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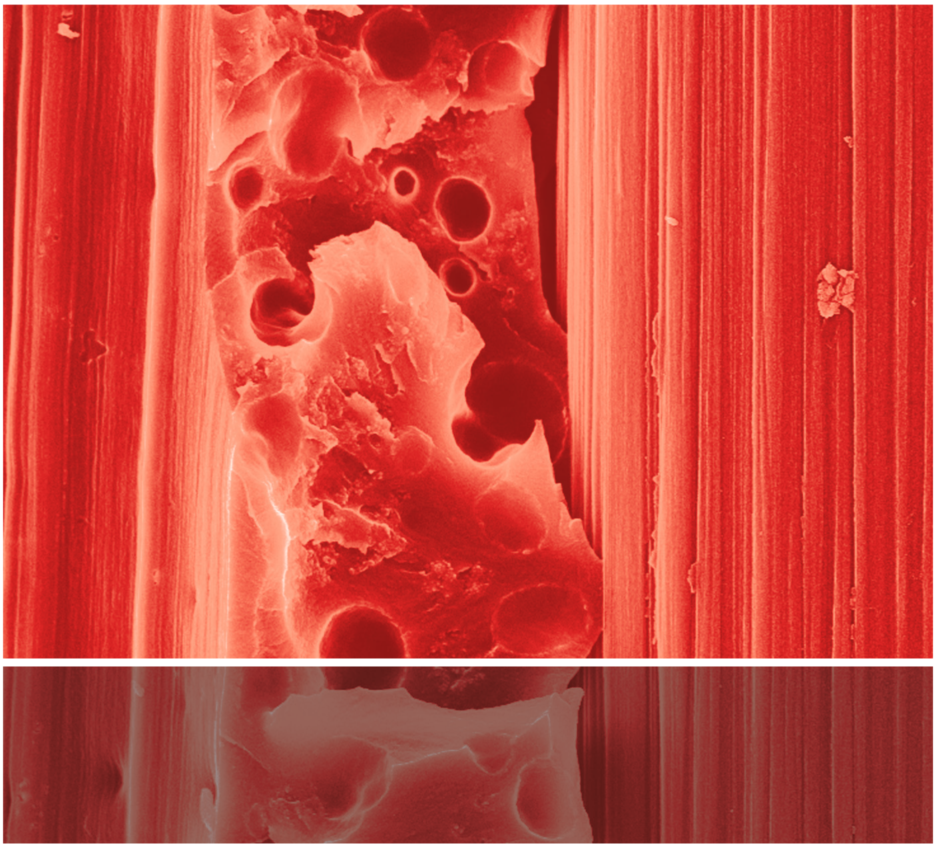

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Short Summary

The properties of cured epoxy resins can be improved significantly by the addition of surface-modified SiO_2 nanoparticles. A linear relationship between the increase of modulus respectively the fracture toughness and the addition level of nanosilica exists for most epoxy curing agents. Compressive strength and fatigue performance can be improved as well.

Combining this modification with the classic toughening concept using reactive liquid rubbers or core-shell elastomers leads to so-called hybrid systems, which are characterized by both high toughness and high stiffness. The fatigue performance is improved further.

Laminates manufactured by using these modified resins exhibit improved performance as well. Regardless if glass or carbon fibers are used as reinforcing material, the relative property improvements of the laminates are much smaller. A linear relationship between the percentual increase in fracture toughness (G_{Ic}) of the cured bulk resin systems and the percentual increase of the G_{Ic} of the laminates made thereof seems to exist; with a conversion factor of 0.18. If the fracture toughness of a fiber-reinforced part shall be increased by 100 %, then instead of the resin used a hybrid resin with a 555 % higher bulk G_{Ic} needs to be used. For the fatigue performance of laminates made from hybrid resins a tenfold increase in cyclic loadings upon failure can be achieved.

In own trials a fast curing epoxy resins system based on DGEBA/IPD/TMD was employed to manufacture carbon fiber reinforced laminates; whose properties were investigated. The cured bulk resin systems exhibit the expected property improvements for the hybrid systems. However, the laminates based on hybrid resin systems, modified with both reactive liquid rubber and SiO_2 nanoparticles, show no further improvements compared to the rubber-only modification but rather slightly lower values for G_{Ic} and G_{IIc}. The ILSS is comparable; the residual strength after impact reduced.

The agglomerates of silica nanoparticles, which were discovered, might be a potential cause. They form during the fast cure in presence of reactive liquid rubber; probably caused by the forced rapid phase separation of the rubber upon cure. Future research will provide further insights.

In summary it can be stated that laminates made from hybrid epoxy resins are tough and stiff and exhibit improved compressive strength as well as excellent fatigue performance. This makes them especially suitable for highly stressed composites parts like in automotive applications.

