

FILM PREPARATION BY INORGANIC-ORGANIC SOL-GEL SYNTHESIS

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ABSTRACT

Film formation by sol-gel techniques is an advantageous method to obtain inorganic coatings. The sol-gel process allows the preparation of prepolymers with suitable viscosities to use various coating techniques like dipping, spraying and spin-on coating. The main disadvantage is the shrinkage of the gel layer during drying or sintering which leads to cracks with layer thicknesses more than some micrometers.

The introduction of organics, causing a decrease of the network connectivity and increasing relaxation ability can help to overcome densification problems. Moreover, in some cases, hardness or abrasion resistance are not too much affected by organics. In these cases, the organics can be left within the inorganic network. The possibilities of inorganic-organic processing techniques will be discussed and examples for film formations will be given.

INTRODUCTION AND GENERAL ASPECTS

Coatings are important for many technical applications. Numerous substrates show surface qualities which have to be improved by coatings for many reasons. Examples are anticorrosive coatings, mainly applied on metals like steel or aluminum but also on chemically less durable glasses, and decorative coatings which are used on all type of substrates and which play an important role in the daily life. Other coatings are used to add special functions to the substrate: improvement of hardness of soft materials; optical functions like reduction or increase of reflectivity, electrochromic effects, light absorption (filters), sensitive coatings, heat insulation and others.

To apply a coating, some basic requirements have to be fulfilled. The adhesion to the surface has to be high enough for the desired application. The adhesion depends on the interaction between the coating and the substrate along the boundary layer and can be reduced by shear stresses e.g. due to a mismatch of thermal expansion coefficients or mechanical loads (bending). The intensity of the shear stresses depend on the moduli of elasticity of the substrate and the coating. Elastic coatings develop lower shear stresses than brittle ones. Therefore, with inorganic coatings (glasses or ceramics), especially with increasing thicknesses, a has to be adjusted very thoroughly to the substrate.

Common coating techniques are vapor deposition methods (e.g. CVD or PVD), liquid coating and laminating techniques (e.g. laminating thin sheets on top of solid substrates). Liquid phase techniques are characterized by the fact that, with a few exceptions, solutions, emulsions or dispersions are used including solvents. Since the solvent has to be removed, a shrinkage takes place. The solid content of laquers based on organic polymers is in the range of about 20 to 30 wt.-%, high

along the film owing to different concentrations of vapor in the vicinity of the film's surface. The transport of solvent vapor away from the film in the gas phase controls this factor.

OBSERVATIONS AND CONCLUSIONS

Aggregated sols produce highly porous films that are typically twice as thick as those derived from stable sols. During their formation, we have observed a slowly collapsing area near the drying front. This extended spongelike region is probably the result of small capillary forces in the large pores created between the large aggregates. It is also likely that these silica aggregates are stiff structures that do not yield readily to the pressures generated by the final capillary collapse of the film.

We have described here a method of imaging through an ellipsometer that can be used to study drying films. The method might be applied, with a little imagination, to unsteady films, as well. Our preliminary analysis of the thickness profile of a drying film implies that curvature or van der Waals effects are significant.

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solid systems may have solid contents of about 50 to 70 %. Shrinkage, in general, is not a problem with organic polymers, due to the possibility of adjusting their relaxation behaviour very easily to the requirements of application. If the polymers are only weakly crosslinked, the chain mobility is high enough to follow the volume reduction caused by evaporating of solvents (figure 1).

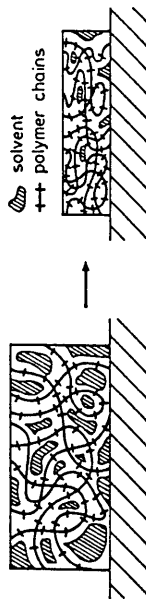


Figure 1. Shrinkage of a solvent containing polymer film.

Liquid coating techniques are widely used in practice and are the most important method for coatings including organic polymers. The most common methods are spraying, dipping, electrophoresis, and spin-on techniques. Powder coating is a variation where a liquid phase (mainly solvent-free) is applied after coating to obtain a closed film on the substrate.

For coatings based on inorganic materials, deposition techniques can be preferably used for thin films. Thicker films require long deposition times, therefore the practical use is limited. Vacuum deposited films, in general, very often show distinct microstructures with pinholes and high performance optical coatings are difficult to obtain in some cases.

