

SYNTHESIS AND APPLICATION OF INORGANIC/ORGANIC COMPOSITE MATERIALS

Helmut K. Schmidt

Institut für Neue Materialien, Im Stadtwald, Geb. 43 A, D-66 123
Saarbrücken, Germany

Abstract: A new type of inorganic-organic composite has been developed using organic monomeric or polymerizable silanes (with appropriate organic groupings like double bonds or epoxides) as monomers or in situ prepared or separately added nano-scale ceramic or metal particles. Due to the small size of the particulate phase, these composites are still highly transparent but show properties at least partially to be attributed to the inorganic phase. The introduction of special functions into these materials has been used for the fabrication of interesting functions like non-linear optical properties, low surface free energy coatings, controlled release properties or special mechanical properties (scratch resistance).

INTRODUCTION

Ceramic polymer matrix composites are well established materials for a variety of industrial processes. Large-scale applications are elastomers and thermoplastic materials, for example, for injection moulding, but also silicones. For a variety of purposes, a filler is indispensable for achieving appropriate properties like strength or wear resistance. With decreasing particle size, the fabrication of composites becomes more difficult due to the large tendency of very small particles (e.g. in the nano range) to agglomerate. This restricts the degree of filling with nano-sized SiO_2 more or less to 20 % by volume. An alternative to mechanical mixing is the in situ preparation of small particles by sol-gel techniques in systems to be polymerized after or during particle growth. In this case, nucleation and growth are the parameters controlling particle size and particle distribution (Refs. 1 - 2). The mobility and the surface properties of particles are the controlling factors for agglomeration. This type of composites, which can also be called "nanocomposites", are of interest for a variety of reasons, for example, to obtain high transparency and, at the same time, to maintain properties attributed to the solid phase of the inorganic particles (glasses, ceramics, metals or semi-conductors). The second point of interest is a consequence of the high surface area of very small particles and, as a result, the high

interface volume. Interfacial phases between ceramics and polymers are known to have structures different from the bulk phase. Effects on different properties resulting from the interface can be expected, especially if the degree of filling is increasing and the particle size remains small at the same time. The question arises whether these interfacial phases are able to determine the material properties substantially. Another question is related to the synthesis of this type of materials, since the building-up of the inorganic as well as of the organic polymeric phase has to take place in one and the same material. If polymerization processes are used, it is of importance to obtain high conversion rates. Furthermore, it is of interest which type of properties can be expected from this type of materials. Interesting properties related to the inorganic phases are optical properties resulting from the physical properties of the inorganic particles (linear properties as well as non-linear properties), mechanical properties related to the inorganic phase like hardness or modulus of elasticity, or adaptive properties like photochromism or electrochromism as well as properties related to the organic or polymeric phase like thermoplasticity, solubility to be used for a variety of coating techniques as well a polymerizability to be used for photolithography.

MATERIALS SYNTHESIS

General Principles

For the preparation of inorganic-organic composite materials, basically different types of synthesis processes have to be used. The first type, as already indicated in the introduction, is related to inorganic synthesis like crystal growth, precipitation or sol-gel techniques. Sol-gel techniques are known for several decades of years in industrial processing. The sol-gel process is based on solution chemistry using soluble precursors undergoing an activation reaction, for example, hydrolysis of alkoxides, and by nucleation and growth processes, small particles are obtained (with a few exceptions like silica) (Refs. 3 - 9). Since the fundamentals of this process are well established in literature, only some special aspects will be mentioned. Through this process, in general, sols are obtained which represent a suspension of fine particles in the nanometer range (several up to 100 nm). These sols are thermodynamically very instable systems due to the large surface free energy of small particulates and only exist if a stabilization of the colloids is present. The stabilization, in general, is an electrostatic stabilization, governed by the pH of the systems, which leads to a surface charge of the particle according to the Stern model (Ref. 10). Changing the pH to the isoelectric point leads to agglomeration and to a so-called "gel", which is a diphasic system with pores either filled with liquids or air. It is very difficult to process these sols into solid high-concentration systems,

since the stabilization mechanisms are disturbed, and uncontrolled agglomeration occurs. To solve this problem, methods have been developed to stabilize the small particulates by strongly bonded tailored molecules to the surface (Refs. 11 - 14). It has been shown that, for example, carboxylic acid can be strongly bonded to the surface of zirconia or alumina particles and amines can be strongly absorbed to metal particles like palladium or gold. If bifunctional molecules are used, additionally having double bonds or hydrolyzable silane groupings, the nano-scale precursors now have chemical reactivities, mainly to be attributed to the type of surface molecules. In this case, zirconia particles with diameters of only 2 nm can be copolymerized to double bonds if methacrylic acid is used as a surface modifier. The general principle of synthesizing and processing of small particles to composites is shown in Fig. 1.