Kurzzusammenfassung

Die Eigenschaften von gehärteten Epoxidharzen können durch den Zusatz von oberflächenmodifizierten SiO_2-Nanopartikeln deutlich verbessert werden. Es besteht für die meisten Härter ein annähernd linearer Zusammenhang zwischen der Steigerung des Moduls bzw. der Bruchzähigkeit und der Zusatzmenge an Nanopartikeln. Druckbeständigkeit und Ermüdungsverhalten können ebenfalls verbessert werden.

Kombiniert man diese Modifikation mit der klassischen Schlagzähmodifizierung unter Verwendung von reaktiven Flüssigkautschuken oder Core-Shell-Elastomeren, so erhält man sogenannte Hybridsysteme, welche sich durch eine besonders hohe Zähigkeit bei gleichzeitiger Steifigkeit auszeichnen. Auch das Ermüdungsverhalten wird weiter verbessert.

Beim Einsatz dieser modifizierten Harze zur Herstellung von Laminaten können an diesen ebenfalls Eigenschaftsverbesserungen beobachtet werden. Unabhängig davon, ob Glas- oder Carbonfasern als Verstärkungsmaterial eingesetzt werden, fallen diese Verbesserungen prozentual deutlich geringer aus. Es scheint eine lineare Beziehung zwischen den prozentualen Steigerungen der Bruchzähigkeit (G_{Ic}) der gehärteten Reinharzhybridsysteme und den daraus hergestellten Laminaten zu existieren; mit einem Übertragungsfaktor von 0,18. Soll ein Faserverbundbauteil um 100 % in der Zähigkeit gesteigert werden, so muss statt des bisher verwendeten Harzsystems ein Hybridsystem mit einem 555 % höheren G_{Ic} eingesetzt werden. Beim Ermüdungsverhalten der Laminate auf Hybridharzbasis kann eine zehnfache Steigerung der zyklischen Belastung bis zum Versagen erzielt werden.

In den eigenen Versuchen wurden unter Verwendung eines schnellhärtenden Epoxidharzsystems basierend auf DGEBA/IPD/TMD kohlefaserverstärkte Laminate mittels RTM hergestellt und untersucht. Die gehärteten Reinharzsysteme zeigen für die Hybride die erwarteten Eigenschafts-verbesserungen. Die Laminate auf Basis Hybridharz, sowohl mit reaktivem Flüssigkautschuk als auch mit SiO_2-Nanopartikeln modifiziert, weisen jedoch keine weitere Verbesserung der Bruchzähigkeit gegenüber der reinen Kautschukmodifikation auf, sondern eher geringfügig niedrigere Werte für G_{Ic} und G_{IIc}. Die ILSS ist vergleichbar; die Restdruckfestigkeit nach Impact jedoch verringert.

Eine mögliche Ursache sind die entdeckten Agglomerate der SiO_2-Nanopartikel. Sie entstehen während der raschen Vernetzung in Gegenwart von reaktivem Flüssigkautschuk; wahrscheinlich verursacht durch die erzwungene schnelle Phasentrennung des Kautschuks während der Härtung. Zukünftige Forschungs-arbeiten werden hier weitere Erkenntnisse bringen.

Zusammenfassend kann festgestellt werden, daß Laminate auf Basis von Hybridharzen gleichzeitig zäh und steif sind und eine verbesserte Druckbeständigkeit sowie ein hervorragendes Ermüdungsverhalten aufweisen. Sie sind daher besonders für hochbelastete Bauteile wie beispielsweise in automobilen Anwendungen geeignet.

1. Introduction

Lightweight construction is one of the key technologies to master the challenges of the 21st century. Be it to enable mankind to exploit renewable energy (just think about rotor blades for wind energy generators) or to reduce consumption of fossil energies in transportation by air, land or sea. In lightweight construction fiber-reinforced composites (abbreviated to "composites" for short) play a very prominent role. These new materials experienced, and are still experiencing, an extremely rapid development. After the initial developments in aerospace applications, and later rotor blade construction, it is now time to think about the extensive use of such composites in automotive construction. The political pressure on European car manufacturers to offer cars low in fuel consumption and low in exhaust emissions is constantly increasing [1.1]. Thus, fiber-reinforced composites offer here a tremendous potential for weight reduction. The optimization of the manufacturing process of composites (see chapter 2.1.), the identification of the best design and the types of fiber reinforcement are of great importance. However, the optimization of the matrix materials is also a very important topic of international research.