SOL-GEL COATINGS

Sol-gel coatings generally have to be applied from a liquid phase (with a few exceptions, e. g. "pyrosols" deposited on hot substrates). There are numerous publications concerning the preparation of sols for coatings [1-7]. The important step is to control the degree of polymerisation in a way that suitable viscosities can be obtained. For film formation, viscosity and surface tension are important parameters which control thickness and surface quality of the film. Sakka has shown that with SiO_2 sol [8] it is possible to obtain mainly linear prepolymers suitable for fiber drawing. More difficulties exist with other systems like TiO_2 , Al_2O_3 or ZrO_2 .

For coatings, it does not seem to be absolutely necessary to prepare chains like prepolymers. Colloidal gel structures basically should exhibit reasonable coating properties, too. Only with increasing particle size, problems with film homogeneity can appear. Of more importance are the solid contents of the coating system and the densification mechanism of the film (figure 2).

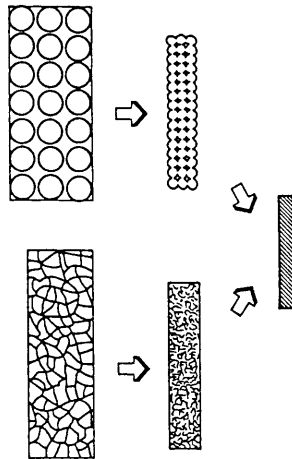


Figure 2. Densification behavior of two different gels (monolithic with a highly crosslinked polymeric network and colloidal; viscous sintering is assumed).

Figures 3a and 3b show monosized SiO_2 powders, synthesized by the sol-gel process in our lab, at room temperature and heat-treated at 1200°C for several minutes and the effect of temperature treatment.

The film layer (thickness $2 - 3 \mu\text{m}$) does not crack during drying at room temperature but cracks during sintering at higher temperatures. Since the shrinkage of the micropellets between room temperature and 1200°C is extremely low, one can conclude that the solid content of the gel particles is very high after synthesis. The pellets exhibit a very low specific surface area, which is in the range of the geometric surface area of the balls [9].

This system shows a good drying behavior (crackfree drying) which might be due to the low interaction forces between the pellet surfaces. In the wet stage, they seem to be able to

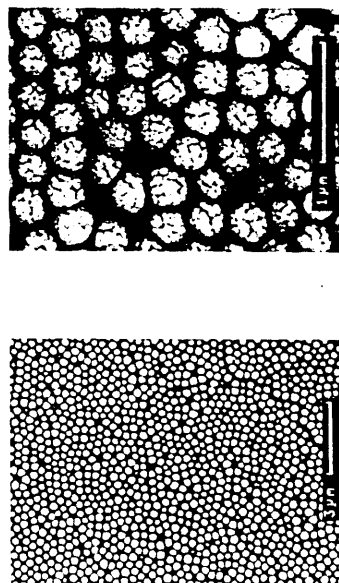


Figure 3a. SEM micrograph of SiO_2 microballs at room temperature.

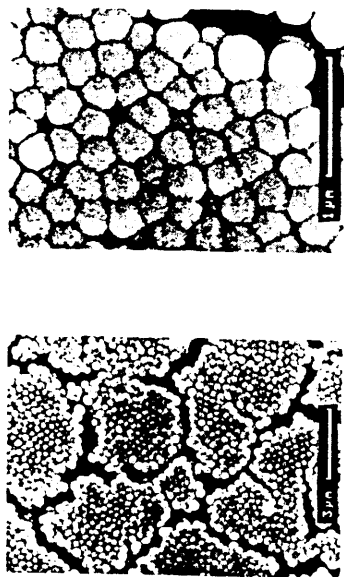


Figure 3b. SEM micrograph of SiO₂ microballs heated at 1 200 °C.

move into a dense packing of spheres. This low interaction between the particles might be either due to adsorbed species on the surface (e.g. organic solvent) or due to unhydrolysed organic radicals (=SiOR). On the other hand, the interfacial tension, caused by the interfacial angle between the pore liquid (e.g. water) and the pore walls prevents the desaggregation of the balls during drying. The "relaxation" of the system is obtained by the mobility of the pellets. Thus, the mechanical strength of the layer cannot be exceeded during the drying process. In the case of a worse relaxation behavior, interfacial tensions may be able to lead to cracks, as shown by [10].

