GENERAL CONCLUSIONS AND PERSPECTIVES

This manuscript tried to give a detailed insight on the development and characterization of novel sub-micro structured composites based on epoxy-amine matrix and on pyrogenic silica. The main objectives of this work were to understand the structure / properties relationship and the mechanisms of reinforcement involved in the behavior of these materials. A large number of properties were characterized at different stages of the processing of the materials depending on the formulation in order to elucidate the influences of the morphology and interfacial adhesion on the final behavior of epoxy / silica composites.

The nature of epoxy-amine comonomers, as well as those of silica surface modification, were varied in order to design finely the interactions developed in the system. Basically, silica surface chemistries used were: hydrophilic, hydrophobic or reactive, i.e. amino or epoxy-modified, in order to induce a potential convalent bonding with the matrix. A common diepoxy prepolymer was combined with really different curing agents: an aliphatic diamino hardener with long polar chains (closer to adhesives formulations, often used in mixtures) generating rubbery systems with epoxy, and a short aromatic diamine (closer to aeronautical high performance formulations) generating glassy systems at room temperature with epoxy.

The dispersion state was optimized from the development of a suitable process. The rheological behavior could be related rather straightforwardly to silica dispersion state into epoxy or amine: for instance, a physical gel behavior characterized the filler percolation as checked by TEM. Silica also influenced the crosslinking step as it was studied by chemio-rheological analysis: silica surface silanols acted as catalyst of epoxy-amine reactions.

The nature of the initial interactions in the system was evidenced as a first order parameter governing the dispersion state (i.e. balance between particle-particle interactions and particle-polymer interactions). For example, for certain types of amino-modified silica, agglomerates were present whatever the processing route employed.

Consequently, dispersion medium and silica surface modification have to be chosen carefully in order to control the initial dispersion state in the suspension, otherwise, as an absence of significant evolution of the morphology during the polymerization was observed, the initial morphology might be frozen from the beginning of the crosslinking of the network (or respectively of the reaction of the reactive groups grafted on the silica surface).
Furthermore, it is advisable to generate the reaction of the potentially reactive groups grafted on silica surface directly in the suspension into epoxy or amine, otherwise, this covalent bonding might be subject to the competition with the reaction leading to the formation of the network. In this work, a large effort was invested in order to check the reaction at the amino-modified silica / epoxy interface from the development of a consistent procedure based on the utilization of different complementary techniques.

Final properties of epoxy / silica composites were characterized in the solid state and related to the morphologies, particularly the mechanical and thermal properties.

The morphologies were investigated via transmission electron microscopy coupled with image analysis and via small angle neutron scattering. Various euclidean and fractal parameters were worked out for a full description of the morphologies at multi-scale depending on the formulation: size of the individual structures (aggregates vs. agglomerates), interfacial area effectively developed between filler and matrix, aspect ratio, percolation trend, occluded matrix, fractal dimensions…

Morphologies were evidenced to depend in a large range on silica surface chemistry. Basically, optimal homogeneous dispersions were achieved for hydrophilic silica whatever the specific surface area, percolation trends were observed for hydrophobic silica, and for reactive silica, a fine tuning of the silica surface chemistry was needed to prevent the formation of agglomerates. The dynamic mechanical behavior could be well connected to the morphology and to the structure of organic-modifier grafted on silica surface. Silica addition resulted in a decrease of the mobility of the macromolecular chains. Glass transition temperature was maintained or increased and the changes were closely related to the interactions developed in the system. Increases in mechanical properties were observed in the linear region and in the fracture region. The range of these enhancements was much greater in the rubbery state than in the glassy state. Adhesion was shown as an important factor in the rubbery state especially in the elastic region. Ultimate properties were furthermore sensitive to the dispersion state.

Relationships between the structure and mechanical properties were discussed as function of the large number of parameters involved such as the size, size distribution, specific surface area, and fractal dimension of the reinforcing filler, interfacial interactions developed in the system, and dispersion state.

To summarize, interactions developed in the system appeared to govern each stage of the process: they determined the rheological behavior of the silica suspensions, the reactivity of the filled systems, the dispersion state of the suspensions, the final dispersion state, and influenced the mechanical and dynamic thermo-mechanical behaviors, through the interactions in the system and morphologies.
The perspectives of applications of the epoxy / silica composites developed in this work are the same as those of neat epoxy but exhibiting greater mechanical properties. For instance, they can be used in the field of structural adhesives, matrices of fiber-based composites in order to design innovative high performance composites structured at various scales, coatings exhibiting increased surface hardness. In addition to mechanical reinforcement, silica can provide increase of other functional properties of the materials: increased fire resistance (as shown in annex D), increased dimensional stability…

Eventually, let us summarize the different still “open” discussions, propositions of improvements, and perspectives arising from this study.

Among not fully answered questions that could need further investigation, may come first the completion of the characterization and quantification of the morphological evolution during crosslinking using finer techniques. Indeed, even if both confocal microscopy and SANS experiments seemed to point out an absence of evolution, their respective resolutions were limited. Ultra-small angle neutron scattering was proposed to complete the study towards larger dimensions. Besides it could be interesting to perform these experiments at various temperatures to tune the competition between the structuration of the fillers and the polymerization of the matrix.

A second topic that might need a deeper understanding is the discrepancy between the results of all the methods carried out for the investigation of the covalent bonding between amino-modified silica and epoxy, leading to the conclusion that the reaction actually occurred, and the limited effect of amino-modified silica on the gelation time of filled epoxy-amine systems whereas this silica behaves as a multi-functional crosslinker in the network.

The approach used in this work for the development of sub-micro structured composites based on fumed silica could be applied for the reinforcement of other natures of thermosetting polymer (some examples for polyurethane and acrylates were reported in the literature section). In each case, an adequate silica surface chemistry would have to be designed.

The trends found in this work for mechanical properties of fumed silica epoxy composites in the rubbery state are in agreement with those generally observed for filled elastomers. For glassy polymers, it can henceforth be supposed that pyrogenic silica reinforcing ability would result in the same trends for other natures of matrix as for epoxy.

In order to enhance further the mechanical properties in the glassy state, especially in order to try to overcome in a larger range epoxy brittleness, it could be proposed to use fumed silica
grafted with thick organic layers to have a "core-shell" like behavior. Besides, it could be interesting to compare the results obtained with pyrogenic silica with those obtained with a colloidal silica sol (individualized primary particles) to elucidate the influence of the fractal structure of fumed silica.

Eventually, this work provided a fine quantification of the morphologies of epoxy / fumed silica composites from different techniques, and of their mechanical properties, the correlation was discussed qualitatively and first order parameters were evidenced. This study can be used as basis for developing quantitative modeling of the properties of composites as a function of the structure (dispersion state, shape, size of the individual aggregates/ agglomerates, interfacial area, fractality, immobilized and occluded matrix) for materials reinforced with pyrogenic silica or other fillers presenting a similar multi-scale organization.