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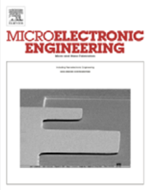

Polymerization conditions influence on the thermomechanical and dielectric properties of unsaturated polyester–styrene-copolymers

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ABSTRACT

The influence of different polymerization conditions like curing agent (MEKP) amount and styrene content on the glass transition temperature, the relative dielectric constant as well as loss factors of unsaturated polyester–styrene-polymer systems after solidification was investigated in depth. With respect to a high average molecular mass and Vickers hardness a curing agent content of 3 wt% is recommendable. Increasing MEKP-concentrations cause a slight elevation of the polymers relative dielectric constant as well as of the loss factor. Regarding an easy film formation using tape casting a.o. higher styrene amounts lower the viscosity of the resin significantly, the relative dielectric constant and the loss factor decrease also. As an average value a relative dielectric constant of 3 under ambient conditions can be obtained.

1. Introduction

Polymer based reactive resins containing acrylates, epoxides, or unsaturated polyester moieties gain more and more importance for modern applications exploiting active or passive photonic as well as electronic properties [1–3]. In the last years huge research efforts have been made focussing on the realization of embedded capacitors consisting of different polymers filled with inorganic dielectrics thus following the tendency for an enhanced integration of resistors and capacitors from the surface (surface mounted devices, SMD) into the printed circuit board (PCB) [4–9].

In most of the cases micro- or nanosized $BaTiO_3$ and related perowskite type ceramics were used as high-*k*-material, dispersed in a polymer matrix [5–13]. Other ceramics like CdO and TiO_2 are suggested as promising candidates applied in polymer–ceramic-composites [14,15]. Core–shell-fillers like Al_2O_3 covered Al, dispersed in an epoxy resin, enable the realization of new complex composites containing metal particles [16]. Typical polymer matrix materials are curable resins like epoxides [6,7,9,11,12,16], acrylates [14], styrene–ethylene–butylene block-copolymers [15,17], polyimides [10,18] or polymer blends consisting of polyamides and bismaleimides [5,8]. Besides an enhanced thermal stability, a higher dielectric constant and a good wetting behaviour of the inorganic filler are aspired polymer matrix properties [4].

In addition to the high dielectric constant and the low dissipation or loss factor the resulting composite's thermomechanical and flow properties must be compatible with the standard process technology for PCBs. Especially the film formation using screen printing, tape casting or, may be in the near future, inkjet techniques play a major role for low cost fabrication [4]. Hence the composite flow behaviour is a key factor for successful film or laminate formation [4,5].

In this paper the influence of different polymerization parameters like curing agent (peroxide) concentration, polymerization temperature and postcure as well as dilution with vinyl monomer (styrene as reactive thinner) on the physical properties and the polymerization behaviour of an unsaturated polyester–styrene-system will be investigated intensely. The used commercial unsaturated-polyester-resin possesses, in contrast to customary unsaturated polyesters, thermoplastic properties after thermal or photochemical curing showing a reversible glass transition around 80–90 °C. These properties have been exploited earlier for the establishment of a micro reaction molding technique for the realization of microstructured polymer, ceramic or metal parts [19,20]. Thermogravimetric investigations of the solidified unsaturated polyester–alumina-composites showed no weight loss up to a temperature of 280 °C [19]. In addition the unsaturated polyester resin was used for the realization of highly transparent solid microoptical components like prisms a.o. [21]. With respect to the realization of highly filled polymer composites a main investigation emphasis was put on the flow behaviour of different unsaturated polyester–styrene mixtures, filled with ceramic or metal fillers [22–24].

The sensitivity of a liquid's viscosity to temperature changes can be described using the Andrade–Eyring Eq. (1), η_1 and η_2 are the apparent viscosities at the two different temperatures T_1 and T_2, R is the gas constant and ΔE_a is the flow activation energy, which depends mainly on the composition of the investigated

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system [25,26]. Large ΔE_a values correspond with an improved sensitivity of the viscosity to temperature changes:

$$\text{Andrade–Eyring} \quad ln\frac{\eta_1(T_1)}{\eta_1(T_2)} = \frac{\Delta E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{1}$$

2. Experimental

A commercially available unsaturated polyester–styrene resin (polymer content: 65 wt%, styrene: 35 wt%, cobalt-pretreated, Carl Roth GmbH + Co. KG, Germany) was used as master solution, other dilutions were prepared by adding styrene. The vendor does not supply any detailed information about the chemical composition of the resin, earlier size exclusion chromatography experiments yielded an average molecular mass around 1700 g/mol of the non-polymerized resin as delivered [27]. After solidification the solid polymer possesses a glass transition temperature around 80 °C, and a good solubility in acetone [28].

The unsaturated polyester–styrene mixtures were polymerized using different amounts of the cold hardener curing agent methylethylketon peroxide (MEKP, supported by the vendor: composition: 25–35 wt% MEKP, 12.5–15 wt% 4-hydroxy-4-methyl-pentan-2-on, 3–5 wt% Butanon, 3–5 wt% H_2O_2 [28]). The samples were mixed under ambient conditions and cured at 50 °C, for comparison some samples were postcured at 120 °C. The vendor suggests a curing temperature between 20 and 60 °C and an optional postcure at 60 °C for at least 2 h [28]. To obtain homogenous and plane parallel test specimen the mixtures were poured into silicone elastomer-based molds (diameter: 58 mm, thickness: 3 mm) and solidified at elevated temperatures.