The capillary pressure p depends on the surface tension γ and the pore diameter (figure 4).

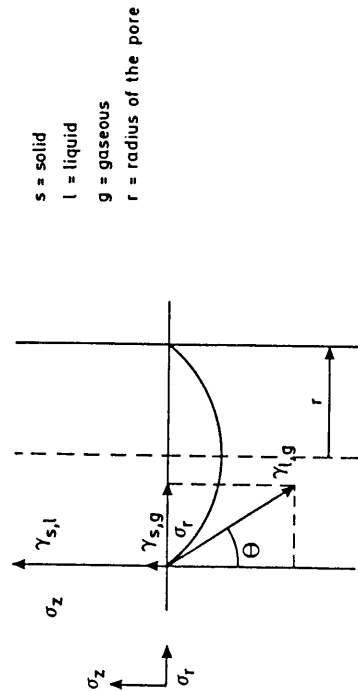


Figure 4. Capillary forces in pores.

σ defines the height to which a liquid can rise against gravity.

$$\sigma_r = \frac{2}{r} \cdot \gamma_{l,g} \cdot \sin\theta; \quad \bar{p} = \frac{2\gamma}{r}$$

$$\sigma_z = \frac{2}{r} (\gamma_{s,g} + \gamma_{s,l} - \gamma_{l,g} \cdot \cos\theta)$$

σ causes local tensions in the form of a ring around a pore (figure 5) and tries to narrow the pore. As long as the material can follow the tension, a plastic deformation and crackfree shrinking can take place. Since, in general, in gels neither pore shape nor pore diameters are constant, a tension zone will be formed during the drying process moving slowly through the material (figure 6).

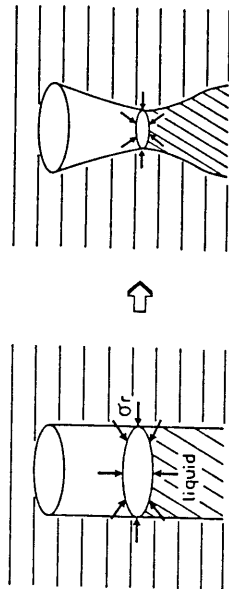


Figure 5. Effect of interfacial tensions on pore deformation.

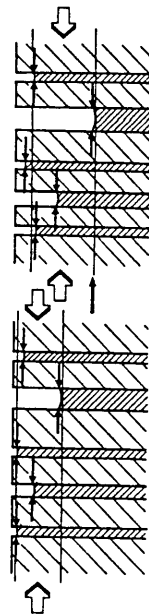
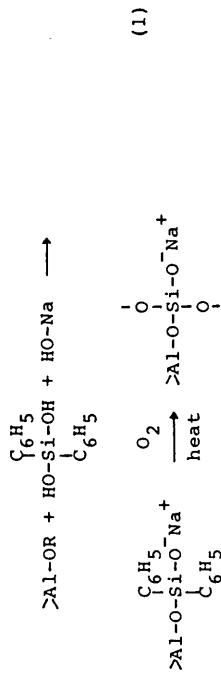


Figure 6. Development of a tension zone during drying.

The tension depends on the pore radius and the interaction between the liquid and the pore wall. For a glass surface (good wetting, contact angle 10°) and an assumed pore radius $r = 5 \cdot 10^{-8} \text{ m}$, $\sigma = 5.05 \text{ MPa}$. For $r = 10 \cdot 10^{-8} \text{ m}$, $\sigma_r = 2.57 \text{ MPa}$. In comparison to that the practical strength of glass is in the range of 50 to 150 MPa. A SiO₂ gel with Si-O-Si bonds and a porosity of 90% in analogy to practical glass strengths should exhibit a "practical" strength in the range of 5 to 15 MPa. That means, capillary forces should be able to cause cracks at

b) The role of organic groupings as network formers. Examples are:
 $\equiv\text{Si-R}'$ (with $\text{R}' =$ polymerizable or polycondensable groupings to be reacted with themselves or organic monomers);
 $\equiv\text{Me}-\text{L}'$ (with $\text{L}' =$ polymerizable or polycondensable ligands).