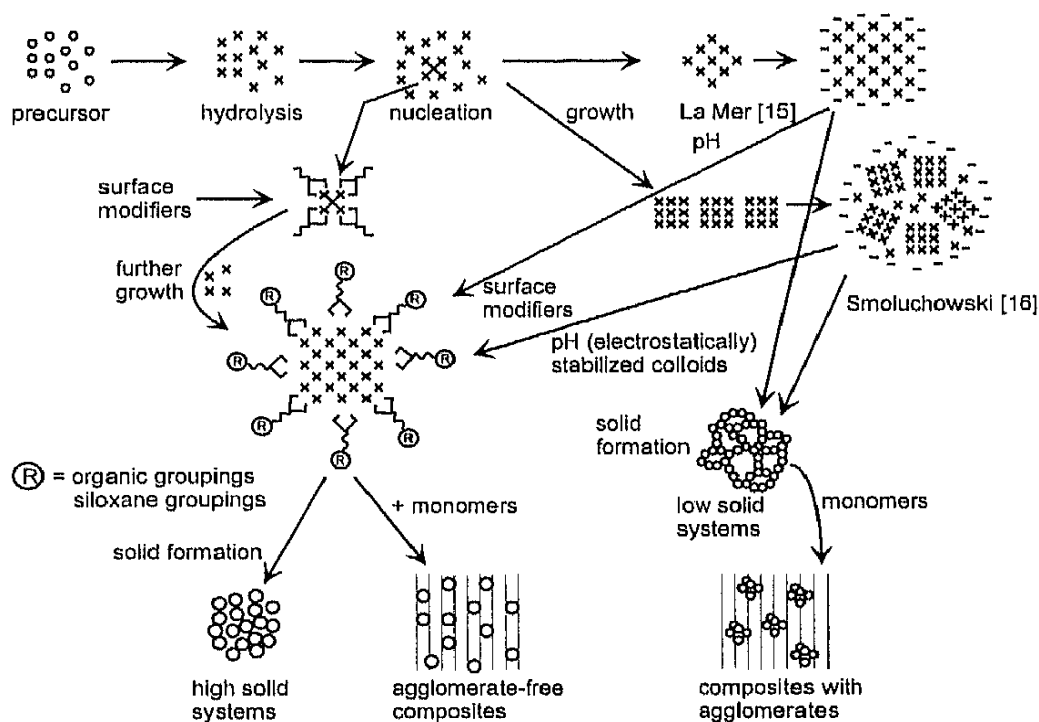


Fig. 1: General principle of the preparation of nano particles with specific reactivities.

This basic principle can be generalized, and a variety of materials has been prepared using this approach (Refs. 17 - 28).

Beside their role as surface modifiers of colloidal particles, silanes can also act as links between inorganic particles or networks and organic chains. For this reason, especially silanes with double bonds for being polymerized or with other reactive groups for building up polymeric chains like epoxides are of interest. Especially with epoxides, a variety of reactions are possible, such as using additional epoxides for

PEO formation, alcoholic groups or amines for additional reactions. Some reaction principles are shown in Fig. 2.

