Investigations of the Morphology of Various Epoxy-based Nanocomposites

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Abstract—Goal of present paper is to assess the applicability of common interphase models on thermoset polymers like epoxy resin. Abstract theoretical constructs like the multi-core-model, the interphase volume model or the interphase power law are examined in order to determine their physical applicability. Samples used were bisphenol-A type epoxy resin with anhydrite hardener and AlN, Al₂O₃, MgO and SiO₂ filler of nanometric dimensions. The samples have previously been examined in terms of their dielectric and thermal properties. Now thermogravimetric analysis and differential scanning calorimetry is utilized in order to assess the structural changes of the polymer. The composites showed consistently higher char content than the base resin would suggest. This additional char could be interpreted as rigid polymer layer that adheres to the particle surfaces, however, differential scanning calorimetry does not support this theory. Primarily, MgO filled samples showed distinct behavior, with significantly reduced T_G, as well as a narrower peak than all other investigated materials.

Keywords—polymer; epoxy resin; composite materials; TGA; DSC; interphase; nanocomposite; nanodielectric

I. INTRODUCTION

Ever since the first materials now known as nanodielectrics showed material properties that were outside the range of expectations, hypothesis about the root of these properties were devised [1]. Nanodielectrics are more than just the sum of their parts and it was quite quickly assumed, that the individual particles may impact the polymer within a certain sphere of influence [2]. This volume was termed as interphase, and must not be mistaken with the interface between particle and host. There are a number of different models based on the concept of an interphase. Among them are the multi-core model, the interphase volume model, the interphase power law or the polymer chain alignment model [3-6]. Some of the models assume a random dispersion of particles, others suggest a periodic lattice to simplify the mathematics. The existence of a distinct polymer phase at the interface between polymer and filler particles has long been suggested for various types of rubber [7]. However, for polymers like epoxy resin (ER) or polystyrene the interphase is still elusive.

For thermosets like ER, much information can be derived from investigating the glass transition temperature. The glass transition temperature T_G, which resembles a peak, is sensitive to various changes to stoichiometry, curing temperature and, of

course, filler materials. When the epoxy structure changes, either the T_G peak is expected to shift or the width of the glass transition changes. It is well known, that polymers can exhibit multiple glass transition peaks, which correspond to different polymer phases [8].

II. EXPERIMENTAL

A. Materials

The materials investigated here are all based on the same bisphenol-A type ER CY231 provided by Huntsman, cured with anhydrite hardener HY925, also by Huntsman. The used filler materials are aluminium oxide (Al₂O₃) and aluminium nitride (AlN) supplied by Sigma Aldrich, as well as magnesium oxide (MgO) supplied by Strem Chemicals. For these fillers the silane coupling agent (SCA) γ -glycidoxypolytrimethoxysilane was used, provided by Sigma Aldrich. Silicon dioxide (SiO₂) used in this study was used in form of NanopoxTM provided by Nanoresins. Unlike the other fillers that were obtained as dry powders, SiO₂ was created by a sol-gel process. Due to residues of this process, the complex permittivity differs significantly from samples with dry powders [9]. Average particle sizes were derived by TEM in previous work and are 60 nm for AlN, 50 nm for Al₂O₃, 22 nm for MgO and 20 nm for SiO₂ [9].

Samples were characterized in terms of dielectric and thermal properties in previous work [10, 11] and prepared as follows: particles were first dispersed and modified in an ethanol solution. Subsequently they were mixed with constituent amounts of resin and hardener, while being subjected to conventional mixing in combination with ultrasonication to help disperse the particles. Samples were cured for 4 h at 140 °C in aluminium molds, treated by a commercially available silicon-based release agent.

B. Characterization techniques

A Perkin Elmer Pyris 1 was used to determine the actual filler content, respectively the residual char of the polymer plus the filler, via thermogravimetric analysis (TGA). Samples of 5 to 7 mg mass were heated in a disposable aluminium pan between 50 °C and 650 °C at a rate of 10 °C/min under oxidizing conditions. One reference epoxy sample was heated in a platinum pan until 950 °C at the same heating rate, in order to assess if additional information can be gathered in the range of 650 °C to 950 °C. The change of mass in this regime was

negligible, hence it was concluded that most of the polymer would incinerate below 650 °C. However, from literature it was known that a residual char between 4 and 10 % of mass could be expected for epoxy resins [12]. Hence the resulting mass needed to be compensated for this char content, in order to derive the precise amount of nanofiller in the investigated samples.

