Radiation Curing Enhancement by Semiconducting Nanoparticles

(No. T4-2215)

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Overview

The curing of polymers by UV light is of great technological importance in, for example, dentistry, advanced manufacturing (3D printing), and various applications such as manufacturing of optical media, biotechnology, and more. Generally, photocuring of thermosetting plastics occurs via UV irradiation of the monomeric liquid, which contains also few percents of a photoinitiatior. The photoinitiator absorbs the light and produce radicals, initiatin g thereby the photocurring process. However, radiation curing thermosets are brittle, and the process is limited to low thickness and transparent formulation. Here we provide a new method for thermoset resins curing using semiconducting nanoparticles that would enable stronger polymers with better elasticity, peeling resistance, adhesion and fracture toughness.

The Need

Cationic photo-cured thermosetting polymers, like epoxy resins and also acrylates are characterized by numerous advantages, such as curing on-demand, low viscosity, good surface adhesion to various substrates, high modulus, zero-VOC (Volatile Organic Compounds) and low level of shrinkage. However, it possesses high brittleness and low fracture toughness. WS2 nanoparticles (NPs) with fullerene-like structures and nanotubes were first synthesized in 19921. They were found suitable for improving the mechanical and thermal properties of polymers upon adding a low percentage of the NPs to the nanocomposite material. However, when incorporating additives like opaque WS2, fundamental issues could be encountered, like absorption of the photon radiation, which is essential to initiate the cationic reaction of the epoxy system. Dark fillers, like WS2, are known to have a shadowing (masking) effect and, as a result, reduce the conversion rate and level of conversion in radiation curing of acrylates and epoxies cured by cation polymerization.

The Solution

Prof. Reshef Tenne in collaboration with a team of polymer experts invented a radical curing method for thermoset resins using semiconducting nanoparticles.

Technology Essence

One remarkable property of illuminated semiconductors is that they absorb light at any energy above the bandgap. Being a semiconductor, WS2 NPs, with absorption edge below about 630-660 nm (1.95-1.85 eV)2, exhibit high absorbance in UV/near-visible light. However, in a matter of a femtosecond time interval, the excited electrons thermalize into the conduction band edge, and their oxidation (reduction) power is determined by the bandgap of the semiconductor. This means that, if excited by UV light, low bandgap materials, like WS2 will have oxidative power not larger than their bandgap. Thus, UV irradiation of WS2 nanotubes or fullerenes cannot sensitize the dye molecules directly because their energy gap (2.05 eV= 610 nm) is appreciably lower than the original UV irradiation. However, they can form superoxide (O2.) or OH. radicals, by oxidizing adsorbed moieties with the surface holes in the edge of the conduction band. These OH. radicals can initiate a chain reaction leading to photoinduced polymerization and cross-linking of the resin. Furthermore, the properties of nanocomposites are affected by the NPs' size, shape, and most importantly, the physio-chemical affinity to the polymer matrix. The interface controls the degree of interaction between the particles and the matrix. By reducing the tendency of the NPs to agglomerate; properly dispersing them in the matrix, as well as controlling the interface interaction, an efficient stress transfer from the matrix to the NPs can be achieved, and the load-bearing capacity of the nanocomposite can be largely improved.

Applications and Advantages

Applications

- Reinforcement of radiation curing of acrylates
- Cation-induced polymerization of epoxies for adhesives
- Matrices for fiber composites and resins for additive manufacturing (3D)

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Advantages

- Enhances the mechanical properties (elasticity (Young's module), yield strength and elongation) of thermosetting polymer films
- Increase the polymer film's fracture toughness
- Improves the polymer film's peeling resistance, strength, and adhesion
- Photocuring process acceleration

Development Status

Tenne and his collaborators invented the use of the dispersed tungsten disulfide fullerene-like nanoparticles (WS2-IF) in acrylate and epoxy resins photocuring. They showed that the curing level was enhanced when the nanoparticles were part of the formulation, covalent bonds were formed between the IF-WS2 nanoparticles (and nanotubes thereof) and the cross-linked matrix, and the adhesion strength was increased. Furthermore, the viscosity showed appreciable reduction upon NPs incorporation compared to neat resins. A synergistic effect was obtained in cases where the WS2 NPs were incorporated in the mechanical properties when compared to the pure acrylate and epoxy resins.

Market Opportunity

The curing of polymers by UV light has profound applicable advantages in fiber composites, structural adhesives, and 3D printing resins, making it suitable for 3D printing, dentistry, optical media and biomanufacturing, and the medical market.

References

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Patent Status

PCT Published: Publication Number: WO 2023/218463