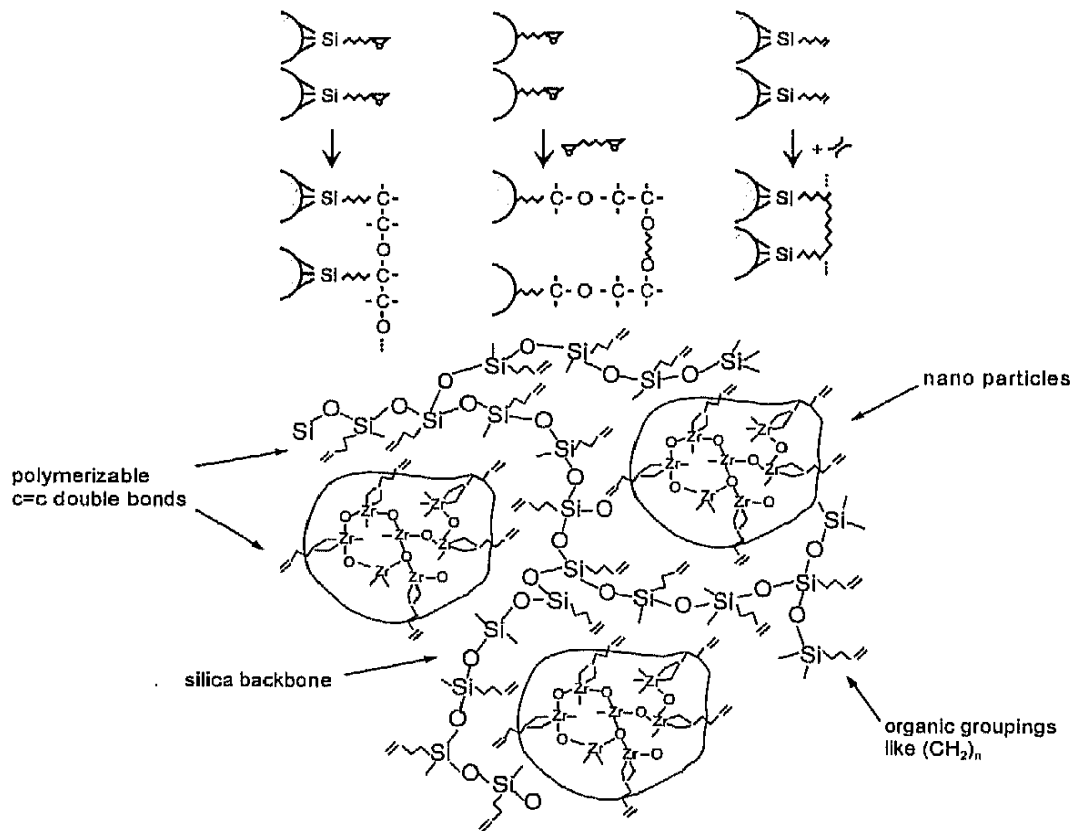


Fig. 2: General reaction principles using functional silanes for inorganic-organic links and model of a ZrO_2 /methacrylic acid (ma)/methacryloxy silane system.

In this connection, it is of high interest to know how far polymerization reactions can be carried out within such systems. For this reason, methacryloxy group containing silanes were investigated with respect to their polymerizability (conversion kinetic) in a non-polycondensed state and compared with the hydrolyzed and prepolycondensed state with and without addition of 2 nm ZrO_2 methacrylic acid surface modified particles according to the model in Fig. 2. The ZrO_2 /ma system was prepared according to Ref. 21. The results are shown in Fig. 3 (Ref. 22).

As one can see from this comparison, the reaction kinetics of the silane and composite systems, in general, are slowed down compared to the pure organic methacrylic compound. However, the conversion rates obtained by integration of the heat flow curve are similar and are all in the range of about 70 %. The unhydrolyzed silane, however, shows a slower reaction kinetic compared to the hydrolyzed composite system, which is of high importance for the composite synthesis. The results show that even in highly complex systems, the conversion kinetics is suitable for composite preparation.

