

Tough and Heat-resistant: New Silicone Particles for Thermosets

Additives. A new generation of nanoscale silicone and core-shell particles is revolutionising the modification of heat-resistant thermosets. Even small additions of the new particles significantly increase the impact strength and fracture toughness of reactive resins and other plastics.

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Highly crosslinking reactive resins, such as hot-curing epoxy resins, bismaleimide resins or cyanate resins are used as structural adhesives, moulding and filling compounds, laminating resins and coatings. Alongside their many advantages such as high elastic modulus, resistance to chemical media and thermal stability under load, cured

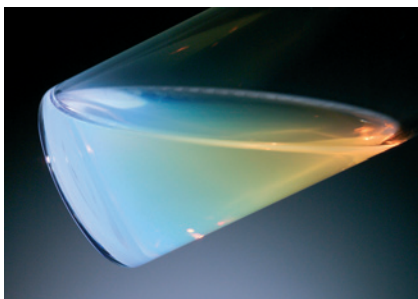


Fig. 1. Nanoscale silicone spheres: homogeneous, opalescent solution of silicone particles with a diameter of about 100 nm

reactive resins or thermosets, particularly those with high degrees of crosslinking, generally have the disadvantage of excessive brittleness.

Over the past twenty or thirty years, there have therefore been many efforts to increase the fracture toughness of highly crosslinked reactive resins. At present, thermoplastic toughening is the solution that offers the most advantageous property combinations. However, the high-temperature-resistant thermoplastic modifiers that influence the toughness of the material are difficult to process. They

considerably increase the viscosity of the resin and are only sparingly soluble in it, which is the reason that their use has essentially remained restricted to CRP structural applications in aircraft manufacture.

The oldest method of increasing the fracture toughness of reactive resins is modification with liquid reactive rubbers. These dissolve without any problem in the resin and bring about only a moderate increase in viscosity as compared with high- T_g thermoplastics. Because of their relatively favourable price and ease of processing, these reactive rubbers are now widely used as toughening agents. However, they have a number of disadvantages, such as reduced elastic modulus, low glass transition temperatures and high water absorption. Resistance to thermooxidative degradation is also lowered.

Unlike with thermoplastic toughening agents, the effectiveness of rubber toughening modifiers is dependent on the network density of the resin matrix: the toughening effect decreases with increasing crosslink density.

In toughening thermosets, both with thermoplastic toughening agents and reactive rubbers, the achievable effect is dependent on the thermodynamically and kinetically controlled process of phase separation during curing. Consequently, the resulting properties are also dependent on many factors that influence the thermodynamics and kinetics of phase separation (e.g. fillers and other modifiers, curing regime). If phase separation is prevented by, for example, over-rapid curing, the toughening effect is only minimal.

Soft Core, "Hard" Shell

To overcome this disadvantage, work has been proceeding for some years now on the development of core-shell particles (Fig. 1). These are preformed rubber particles with a soft, flexible rubber core and "hard" outer shell. These particles can be incorporated into the reactive resin matrix. The advantage is that, with suitable dispersion, the morphology of the system with its "islands in the sea" structure is predetermined. The matrix is therefore no longer influenced by thermodynamic and kinetic factors during curing.

The majority of the relevant literature is, however, confined to core-shell particles in which the soft, flexible core is produced from organic rubbers, e.g. acrylate- or butadiene-based. The above-mentioned disadvantages of the reactive, organic liquid rubbers are therefore only partially overcome; similarly, the organic rubber grades do not achieve the

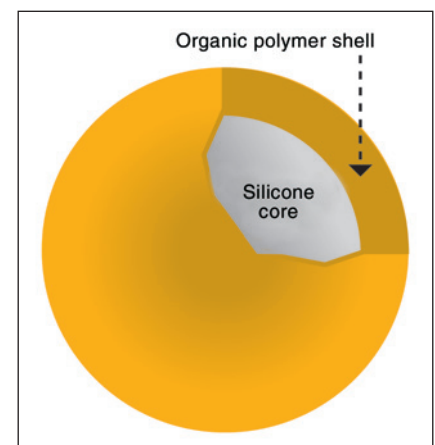


Fig. 2. Core-shell particles: soft flexible silicone core with a grafted-on acrylate polymer shell

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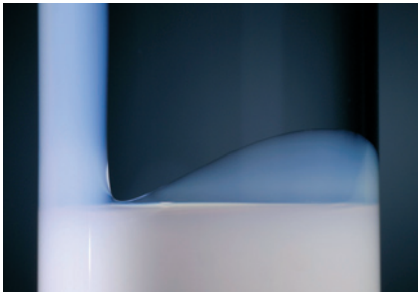


Fig. 4. Masterbatch: dispersion of core-shell particles in an epoxy resin

high-temperature resistance often required [1].

