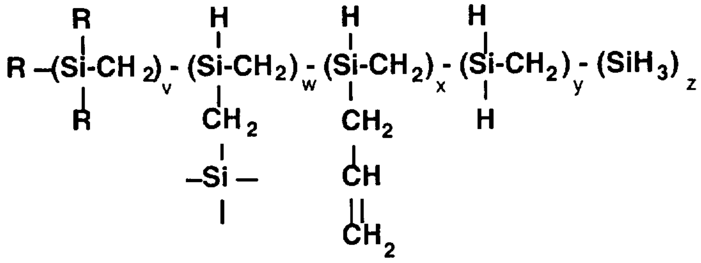
INTRODUCTION

The suspension of inert particulate fillers[1-3] in a preceramic polymer is of interest for reducing the number of infiltration/ pyrolysis cycles required for matrix densification in fabricating a ceramic matrix composite. Incorporation of particulates also may be used to influence thermal conductivity. Reproducibility of the rheology of the suspension is necessary for attaining consistent composite properties. This study attempts to identify the polymer characteristics required to produce low viscosity slurries, to determine the influence of molecular weight, molecular structure, and residual solvent on the polymer/ powder interactions, and to use a polymer/ filler/ dispersant system to infiltrate rigidized fiber preforms.

Earlier work[4] reported on the development of a 0.15-0.20 N·s /m^2 polymer/ filler system using a polyhydridocarbosilane (AHPCS) having 7.5% allyl substitution (Starfire Systems), a UF 10 SiC powder (Starck) and a glycol copolymer dispersant (Dow EP 530). Based on those findings, we undertook a design of experiments study to optimize particle size, filler loading and dispersant concentration, only to find we were unable to reproduce the low viscosities reported for the original polymer with newer batches of material. The study therefore evolved into a characterization of newer polymer batches, and comparison with the older batches, to elucidate the variations in molecular weight and polymer structure giving rise to the higher viscosity dispersions using the newer material.

EXPERIMENTAL

AHPCS, whose nominal structure[5,6] is shown in Figure 1, was purchased from Starfire Systems Polymers having both 5 and 7.5% allyl substitution, based on the number of Si atoms, were characterized by gel permeation chromatograpy (GPC), ^{1}H and ^{29}Si nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).



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Viscosity measurements using a rotating spindle and cylinder were used to determine new ratios of polymer, filler and dispersant with viscosities suitable for infiltration into 2-D preforms.

Preforms were of 5HS CG Nicalon fiber, coated with BN and overcoated with CVD SiC, having nominally 26.5% porosity (Honeywell Composites). The preforms were infiltrated under vacuum, the polymer cured to 200°C under 6.89 MPa argon pressure, then pyrolyzed free standing to 1200°C and held at the final temperature for 30 minutes. Composite panels were sectioned, polished, and characterized by optical and field emission microscopy.

RESULTS AND DISCUSSION

Four batches of AHPCS, two having 7.5% allyl and three with 5% allyl concentrations, were characterized. An additional batch of 5% allyl polymer was screened, but was not included in the full characterization because it was of significantly higher viscosity on receipt than the other materials, and further increased in viscosity under refrigerated storage of a few months. All materials discussed are denoted by their synthesis date. Some of the 7.5% allyl material from the initial filler study[4], batch

970507, was still available, had not increased in viscosity under refrigerated storage of >2years, and was freshly characterized for comparison with more recently purchased materials. The newer materials which were included here had neat polymer viscosities of 0.100-0.125 N·s /m^2 at 25°C, and were more viscous than the 970507 polymer. Two separate polymers, the 7.5% allyl 980220, and 5% allyl 990319, each were mixed with 25 volume percent UF 10 SiC powder and 0.06% EP 530 copolymer, the ratios determined in the earlier work to produce suspensions of nominally 0.150-0.200 N·s /m^2 using the 970507 polymer, only to find the slurries so stiff as to leave the impression of the mixing blade in the filled polymer, whereas repeating the same filler and dispersant ratios with the stored 970705 yielded very pourable mixes. Some improvement was attained by drying the powders overnight under vacuum at 150°C, but this still did not produce a low viscosity system.