If the model of a network relaxation is valid for an improvement of the densification behaviour, one should be able to obtain crackfree films after drying. Therefore, a material was prepared with the composition $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}$ with the molar ratio of $\text{Si}:\text{Al}:\text{Na} = 82:9:9$ by sol-gel technique. The Si was completely added as $\theta\text{-Si}(\text{OH})_2$, thus leading to a twofold cross-linking Si unit (1), which can be transformed into a $[\text{SiO}_4]^{4-}$ tetrahedron by oxydation.



For preparation, $\text{C}_6\text{H}_5\text{Si}(\text{OH})_2$ was dissolved in a mixture of toluene and ethanol, a solution of NaOH in ethanol was added and the solvents were evaporated. To the remaining solid a solution of Al(o-but)₃ in a mixture of toluene and propanol was added. The suspension clears up to a transparent solution, which, after removal of the solvent and addition of toluene, can be directly used for coating. The infrared spectra of the room temperature dried material shows a surprisingly low OH content (figure 8), compared to the unreacted $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$, indicating that 90 to 95 % of the $\equiv\text{SiOH}$ groups had been reacted.

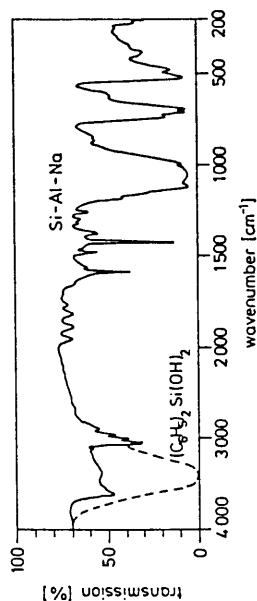


Figure 8. IR spectra of the room temperature dried film of the system $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}(\text{C}_6\text{H}_5)_2$

weak points of the gel, if relaxation cannot reduce the tensions. This consideration is basically valid for films, too, since the substrate plays the role of the wet unshrunk center of a monolith (figure 7).

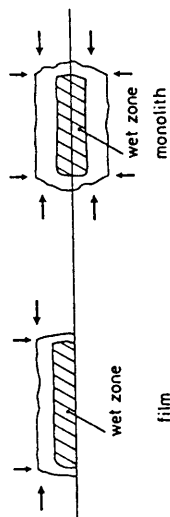


Figure 7. Comparison of a film and a monolith during drying.

If relaxation or strength are high enough, monolithic gels can be prepared. In the case of the "monolithic" film, an additional prerequisite appears: The tension acts along the surface, whereas the densification has to go perpendicular to it. That means, that the material has to undergo a unidirectional shrinking process and one has to look for mechanisms to increase the plastic deformation behavior of gels in order get perfect layers, especially, if thicker layers are required. Means are:

- to reduce interaction between gel particles
- to reduce the network connectivity in order to reduce the three-dimensional crosslinking
- to establish high temperature densification mechanisms which allow plastic deformation (e.g. viscous flow).

ORGANIC PROCESSING

As indicated above, plastic deformation should be able to enhance the film formation ability of a system. The addition of organic "thinner" to an inorganic network does not necessarily decrease viscosity, but if this leads to a reduction of covalent or other bonds, plasticity can be increased. Two basically different paths are possible: to block a reaction site of an inorganic unit by reaction (e.g. adsorption) with an organic molecule or to substitute an $\equiv\text{Me-X}$ bound (e.g. -OR) by an organic radical. For the first reaction, complex formation like reactions with a chelating ligand can be taken into consideration, for the second one, especially for SiO_2 , $\equiv\text{Si}-\text{C}$ bonds are suitable. Reaction principles for $\equiv\text{Si}-\text{C}$ -containing compounds in connection with sol-gel techniques are described elsewhere [11-14]. Different possibilities for an inorganic network modification exist:

- a) The role of organic groupings as network modifiers. Examples are:
 $\equiv\text{Si-R}$ (with $\text{R} = -\text{CH}_3$; $-\text{C}_6\text{H}_5$ or organofunctional groupings);
 $\equiv\text{Me}-\text{L}$ (with $\text{L} =$ complexing ligand, blocking reactive sites and thus acting as modifiers or as flexible connections between inorganic units).

Figure 9 shows a microscopic photograph of a film (about 20 μm thickness). The drying leads to a crackfree coating. After burning out the organics at 600 $^{\circ}\text{C}$ cracks appear, but there are relatively large areas of continuously thick crystallized films (figure 10).