1.1. Motivation

Silica nanoparticles have been available as concentrates in epoxy resins in industrial quantities for more than 10 years now. They are used to improve the mechanical properties of epoxy resins and fiber-reinforced composites made from these modified epoxy resins. They do increase the toughness of epoxy resins, however not to the same extent as traditional tougheners like reactive liquid rubbers or core shell rubber particles do. Nevertheless, when combining the nanosilica modification with a toughening of the epoxy resin there seem often to exist synergistic effects. After many own research work in this area, many papers published, and common research projects with universities and institutes the need arose to summarize and integrate the many results. Other research groups, active in similar or related fields, have published often similar results but sometimes contradictory results as well. Unfortunately very often either bulk resin systems or fiber reinforced composites have been investigated - but not both. Also, the many individual results based on totally different resin/fiber-combinations made the preparation of an overview mandatory.

Of course the question needs to be asked, if fundamental laws or correlations between the modifications and property improvements exist. Especially with regard to a potential synergy between rubber-modification of the epoxy resin and the addition of silica nanoparticles. The same question is also valid for the transfer of property improvements of the bulk resin into the fiber reinforced composite as a function of the different modifications and fiber reinforcements. To have the possibility of predicting the composite performance from bulk resin performance would be also extremely helpful for industrial formulators, who can then validate the predicted results from their own test programs on the composites.

1.1.1. References

[1.1] Regulation (EC) No 443/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL; Official Journal of the EU, 05.06.2009, L 140/1

1.2. Objectives and structure

It is the intention of this work to provide an overview of the actual state-of-the-art of the research regarding the mode of action of SiO_2 nanoparticles in modified epoxy resins and fiber-reinforced composites made thereof, to evaluate the different results and, if possible, to identify fundamental correlations. One example would be the potential existence of a relationship between the properties of an optimized resin matrix and the properties of the resulting fiber-reinforced composite.

First the modification of epoxy resins with SiO_2 nanoparticles regarding the achievable property improvements of cured bulk resins needs to be investigated – this will be the subject of chapter 3.1. Secondly, the so-called hybrid epoxy resins, that is epoxy resins modified with both a rubbery (i.e. elastomeric) toughener and silica nanoparticles, will be evaluated with a focus on mechanical properties in chapter 3.2. Thirdly, the use of nanosilica-modified epoxy resins in fiber-reinforced composites based on glass or carbon fibers is the subject of further investigations in chapter 3.3. One of the essential questions here is whether property improvements found for modified bulk epoxy resins will be found for fiber-reinforced composites as well. Fourthly, of course the same question is even more important for fiber-reinforced composites made from hybrid epoxy resins which will be investigated in chapter 3.4.

Finally, the insights obtained from the above studies will be verified by investigating a bulk epoxy resin system and a composite made by using a common resin system of major industrial importance in chapter 3.5. A carbon fiber-reinforced system based on a fast-curing epoxy resin system, as typically used for manufacturing automotive parts, was selected to perform this task.

To obtain a clear structure of this work it is divided in these five work packages (chapters 3.1. - 3.5.). To ensure a correct interpretation of the many different results from many individual sources as well as the results of my own work the single work packages have been published up front in renowned scientific journals.

As each work package has is a separate chapter and coherent in itself, the necessity arose to use graphs or pictures several times. Examples are the SEM picture of core shell elastomers used in chapters 2.4.3. and 3.2., or the SANS curve for the particle size distribution presented in chapters 2.5.1. and 3.3., or the TEM picture of the silica nanoparticles shown in chapters 2.5.1. and 3.2. This recurrence is necessary to give a clear and readable structure. In the bibliography the cross-references are given.

2. State-of-the-art of the science and technology

2.1. Manufacturing technologies for fiber-reinforced composites

The manufacturing of fiber-reinforced composites is based on quite a few very different processes [2.1.1], [2.1.2]. An excellent overview on actual technologies especially used for epoxy resins as matrix materials is given by Constantino et al. [2.1.3]. As each manufacturing technology implies specific requirements regarding the processability of the resin/hardener system used, this affects the formulations which potentially could be used. Thus the most important manufacturing technologies for fiber-reinforced composites based on epoxy resins will be introduced briefly in the present chapter.

General trends are the increasing automation of the manufacturing processes and the reduction of the cycle times in order to reduce the process costs. Therefore, much work has been performed on resin systems which enable cycle times of 3-5 minutes to be achieved – which is one of the requirements of the automotive industry [2.1.4]. In the near future even the fully automated production of large rotor blades for wind energy generators will be possible [2.1.5].

Sometimes single parts are manufactured by different methods and assembled to form larger structures afterwards. If you have a close look at the chassis of the Porsche 918 Spyder (Figure 2.1.1) you will discover that the monocoque is manufactured using a resin transfer molding (RTM) process. The engine support however, being subject to much higher operating temperatures, is made using prepreg technology in combination with an autoclave cure [2.1.6].

Figure 2.1.1: Rolling chassis of the Porsche 918 Spyder [2.1.6]