With soft, flexible cores based on silicone rubber, however, it is possible to overcome these disadvantages. For example, resistance to thermooxidative degradation is very high and water absorption low. The toughening mechanisms that provide rubber-elastic properties also operate far more efficiently when an elastomer is used as the toughening component. The reason for this is that below the glass transition temperature of the rubber phase, these mechanisms are not effective in the same way. In the case of core-shell particles with a silicone core, which has a glass transition temperature far below $-100\text{ }^{\circ}\text{C}$, toughening is ensured even under low-temperature conditions. Last but not least, silicones also have exceptional electrical and dielectric properties, which make them particularly suitable for use in electronics applications.

The synthesis of silicone and core-shell particles is carried out in an aqueous microemulsion process. In this process, different silane components are hydrolysed in the presence of a special catalyst system and then undergo a condensation reaction, which results in elastomeric (or highly crosslinked) silicone particles [2]. Depending on the end property required, these “silicone cores” can then be surface-modified, surface-functionalised or graft polymerised with an organic acrylate copolymer, which gives rise to core-shell particles (Fig. 2).

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The synthesis process permits stepwise particle formation and leads to customised, monomolecular giant molecules with diameters of up to several hundred nanometers. These “nanoscale silicones” are hundreds to thousands of times smaller than the diameter of a hair. It is precisely the “nanoscale” of the tiny particles, which – after homogeneous dispersion – creates a very large “internal” surface in the target system and, in combination with the elastomeric properties of the particles, leads to very high efficiency in toughness improvement.

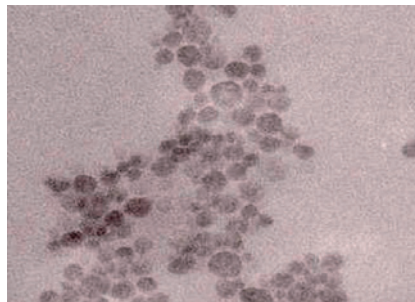
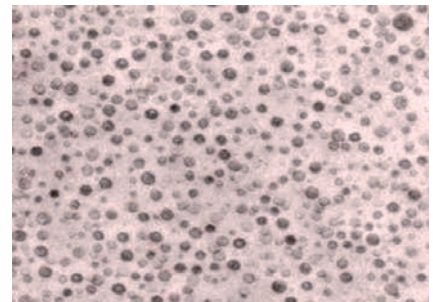


Fig. 3. Agglomerates (left) and homogeneous particle dispersion (right) in the resin: transmission electron micrographs showing dispersion of conventional powders and core-shell particles in the material



Practical Example

A practical example will serve to illustrate this: blends with different contents of core-shell particles were produced from an aromatic bisphenol A epoxy resin (grade: Epikote 828, manufacturer: Resolution) and cured at 120 to 180 $^{\circ}\text{C}$ with diaminodiphenyl sulfone (DDS) in the form of 4 mm-thick sheets.

The problem frequently encountered in incorporating nanoscale particles into reactive resins is agglomeration. This results in undesirable rheological effects and a reduction in the potential of the particles to optimise mechanical properties.

At Wacker Silicones, the nanoscale silicone particles have been modified to permit agglomerate-free, fully homogeneous dispersion of core-shell powders. This has also been assisted by special surface modification of the particles. The company also supplies predispersions of the particles in different epoxy resins as masterbatches under the name Genioperl M. These then only have to be mixed with the remaining formulation, requiring minimal dispersion effort (Figures 3 and 4).

From each of these sheets, three solid tensile test specimens were then cut with a CNC milling machine [3 and 4]. The fracture tests were carried out on an Instron 4456 at a crosshead speed of 1 mm/min. During the test, the crack

length was automatically recorded using new optical measuring technology known as “optical crack testing” (OCT; Fig. 5), which has now become commercially available [5 and 6].

By using OCT in the fracture tests on epoxy resins toughened with the silicone particles described above, it was possible to differentiate sheets with poor particle dispersion from those with good dispersion. In sheets with poor dispersion, there are macroscopically inhomogeneous zones. The crack passes alternately through a zone rich in core-shell parti-

cles, which has higher fracture toughness, and a zone with a significantly lower concentration of particles, which consequently has lower fracture toughness.