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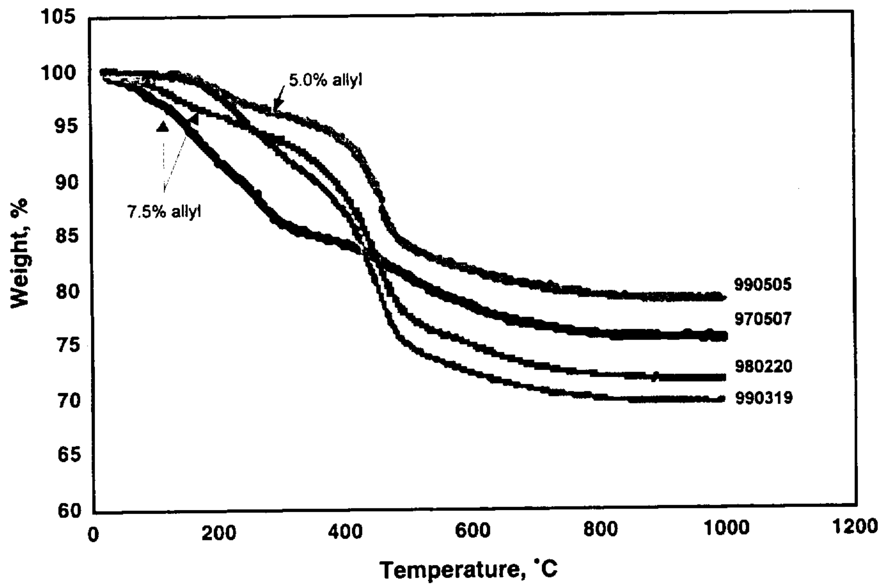
A comparison of polymer structure, based on ^1H and ^{29}Si NMR and GPC, is summarized in Table I. It is evident that the original 970507 batch, even after substantially longer term storage, is much lower in molecular weight and more monodisperse than the other materials, which show more of a bimodal molecular weight distribution, and hence greater polydispersity. It is interesting to note that this batch also has the smallest number of SiH_3 moieties, indicating that, although this is the lowest molecular weight material, it is not comprised of short, linear chains, which would require a high number of end groups, but probably includes a substantial number of low molecular weight cyclics. It is also the only polymer which had fully substituted Si groups. The higher molecular weight polymers also had substantial SiH_3 species, suggesting a significant degree of branching. The higher molecular weights of the three newer batches is attributed by Starfire Systems to their deliberate attempts to strip solvent in their current synthesis procedures. This has resulted in more consistent materials, but has reduced shelf life to a period of months for the 5% allyl polymers, with longer storage times (about 18 months) for the 980220 7.5% allyl batch.

TGA behavior of the four batches is compared in Figure 2. The 970507 polymer, containing residual THF and toluene, as determined by ^1H NMR, begins to lose weight below 100°C, whereas the other polymers did not show weight loss below 150°C. 990505 polymer has the highest char yield (79%); however, the 970507 polymer, despite its highest solvent content, has a char of 75.5%, and the smallest weight loss in the 500°C regime.



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The initial filler loading chosen was 20 volume percent, with EP 530 levels of 0.1 and 0.2 percent in the AHPCS polymer; these produced slurries of > 1.0 N·s /m^2 using the newer polymers, which exhibited marked shear thinning behavior. The glycol level was reduced by diluting the EP 530 in dried THF, as it was too viscous to handle in microliter syringes for use with small batch sizes of filled materials. Using this approach slurry viscosities of < 0.500 N·s/m^2, with little rate sensitivity, could be achieved at glycol concentrations of 0.01-0.02% (Figure 3). For comparison, viscosity measurements were made using additions of 0.1% THF and no glycol, which demonstrated that glycol addition does reduce viscosity beyond that achieved by small solvent addition alone. Surprisingly, UF 15, with a higher surface area, produced lower viscosity mixtures than UF 10. Comparable rheological behavior was