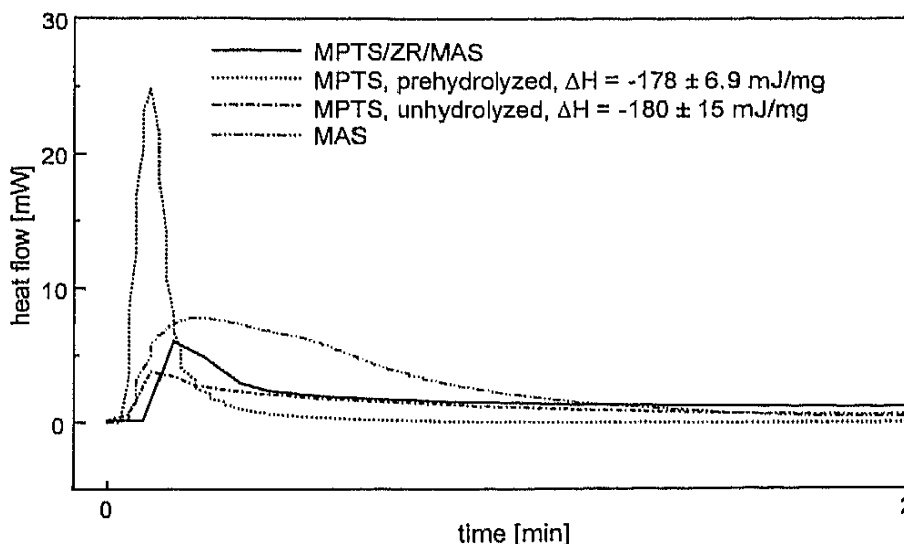


Fig. 3: Comparison of the conversion kinetics for non-hydrolyzed and prehydrolyzed methacryloxy group containing silane with pure methacrylic acid and the composite system surface-modified zirconia plus methacryloxy silane (after Ref. 22) by a calorimetric measurement. The heat is directly proportional to the conversion.

In further experiments, the temperature dependence of the conversion rate has been investigated, and it could be shown that at 120 °C conversion rates above 95 % could be obtained.

The question of the detection of interfacial phases has been investigated with ZrO_2 nano particle systems with organic matrices, prepared from aramide monomers (Ref. 29). ZrO_2 nano particles have been prepared from $Zr(OR)_4$ in presence of the organic monomers, which then have been reacted to aramide. In Fig. 4 a DMTA plot is shown, which compares systems with different degrees of filling. The plot shows that the unfilled polymer shows a T_g of about 340 °C. With increasing content of ZrO_2 (2 nm particle size), the "polymeric type" of T_g is substituted by a second one at about 440 °C. Since the particles consist of ZrO_2 , this peak cannot be attributed to the T_g of the inorganic phase and, as a hypothesis, it is attributed to an interfacial phase around the small particles.

It is not quite clear so far what this interfacial phase means with respect to mechanical properties, since these investigations have not yet been finished, but it is of basic interest: If these phases can be used to tailor the mechanical properties of the systems, so-called interfacial phase-determined systems can be prepared.

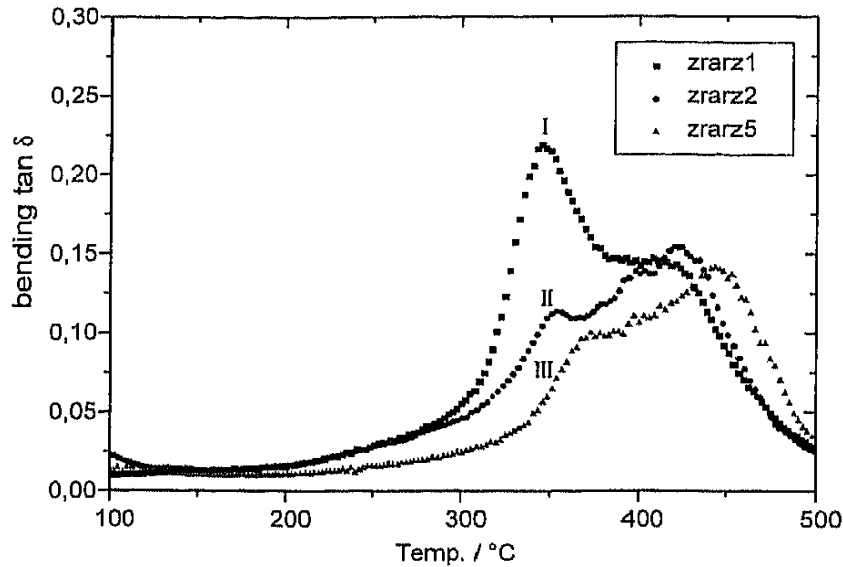


Fig. 4: DMTA plots from an aramide type of polymer made from 1.4 and 1.3 phenylene diamine, terephthalic acid dichloride $Zr(OR)_4$ (ratio: 35:15:50:x) with different degrees of nano particle fillings of ZrO_2 ; particle size: 6 nm. I: $x = 2.5$, II: $x = 5$, III: $x = 15$ (after Ref. 29).