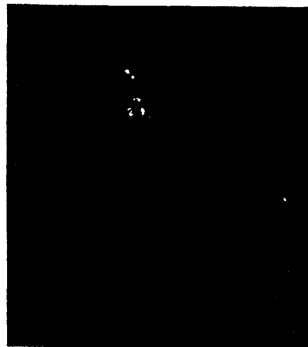


Figure 9. Photograph of the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$ film (room temperature dried; bar: 100 μm)

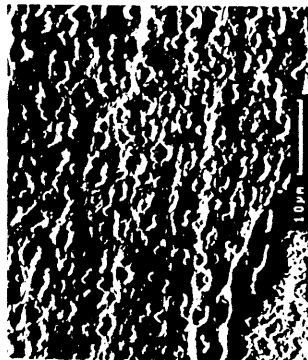


Figure 10. Fired coating of the system $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$ on Al_2O_3 (left cornef)

An ideal random distribution of the organics in the coating should lead to a uniform pore size and random pore distribution. The material should exhibit a perfect sintering behavior (viscous flow). The crack formation can be explained by inhomogeneities due to phase separating effects or related phenomena, as shown in figure 11. The TEM micrograph shows a microstructure with inhomogeneities in the range of 5 nm in the one and 20 to 30 nm in the other dimension (arrow).



Figure 11. TEM micrograph of a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3/\text{SiO}_2$ particle, dried at 110 $^{\circ}\text{C}$; bar: 60 nm

The preparation of Al_2O_3 coatings from sols leads to very poor (figure 12a) coating qualities, if a sol obtained from pure $\text{Al}(\text{i-prop})_3$ is used [15]. The addition of glycerol (25 vol.-%) leads to an increased viscosity after several hours at room temperature (40 mPa·s). Coatings with this sol lead to 2 - 3 μm thick coatings with only a few cracks (probably due to the non-optimized coating techniques, figure 12b).

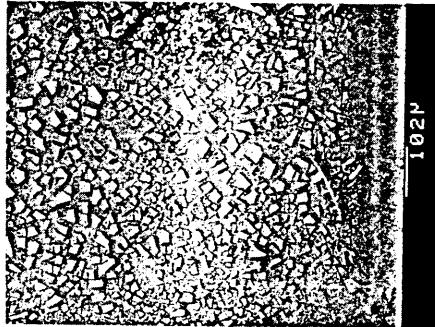


Figure 12a. Al_2O_3 coating with the non-modified gel (densified at 800 $^{\circ}\text{C}$)

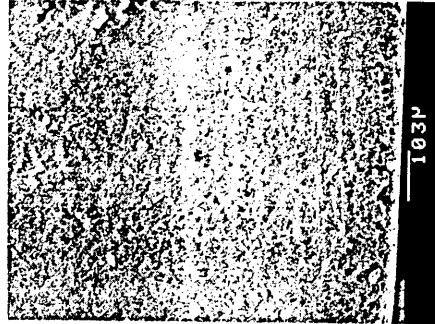


Figure 12b. Al_2O_3 coating modified with glycerol (densified at 800 $^{\circ}\text{C}$)

TEM shows a microstructure with inhomogeneities only in the range of some (1 - 2) nm. In the TGA/DTA scan, the burn out of organics can be observed between 300 and 500 $^{\circ}\text{C}$, and crystallization peaks appear at 700 and 1 200 $^{\circ}\text{C}$ (γ and α phases). It can be concluded that organic processing in combination with high homogeneity leads to a good film formation behavior.

Another example is the Al_2O_3 formation of sol with complex ligand blocked reaction sites. As a complex ligand, acetylacetonone (acac) was used. Therefore, aluminumbutoxide was dissolved in propanol and acetylacetonone was added (Al: acac = 2:1). During this reaction, the substitution of one OR-grouping against one acac grouping takes place (2).



The subsequent hydrolysis (water diluted in propanol) at pH 4.5 leads to a clear, slightly viscous sol which can be used for coatings. Figure 13 shows a crackfree coating, densified at 1 200 $^{\circ}\text{C}$.