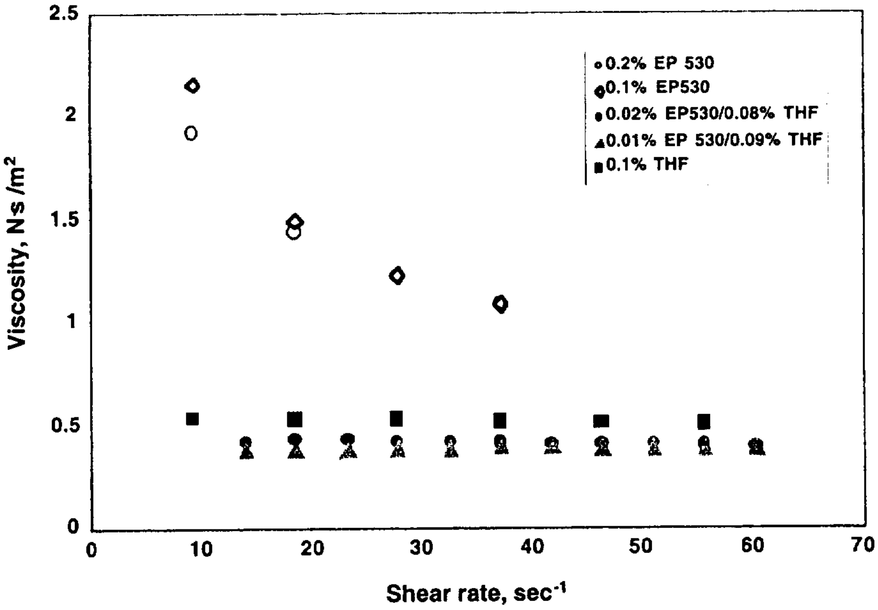

Figure 3: Effect of glycol/ THF additions on viscosity shown for 980220 polymer, 20 v/o UF 15 filler. Polymer and filler with THF alone is shown for comparison.

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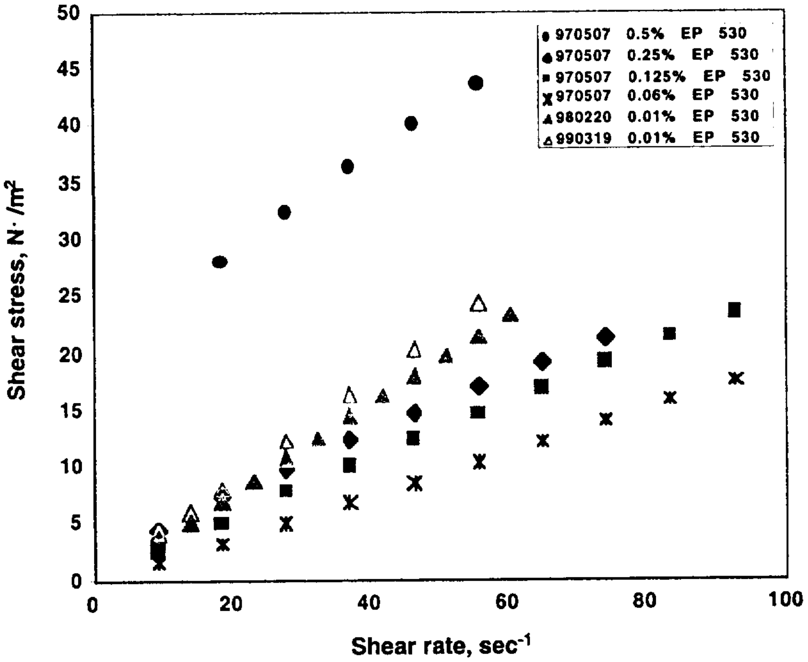
A plot of shear stress vs. shear rate was used to compare the rheological behavior[9] with varying glycol additions for three batches of AHPCS (Figure 4). Glycol concentration is seen to have a significant effect on polymer filler interaction. In the 970507 batch slight shear thinning was observed glycol levels of 0.25 and 0.50%. At 0.5% glycol, a threshold shear stress also is seen (*i.e.* the line no longer intersects the origin). The higher molecular weight materials 980220 and 990319 both exhibited very similar behavior when compared in this manner, despite their molecular weight differences (Table I). The increased slope of the stress-strain curve for the 98 and 99 polymers, relative to the 97 batch, is indicative of stronger polymer/ filler interactions, even at lower glycol concentrations, which results from the presence of a higher molecular weight fraction, and the reduction of residual solvent, which acts as a plasticizer.