Low-temperature DMA (Fig. 6) clearly shows the two separate relaxation peaks of the silicone rubber and the epoxy resin, as would be expected for two-phase mor-



Fig. 5. Reliable determination of fracture toughness by optical crack tracing (photo: Fraunhofer IZM)

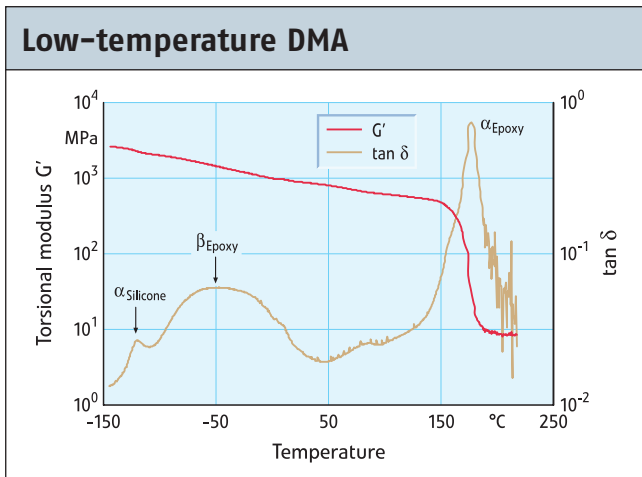


Fig. 6. Two-phase morphology with relaxation peak of silicone rubber below -100 °C (source: Fraunhofer IZM)

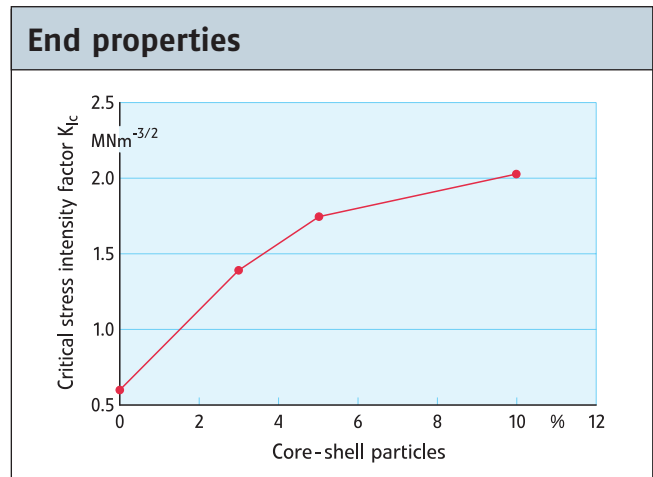


Fig. 7. Fracture toughness of bisphenol A epoxy resins as a function of content of core-shell particles

phology. The tests led to the conclusion that in the case of core-shell particles with a silicone core, a sharp increase in K_{Ic} is recorded, even with low particle content. At the same time, it is known that, in the case of organic rubbers, fracture toughness tends to increase proportionally with content up to 15 % addition. Consequently, with organic rubbers, higher toughening agent content is necessary to achieve corresponding fracture toughness.

With organic rubber toughening agents, many end properties of the thermoset, such as glass transition temperature, water absorption, heat resistance, flame retardancy and electrical/dielectric properties, can be adversely affected. The need to use a high content of organic rubber to achieve a certain increase in fracture toughness has a significant negative effect on the balance of end properties (Fig. 7).

Leadfree Soldering Possible

The new nanoscale silicone elastomer and core-shell particles have already been optimised for use in many different epoxy-based formulations and applications. For example, electrical and elec-

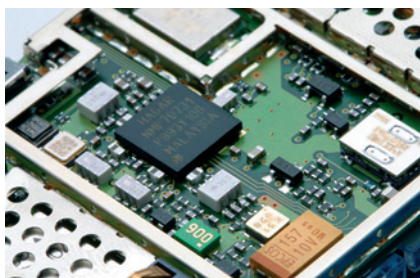


Fig. 8. Inner workings of a cell phone: through the use of nanoscale silicone particles, significant improvements can be obtained in electronic encapsulation materials and adhesives

tronic components cast or encapsulated with silicone-toughened epoxy resin systems have exceptionally high resistance to heat and temperature changes – a requirement specified by many end users for automotive and telecommunications applications

Processing requirements for materials are also continually increasing, which is leading to new materials with improved properties. An example of this is the lead-free soldering process in electronics, which has meant an increase in the temperature stress on the component during soldering from 230 to over 250 °C.

The use of nanoscale silicone particles as a toughening agent now enables components to withstand the stress of lead-free soldering because the particles significantly increase the resistance of resin formulations to so-called “popcorn cracking”. This property also opens up promising applications for core-shell particles in the field of electronic coating materials. These include so-called solder resists or adhesives in the electronics sector (Fig. 8). Toughening with silicone and core-shell particles can also significantly increase the fracture toughness values and heat resistance of potting compounds, which today are used for a whole series of automotive components, including some in the engine compartment.

The unique low-temperature flexibility of silicones, which is due to the low glass transition temperature of silicone elastomers (below -100 °C) is exploited in improvement of epoxy-based structural adhesives. Other target properties, such as resistance to aggressive chemicals, are not adversely affected by the nanoscale silicone particles. On the contrary: in many cases they are even improved.

With the development by Wacker Silicones of new nanoscale silicone and core-shell particles for extremely low-viscosity resin formulations and transparent materials and coatings, the spectrum of possible applications for this highly promising compound class can be substantially broadened in the near future. ■

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