In order to determine the T_G , differential scanning calorimetry (DSC) was used. The instrument in question is a Perkin Elmer DSC 7, where samples with a mass of 10 mg were placed in an aluminium pan under nitrogen atmosphere. Heating rate was 10 °C/min, same as for the TGA, and resulting data was analyzed with Pyris software provided by the manufacturer.

III. RESULTS

A. TGA

A comparison for typical TGA traces for neat ER, compared to Al_2O_3 and MgO filled composites is shown in Fig. 1. Most investigated composites show three distinct areas. There is relatively little mass loss until about 300 °C. The mass loss in this area can be attributed to moisture and varies for different composites, averaging at 2.5 %. No obvious correlation between mass loss below 300 °C and the fillgrade or filler type could be established. It is assumed that variations of the ambient humidity on the day of the measurement has more impact on this value than the sample structure or filler content.

The second region of interest is between 300 and 600 °C. Here most of the polymer decomposes, with primary decomposition occurring between 350 and 500 °C. There seems to be not much change or improvement of the onset temperature for decomposition. In fact, for a number of composites this temperature tends to be lower than for neat ER samples. Table I shows the actual weight of the particles and the deviation from the nominal fillgrade. The residual char for epoxy was 5 % of mass, taken as average from five samples. Samples with 10 % of MgO show quite distinct behavior above 400 °C, as shown in Fig. 2. This delay in mass loss cannot be observed for samples below 10 % nominal fillgrade.

Above 600 °C a minor decrease of weight can be measured, but the weight generally stabilizes at 650 °C.

B. DSC

Fig. 3 shows the compiled data for the T_G peaks as a function of fillgrade. Values for AlN have been presented earlier [13], but are included for convenience. In order to prevent influence from incomplete cure, as established in [13], samples were post-cured for 24 h at 120 °C. The width of the glass transitions is shown in Table II for samples with comparable actual fillgrade. It is apparent that most of the composites have comparable glass transitions to the neat epoxy, with the exception of MgO. After post-curing no indication for secondary peaks could be found in any of the samples. It is noticeable that T_G for MgO filled samples is markedly lower than for the rest. Combined with the peculiar behavior of the 10 wt% MgO-ER composite in terms of TGA.

Fig. 1. TGA between 100 and 650 °C for neat ER and composites with a nominal filler loading of 5 wt% of nanoscale Al_2O_3 and MgO.

Fig. 2. TGA between 300 and 650 °C for MgO-ER composite with nominal filler loading of 10 wt.% compared to unfilled ER, noticeable that the composite reaches a steady state later than other composites.

Fig. 3. Glass transition peaks for various fillgrades (vol %) and different filler types. Noticeable the significantly lower T_G for MgO composites. AlN data taken from [13].

TABLE I. SAMPLE FILLGRADES DERIVED FROM TGA.

Filler type	Nominal particle weight %	Derived particle weight %	Deviation in %
Neat ER	Reference	Reference	Reference
AlN	0.5	2.64	2.14
AlN	2	5.69	3.69
AlN	5	8.55	3.55
AlN	10	11.91	1.91
Al ₂ O ₃	0.5	0.56	0.06
Al ₂ O ₃	2	3.38	1.38
Al ₂ O ₃	5	10.9	5.9
Al ₂ O ₃	10	6.22	3.78
MgO	0.5	5.4	4.9
MgO	2	6.1	4.1
MgO	5	10.93	5.93
MgO	10	14.13	4.13
SiO ₂	0.5	2.15	1.65
SiO ₂	2	2.58	0.58
SiO ₂	5	5.7	0.7
SiO ₂	10	11.1	1.1

IV. DISCUSSION

While there is an indication for distinct interphase volumes in various types of rubber filled with carbon black [14], previous work casts doubt if ER has distinct interphase volumes. These volumes are commonly used for explanation if values for the complex permittivity fall outside the Wiener bounds [15]. The reasoning is that polymer chains near the particle surfaces are restricted in their mobility, thus resulting in much lower effective permittivity than the rest of the polymer. Approaches were made both with random particle dispersion and with periodic lattice models [15, 16]. From a mathematical standpoint the only real difference between these two approaches is the linearity, or lack thereof, in areas I and IV, as indicated in Fig. 4. Periodic lattice models are dominated by linear increase of the interphase in area I and a linear decrease in area IV. Transitional areas II and III account for a narrow band in between, where the interphases of neighboring particles start touching, until the material consists solely of interphase in area IV. Models based on random agglomerations tend to have less linear regions I and IV, but the overall behavior with a distinct maximum of the available interphase does not change.