On the basis of the rheological characterization, slurries of 20 volume percent UF 15 in AHPCS 990319, with 0.01% EP 530, 0.09% THF, were selected for matrix infiltration. Slurry density was calculated at 1.43 g/cm^3; final matrix density was determined from flash as 2.91 g/cm^3, a 51% decrease in volume. Based on this shrinkage, 7 infiltration/ pyrolysis cycles would be required to achieve 99% density, as compared with the 10 cycles typical for neat polymer.



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Characterization of several batches of AHPCS revealed that more recently synthesized materials have a more bimodal molecular weight distribution than older materials, with less cyclic content and more branching. There is also less residual solvent. However, efforts to remove solvent increased molecular weight and led to materials with shorter refrigerated shelf life. Once viscosity of stored materials started to increase, it continued to increase rather rapidly.

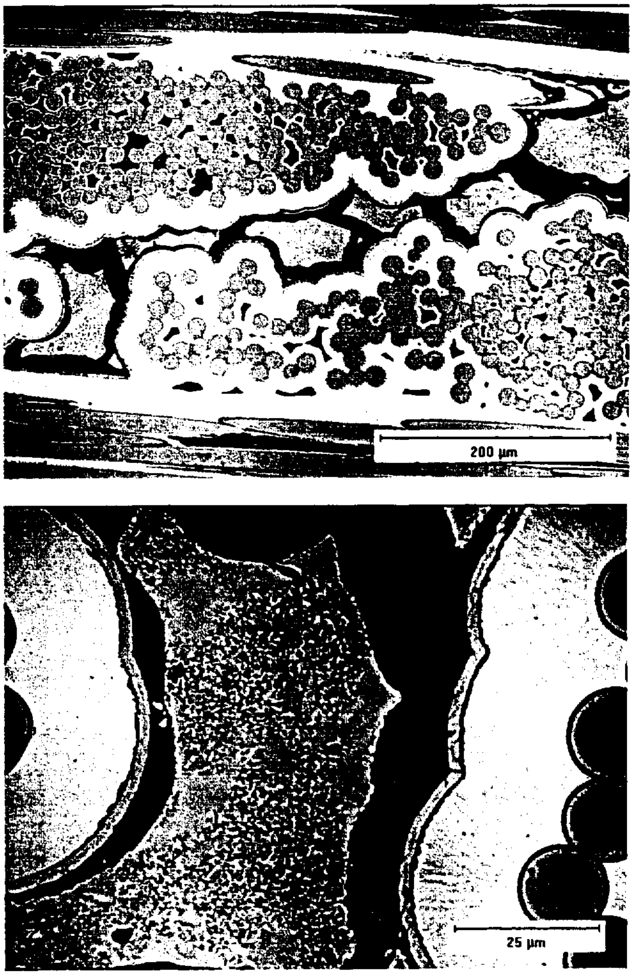

Figure 5. Optical micrographs of composites show shrinkage of filled polymer matrix "islands" following single infiltration, cure and pyrolysis to 1200°C.

The higher molecular weight materials were less exothermic during curing, evidence of a higher degree of chain extension in the as-produced material.

Moderate molecular weight materials could be loaded with a SiC filler at levels of 20 v/o, while maintaining rheology suitable for preform infiltration. The use of fillers at this loading level would be expected to decrease the number of cycles required for densification from 10 to 7. Rheological behavior is sensitive to adsorbed moisture, which was controlled by vacuum drying of powders.