EXAMPLES FOR MATERIAL DEVELOPMENT

Gradient Coatings

Based on the methacryloxy silane zirconia methacrylic acid system, coatings can be prepared, which can be photocured, showing a high abrasion resistance compared to common polymers. If, in addition to the basic system, silanes with perfluorinated side chains are added, coating systems with low surface free energy are obtained. In Fig. 5 a flow chart of the preparation is shown.

It has been shown (Refs. 17, 19) with an even smaller amount of fluorinated silane (< 0.6 mole %) surface free energies below those of polytetrafluoroethylene are obtained. ESCA (electron spectroscopy for chemical analysis) profiling shows that the fluorinated units are enriched in the surface (factor of 10 - 20) compared to the bulk, and that polar groups are found in the interface to the substrate as far as the substrate has a certain polarity. Based on this system, a variety of low surface free energy with a dust-repellent or antisoiling effect has been prepared (glasses, plastics, metals). Coated glass will be introduced into the market in the near future. Metals have been successfully coated for industrial processes, for example, for carpet fabrication, as an antisticking conveyor belt system which now has been running for over one year without any problems. These systems are highly transparent and scratch-resistant (below 2 % haze after 100 revolutions in a taber abrader).

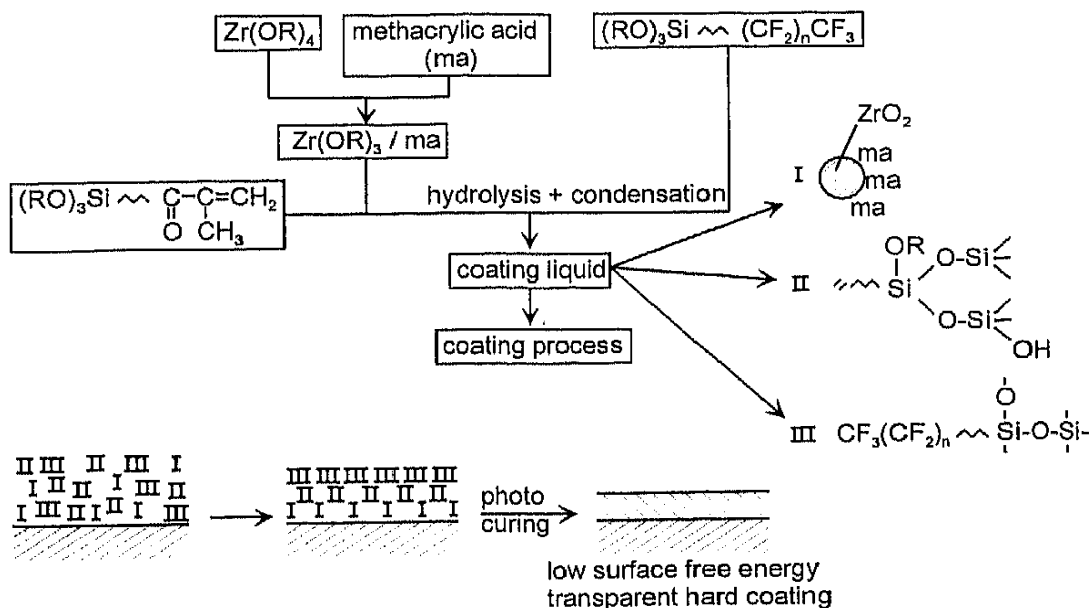


Fig. 5: Flow chart for the preparation of the low surface free energy gradient system.

Controlled Release Systems

By the introduction of tensides into composites having an at least partially hydrophilic matrix (produced from epoxy silanes through ring opening by water addition), controlled release transparent coatings can be prepared, leading to antifogging behavior (Ref. 17). These systems applied on mirrors, for example, prevent them from fogging without decay over the testing period (up to now several years). Fig. 6 shows the flow chart of the principles of the system. Due to the tenside release under H_2O condensation conditions, the formation of droplets causing the "fog" effect is suppressed and substituted by a homogeneous film condensation.