Fig. 5 shows the change of the real part of the permittivity as a function of fillgrade. It is apparent that the minimum of permittivity is at much lower fillgrades than interphase volume models usually would suggest. The minimum for the real permittivity seems to be between 1.2 and 2.3 vol.% for all investigated filler types. Interphase volume models would suggest that such a minimum would be found for interphase volumes above 10%, considering the average size of particles discussed here. This could be explained by a relatively large extent of the interphase layer, exceeding 20 nm. However, neither the position of the T_G peak (see Fig. 3), nor the width of the glass transition (Table II) change significantly for most of the investigated samples. If the interphase would be so distinct from the neat polymer, there should be a discernible difference in terms of T_G and/or width of the glass transition.

Fig. 4. Illustration of the total interphase volume as function of filler volume, and thus the general areas defined by interphase volume models [13].

Fig. 5. The real part of the complex permittivity for various nanofillers as a function of filler volume, data from [9, 10], adjusted by actual filler content derived via TGA.

TABLE II. WIDTH OF THE GLASS TRANSITION AS DERIVED FROM DSC.

Sample	Fillgrade in wt.% (actual)	Average particle size	Glass trans. width
Neat ER	Reference	-	9.8 °C
SiO ₂ 2%	2.58	20	8.54 °C
MgO 0.5%	5.4	22	7.5 °C
Al ₂ O ₃ 2%	3.38	50	9.37 °C
AlN 0.5 %	2.64	60	9.6 °C

The only filler type not following the trend is MgO. Magnesium oxide seems to cause the largest alterations to the polymer matrix. In MgO filled samples, a significant reduction of the T_G can be observed for all fillgrades, as well as a more narrow range of the glass transition itself. MgO samples also exhibit the strongest reduction of the real part of the complex permittivity across the entire range measured here. Since the residual char of MgO was significantly higher than for all other particle types, it was suggested that the additional weight might be due to additional bound polymer on the particle surfaces, which like the residual char of regular ER is more resistant to heat. Raman spectroscopy was utilized in order to investigate the

Fig. 6. Illustration of the effect small particles can have on a polymer being subjected to combustion, from left to right: composite prior to combustion, 30% of polymer consumed, 50% of polymer consumed.

char residue, but results were inconclusive, since the inorganic filler overshadows any carbon-based signals. It has been reported that nanoparticles can improve thermal stability and flame retardant properties with filler content as little as 5% by weight [17]. This was attributed to the high specific surface area and it is feasible that the MgO-ER samples show a similar resistance to combustion, as illustrated in Fig. 6. The non-combustible particles can form a protective layer, hindering consumption of the polymer, compared to unfilled epoxy or polymer with a higher concentration of embedded particles. The investigation of the MgO-ER residues is subject of future work.

V. CONCLUSIONS

A number of nanocomposites with different filler types have been investigated with thermogravimetric analysis and differential scanning calorimetry and earlier work re-evaluated in light of new data. TGA was used in order to determine the actual fillgrade of the composites, which was generally higher than the nominal fillgrade used for original analysis. With the adjusted weight- and resulting volume percentages, it could be observed that the minimum for the permittivity tends to be between 1.2 and 2.3 vol.%. TGA also showed a delayed weight loss at higher temperatures for MgO samples with more than 10wt.% of filler, the cause of which needs further examination, since Raman spectroscopy was inconclusive.

The glass transition peaks and the temperature range of the glass transition were investigated with DSC. For most investigated samples, no significant change in the glass transition could be observed. The peaks shift slightly but no pattern emerged, while the width of the glass transition was consistent for non-MgO-filled samples. Again, MgO shows distinct behavior, having a significantly reduced T_G and a narrower peak. Further work is necessary to fully understand the cause of these differences.

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