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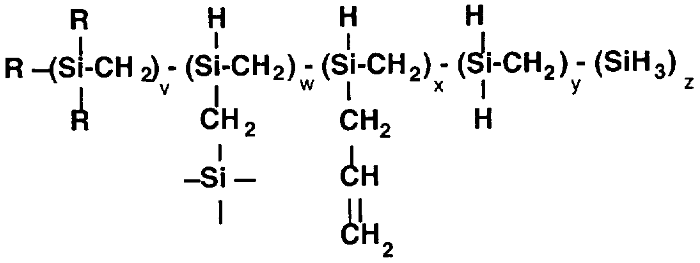

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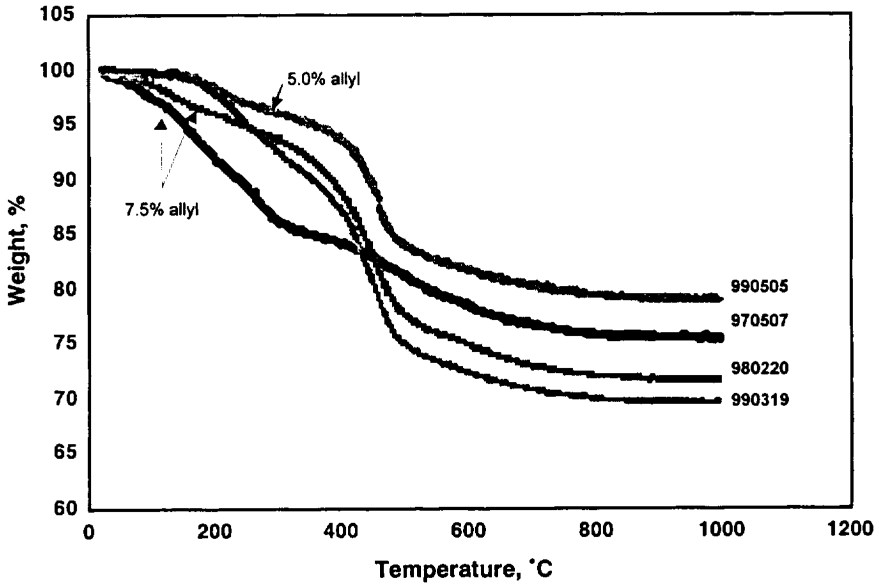

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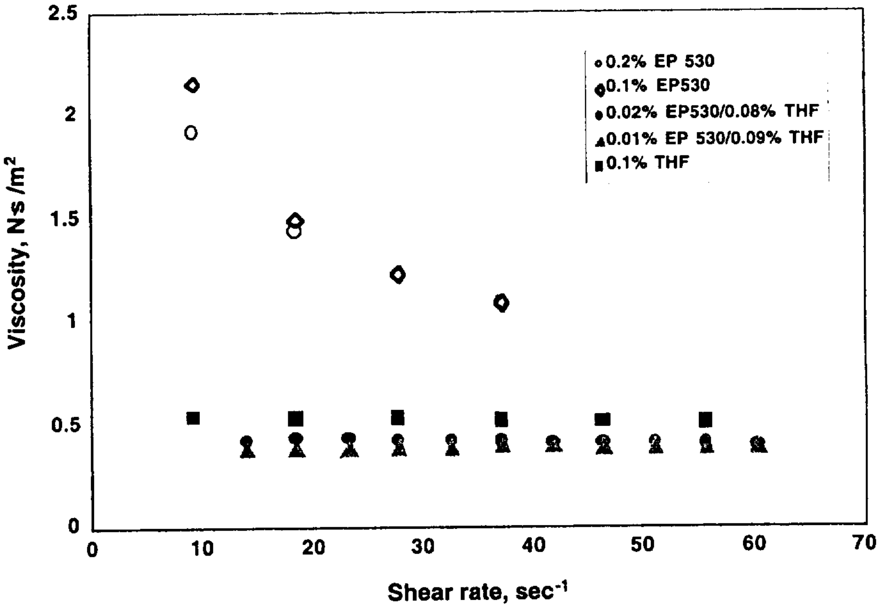