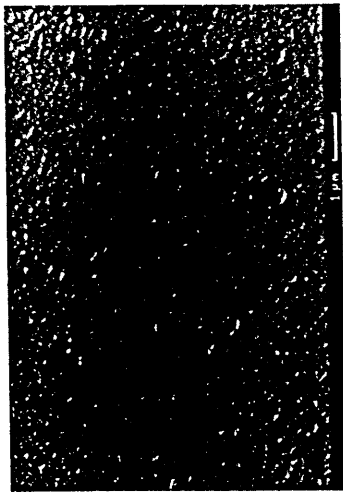
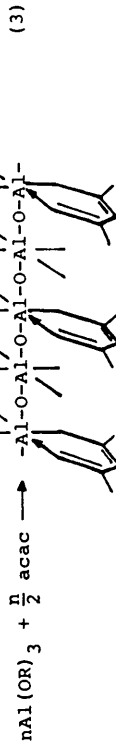


Figure 13. Al₂O₃ coating on a silica substrate (thickness: $\approx 1 \mu\text{m}$).

Without complex former, no continuous coating can be achieved. DTA/TGA shows again burnout of organics at 300 - 500 °C and crystallization peaks at 750 and 1150 °C. The improved film formation behavior is attributed to the fact that the complex former blocks sites for condensation (3) and thus leads to "flexible" gels.



COATINGS CONTAINING ORGANICS

In some cases it is advantageous to have organics present in the final coating. On soft substrates, like organic polymers, inorganic coatings have a poor adherence due to a mismatch and differences in moduli of elasticity. Inorganic organic polymers based on Si, Al, Ti, Zr, Sn, and other alkoxides, crosslinked with Si-epoxy components or Si-methacryloyl components show excellent abrasion resistance and can be densified at temperatures of 70 - 150 °C [16]. These types of coatings can be applied with thicknesses up to 100 μm . In connection with diffusion barrier pigments, like mica or glass flakes, coatings have been developed for corrosion protection [17] and for electronic substrates [18]. With special organofunctional groupings, the coatings can be applied for sensors [19].

CONCLUSIONS

Theoretical considerations and practical experiments show that sol-gel coating techniques can be improved by use of organics during processing. The main effect seems to be based on a better relaxation behavior during the indispensable shrinking

process. Since the field of organic additives is very wide, an interesting potential for further work exists.

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POLY [BENZOBIS THIAZOLE] (PBT)/SOL-GEL MICROCOMPOSITES

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INTRODUCTION

The objective of this Small-Business Innovative Research (SBIR) effort is to expand on work reported previously [1] and further develop a new class of microcomposite materials which combine the outstanding properties of ordered polymers and the excellent compressive strength of glass. In Phase I we demonstrated adverse property changes in poly(p-phenylene benzobisthiazole) (PBT) ordered polymer films by infiltrating sol-gel glass reagents. During Phase II we have addressed the following areas: sol-gel infiltration process; effect of sol-gel glass composition; tensile strength characterization, microcomposite UV resistance, lamination process, compressive strength determination. The following subsections present the work conducted to date.

Ordered Polymers

An ordered polymer such as PBT, is characterized by a rigid rod-like molecular structure which gives it extraordinary mechanical properties. Figure 1 illustrates the molecular structure of PBT fibers with extremely high strength and stiffness, low weight, and excellent thermal resistance as shown by comparison with other fiber properties in Table I, [2-4]. PBT films having biaxial strength are produced for the first time by Foster-Miller, Inc., under an ongoing U.S. Air Force contract F33615-83-C-5120.

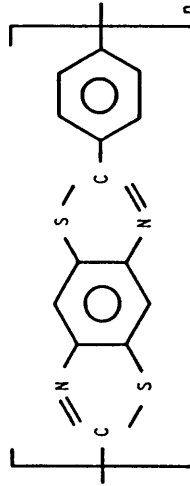


Figure 1. PBT - Poly(p-Phenylene Benzobisthiazole)

The film form has advantages over fiber because it can be more readily processed into sheets, beams, stiffeners, tubes and other structural shapes. In order to gain strength in more than one direction, fibers must be woven or unidirectional plies laid up at various angles. Biaxial strength films already have multidirectional strength. A laminated composite made from high strength, high modulus PBT film can provide better strength-to-weight performance and be simpler to fabricate than graphite kevlar® fiber composites. Although the tensile strength and modulus are lower for the film than the fiber, the composite properties of the film can be superior because of higher volume fraction of film, reduced interlaminar shear stress from ply mismatch, and no degradation of properties due to weave geometry. PBT films can be used to build high strength, thin-walled structures without the limitations imposed by yarn diameter and weave thickness [5].