The average molecular mass and the molecular mass distribution were measured using a size exclusion chromatography setup (ThermoFinnigan AS 100 vial sampler and ThermoFinnigan P100 pumping unit) with tetrahydrofurane (THF) as solvent, which dissolves the cured solid polymer. The chromatography columns (precolumn plus 4 columns 300 × 8 mm: 1 × 10E4Å 5 μm, 1 × 10E3Å 5 μm, 2 × 100Å 5 μm) were fixed to a constant temperature of 25 °C. Output signals were detected with a Showa Denko K.K. RI 71 infrared refractive index analyser. The densities of the solid polymer specimen were determined via the Archimedes method in deionised water. The glass transition and decomposition temperatures were measured using a Mettler-Toledo FP900 equipped with a FP85 DTA cell using large aluminum crucibles (160 μl volume, heating rate 10 °C/min, standard air atmosphere). The accuracy of the measured temperatures is around ±2.5 °C. The Vickers hardness was measured using a Paar Physica MHT-10 microhardness tester under ambient conditions. All dielectric measurements were performed applying an Agilent/HP4149A impedance analyzer in combination with an Agilent 16451B sample holder. The temperature dependent dielectric measurements were performed using an Espec SH261 temperature chamber in the range of −60 up to +70 °C. All viscosity measurements were performed at three different temperatures (20, 40, 60 °C) in the shear rate range between 1 and 100 1/s using a cone and plate rheometer (CVO50, Bohlin) using a semi-closed measuring chamber avoiding styrene evaporation. The experimental uncertainty of the obtained viscosity data is in the range of ±5%.

3. Results and discussion

3.1. Influence of the initiator amount on the curing behaviour

Fig. 1 shows for the different MEKP concentrations the increase of the resin's viscosity (resin composition: 65 wt% polymer, 35 wt% styrene) with time as a measure for the polymerization reaction progress. The measuring temperature was 25 °C, the investigated shear rate 100 1/s. With respect to avoid damage at the rheometer measuring system the measurement was interrupted when the viscosity values exceeded 10 Pa s. Very small initiator amounts (0.6 wt%) cause a long inhibition time more than one hour prior to a remarkable viscosity rise. Higher MEKP amounts cause a slight initial viscosity drop due the very low MEKP viscosity and, more remarkably, a pronounced reduction of the inhibition time. With respect to applications a compromise between rapid curing and stable composite processing, e.g. screen printing, has to be found, here a MEKP amount around 3 wt% seems to be applicable.

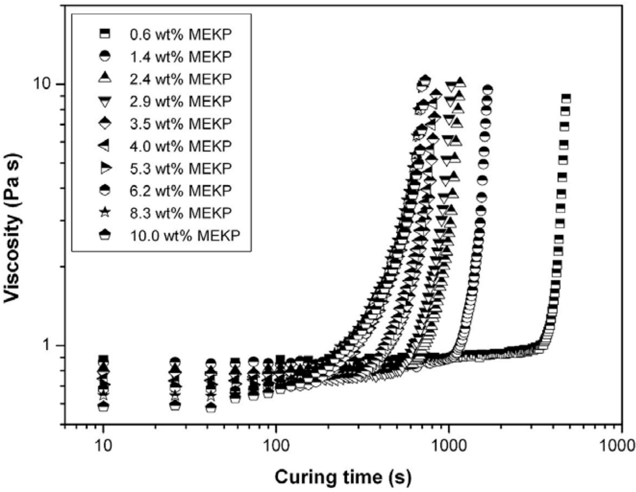

Fig. 1. Time dependent resin (65 wt% polymer, 35 wt% styrene) viscosity increase for the different MEKP concentrations (temperature 25 °C, shear rate 100 1/s).

3.2. Influence of the initiator amount on the thermomechanical properties

Fig. 2 shows the dependence of the polymer's average molecular mass on the initial MEKP amount investigating a composition containing 48 wt% styrene. Largest M_W-values between 6300 and 7300 g/mol can be achieved using a MEKP amount between 1.5 and 3.5 wt%. The resin vendor suggests a MEKP concentration of 3 wt%. Despite the vendors recommendation of a postcure at elevated temperatures only a negligible rise of the average molecular weight M_W can be found experimentally (postcure temperature: 120 °C). Larger MEKP-concentrations (10 wt%) result in a pronounced M_W-reduction down to a M_W-value of 3000 g/mol, which

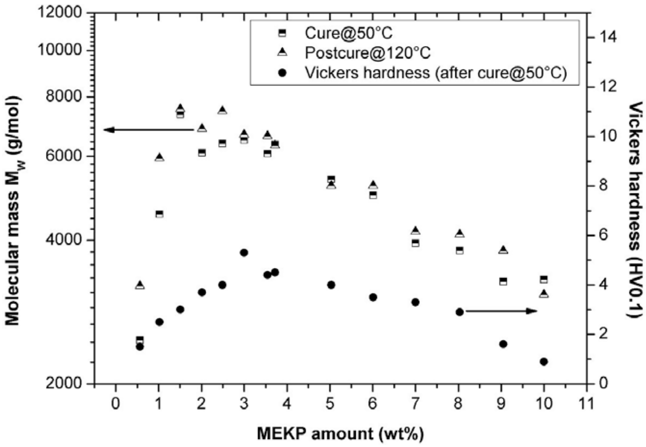

Fig. 2. Change of the average molecular mass M_W and Vickers hardness with MEKP amount (mixture with 48 wt% styrene).