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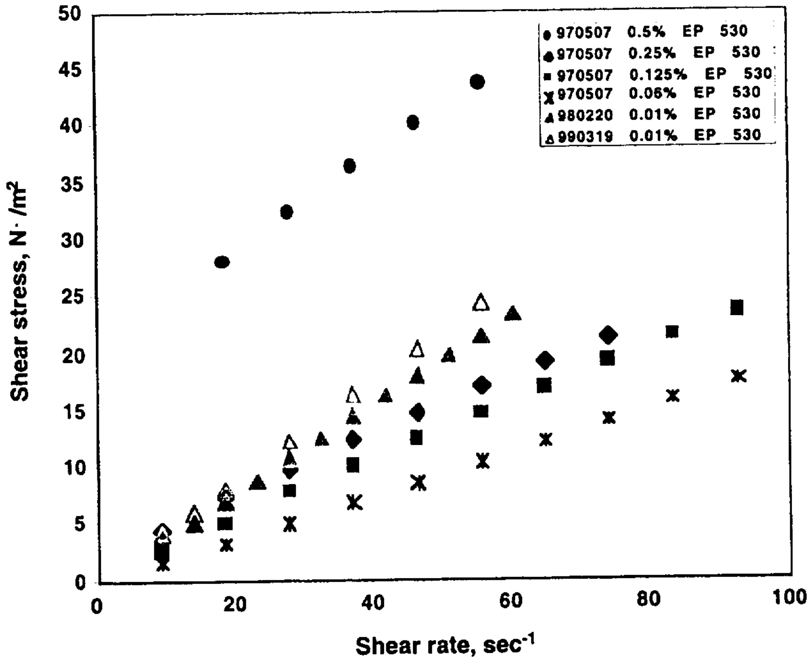

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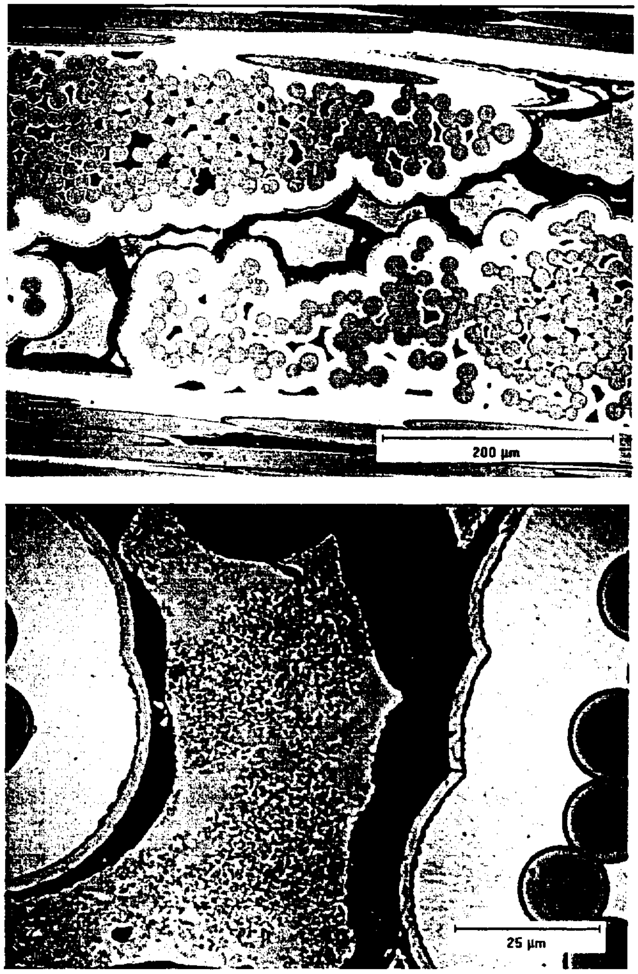

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Control of molecular weight appears critical in maintaining reproducible control of rheology for filled systems. Achieving optimal filler loadings and dispersant concentrations is strongly dependent on controlling the high molecular weight fraction in materials exhibiting a bimodal molecular weight distribution and maintaining polymer viscosities of 0.125 $N \cdot s/m^2$ or less.

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