

PolyTherm – Polymers for Thermally Demanding Applications Programme: COMET – Competence Centers for Excellent Technologies

Programme line: K-Projects

COMET subproject, duration and type of project:
Cationic curing of epoxy thermosets with tailored properties based on simulation methods, 04/2017-03/2021, strategic project

3D printing of polymeric high- κ dielectrics: Production of moldings with low shrinkage during the printing process

The production of three-dimensional moldings is termed 3D printing. The layer-by-layer structure is generated by computer-controlled processes from liquid materials according to specified shapes. The layers are hardened individually, e.g. by chemical crosslinking. This chemical crosslinking generally results in a volume shrinkage, which leads to geometrical deviations between the printed and the specified form. In a cooperation among the MU Leoben, the TU Graz, the University of Southampton, the Politecnico di Torino and the PCCL, a resin system was developed that exhibits low volume shrinkage and tailored dielectric properties.



High- κ dielectrics

Dielectrics is the collective term for electrically non-conductive or only weakly conductive materials, i.e. for materials in which charge carriers are not or only barely mobile, so that no current can flow through these materials. Because of these properties, dielectrics are used ubiquitously in capacitors, cables, high-frequency devices and high-voltage components.

The trend towards miniaturization, for example in microelectronics, continues unabatedly. The advantages of miniaturization are manifold and range from resource efficiency (less use of material for the production of components) to lowered power consumption in highly integrated circuits and higher switching speeds. However, this miniaturization favors the generation of leakage currents. For this reason, dielectric components with special properties must be used in these components.

The special dielectrics are the so-called high- κ dielectrics, i.e. materials that have a higher dielectric constant than silicon dioxide or silicon nitride. If, for example, such a high- κ material is used as an insulator in a capacitor, its capacitance can be obtained in the course of miniaturization even with higher layer thicknesses of the insulation, while at the same time the leakage currents are drastically reduced.



3D printing of molded specimens from polymer solutions

Among the numerous 3D printing processes, the so-called digital light processing DLP process for the 3D printing of photopolymers, i.e. polymers that undergo chemical reactions under radiation, is particularly suitable.

A height-adjustable platform is placed and illuminated in the resin formulation in a DLP printer; the shaped body is built up layer by layer by the height movement of the platform.

The main advantages of DLP technology are high accuracy and resolution as well as the generation of smooth surfaces. The disadvantage is the volumetric shrinkage, which occurs due to the polymerization and crosslinking reactions of the liquid resin.

Resin mixtures based on expansion polymers

In the strategic project of the K-Project PolyTherm, spiroorthoester monomers were used in resin formulations. These are monomers that can undergo ring-opening during the crosslinking reaction. Since this ring-opening induces volumetric expansion, the volume shrinkage during the chemical crosslinking reaction thus can be compensated for. This spiroorthoester was 3D printed together with an ethylene glycol vinyl ether (Figure 1). While the shrinkage was reduced by 2 percentage points, the dielectric constant rose to values of up to 100 at frequencies of 50 Hz.



Figure 1: 3D printing of photopolymers.

Results and effects

Resins that show shrinkage during the hardening reaction often tend to crack and detach from the surfaces (so-called delamination). Since this material damage significantly reduces the insulation effect, the volume shrinkage must be assessed particularly critically. If such dielectrics are used as resin for insulation against current flow, the targeted protective effect of the resin is no longer guaranteed without restriction, which can lead to component failure.

The curing reaction of the resin mixture developed in the K-Project PolyTherm was set up such that it can be carried out either by heating the resin mixture or by irradiating the resin mixture. If UV light is selected as the trigger for the curing reaction, the 3D printing of the resin mixtures shown here is possible as well.

The 3D-printed resins show high dielectric numbers of up to 100 (for comparison: from a dielectric number greater than 3.9, the reference value of silicon dioxide, materials are referred to as high-κ materials). Despite this high dielectric constant, these materials exhibit conductivities as low as 10⁻¹¹ S/cm.

In a cooperation among the MU Leoben, the Graz University of Technology, the University of Southampton, the Politecnico di Torino and the PCCL, a resin system was developed in the K-Project PolyTherm, from which three-dimensional electronic materials of the next generation can be printed using digital light processing techniques.

Contact and information

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