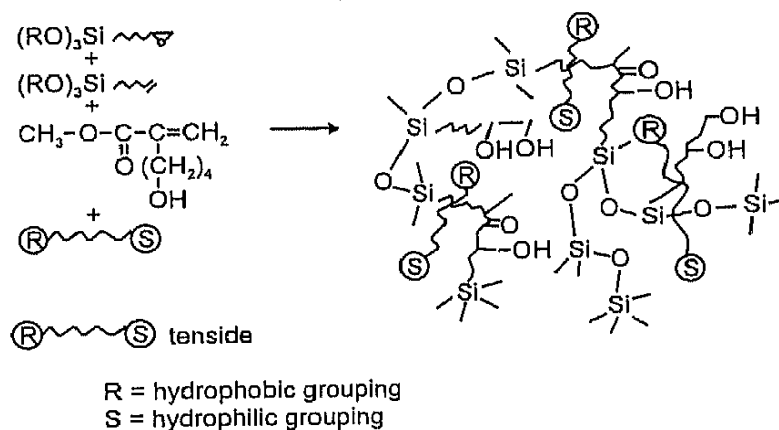


Fig. 6: Synthesis and structural model of an antifogging transparent controlled release coating for glass surfaces.

Scratch-Resistant Systems

The addition of nano-scale γ -alumina to epoxy silane-based alumina alkoxide-derived composites leads to a very special structure, as proved by infrared and NMR spectroscopy, leading to extremely high scratch resistance for the protection of plastic surfaces. In Fig. 7, a structural model of this composite is shown. The epoxy silane is transformed to a polyethylene network, and due to the catalytic effect of the γ -alumina on the epoxy group, the alumina particles are surrounded by this network, additionally linked to the inorganic backbone by the Si-O-Al bonds.

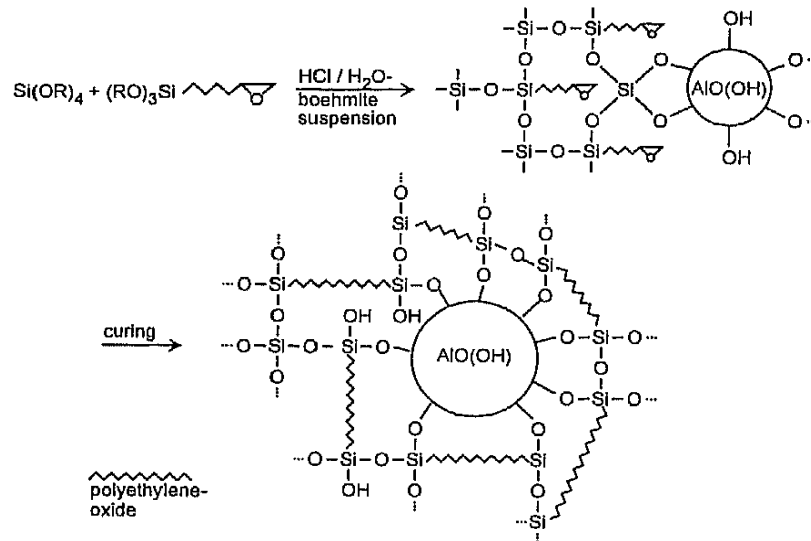


Fig. 7: Reaction scheme and structural model of the GPTS/TEOS/boehmite-based material.

This system, applied as a coating on $\text{CR}^{39\text{®}}$, leads to an extremely high scratch-resistant system, which exceeds the scratch resistance of conventional hard coatings by the factor of three in a diamond scratch test and by the factor of 2 in a special test for eye glass lenses where the coated lens is tumbled in a drum together with abrasive materials. The system has been introduced into the market in June 1994 very successfully.

Optical Systems

Due to the possibility of tailoring the content of inorganics and the techniques for avoiding agglomeration and keeping the particle size very small, optical properties of these systems are of interest. This is useful for passive optics due to the possibility of tailoring the refractive index, but as well as from the good mechanical surface properties, the possibility of using photolithography or embossing for microengineering. Based on these properties, waveguide materials have been prepared (Ref.

21) for channel waveguides, but also for optical gratings or microlens arrays. The introduction of metal colloids into these systems leads to composites with high third-order non-linear susceptibilities (Ref. 25)

PERSPECTIVES

The described systems show that the presented type of inorganic-organic nanocomposites represents a type of material with the potential of material tailoring in a wide range. This has mainly been investigated for a variety of coatings at present, but first results obtained from bulk materials show that interesting properties like a high chemical stability combined with a high thermal stability and very good optical properties can be obtained. The very good optical properties are first based on the nanoparticulate inorganic phase, which second prevents the crystallization of organic polymeric systems.

Especially the option of tailoring a new interfacial phase-determined composite may open an interesting new field for polymer matrix composites.

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