Complex specific heat capacity of two nanocomposite systems

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Abstract

Thermal investigations on two selected model-nanocomposites have been made. They differ with regard to the type of the anorganic nanoparticles that have been filled into an organic oligomer matrix. The properties of nanocomposites may vary between those of a simple mixture of independent components and those of a system, where specific interfacial interactions between the constituting parts lead to 'new' properties. Depending on the type of the nanoparticles filled into the matrix, the resulting properties might be closer to one or to the other extreme. We used temperature modulated differential scanning calorimetry (TMDSC) to investigate a matrix of the oligomer diglycidyl ether of bisphenol A (DGEBA) filled either with SiO_2- or Al_2O_3-nanoparticles. The dependence of the complex specific heat capacity (c'_p) on the concentration of nanoparticles shows a clear difference between the two systems as far as the glass transition of the oligomer is concerned. The SiO_2 composite seems to behave more like a simple mixture, whereas the Al_2O_3 composite shows 'new' properties.
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1. Introduction

Nanocomposites play an increasing role as tailor-made materials for sophisticated technical applications. In that field high performance adhesives [1–3] often based on epoxies represent an important domain. It seems that the technical evolution of nanocomposites progresses much faster than the physical understanding of the interaction mechanism at the interface between nanoparticles and matrix on one hand, and the consequences for their global physical and chemical properties on the other.

It is this situation, which encourages activities leading to a better understanding of the physical properties of selected model-nanocomposites like diglycidyl ether of bisphenol A (DGEBA) filled with Al_2O_3- or SiO_2-nanoparticles.

It is worth noting that the outstanding physical properties of nanocomposites result from the chemical or physical pro-

cesses taking place at the interfaces between the nanoparticles and the surrounding matrix. Consequently, (i) the nature of specific molecular interactions between the nanoparticles and the matrix molecules, (ii) the concentration and (iii) the diameter of the nanoparticles play a pertinent role. As far as molecular interactions at the interfaces are concerned we can distinguish two scenarios:

(1) The matrix molecules at the surface of the nanoparticles undergo specific tight bindings (chemisorption and physisorption) so that the hydrodynamic radius of the nanoparticles is affected.
(2) The interfacial interactions have no influence on the hydrodynamic radius of the nanoparticles. Then, however, there remains the effect of excluded volume by the nanoparticles and its influence on thermodynamic and hydrodynamic properties of the nanocomposite.

Taking into account that the interactions in question may depend strongly on temperature, the latter may play a crucial role for global physical properties.

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Preliminary investigations (infrared spectroscopy) seem to show that the DGEBA-x% Al$_2$O$_3$ system (x%: mass percent) belongs to class (1), whereas the DGEBA-x% SiO$_2$ system belongs to class (2) of nanocomposites. The aim of the current paper is to show the impact of these two very different interaction scenarios on the specific heat capacity and in turn to show what specific heat capacity measurements can teach us about the interaction mechanism in nanocomposites.

2. Experimental

2.1. The oligomer matrix

The basic material for our nanocomposites is diglycidyl ether of bisphenol A of commercial grade (DER 331 from DOW Plastics). Fig. 1 shows the structural formula of the oligomer. The molar mass is 340 g/mol. The melting point of DGEBA is at 315 K [4] but the tendency to crystallize is low and the material easily can be undercooled. The glass transition temperature appears at 257 K. At ambient temperature the viscosity of DGEBA is rather small, and therefore the oligomer can easily be filled with nanoparticles.

2.2. The nanoparticles

The primary Al$_2$O$_3$-nanoparticles have a mean diameter of 13 nm and a specific surface of 100 m^2/g. Manufacturing of the particles, however, yields two kinds of clusters known as aggregates and conglomerates. Whereas the primary particles within the aggregates are interconnected by so-called agglomeration necks (chemical bonds), the conglomerates are held together by van der Waals interactions [5]. In order to reduce the size of the clusters and to get a homogeneous distribution, the Al$_2$O$_3$-nanoparticles have been mechanically dispersed into the DGEBA melt using a dissolver, a pearl mill and ultrasound. TEM pictures confirm an almost homogeneous distribution of nanoparticles of a mean diameter of 35 nm dispersing destroys conglomerates, whereas aggregates remain intact.

The SiO$_2$-nanocomposites were received from Hanse Chemie (Geesthacht, Germany). The nanoparticles had directly been synthesized within the DGEBA matrix. TEM pictures show a homogeneous distribution of SiO$_2$-nanoparticles with a mean diameter of about 15 nm.

2.3. Instrumental

Specific heat capacities were measured using temperature modulated differential scanning calorimetry (TMDSC) performed on a highly modified Mettler Toledo DSC 821^e instru-
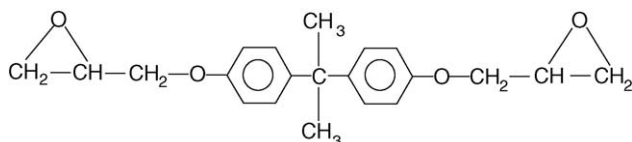
ment adapted to a temperature range extending from 20 to 600 K [6,7]. According to Schawe [8], controlling the oven by the temperature program $T = T_0 + \beta t + A_{TB} \sin \omega t$ yields an heat flow HF$[T(t)] = c_\beta(T)\beta + A_{HF} \cos(\omega t - \varphi)$ between sample and reference: the first term is the contribution to HF depending on the mean heating rate β and the second term is representing the system response to the periodic perturbation. Real and imaginary parts of the complex specific heat capacity are calculated from the amplitude $A_{HF} = \omega A_{TB}|c(T, \omega)|$, that is proportional to the module of specific heat capacity, and the phase shift φ between HF and instantaneous heating rate:

- the real part $c'(T, \omega) = |c(T, \omega)| \cos\varphi$ is the so-called specific storage heat capacity describing the periodic heat transfer between sample and environment;
- the imaginary part $c''(T, \omega) = |c(T, \omega)| \sin\varphi$ is known as specific loss heat capacity that takes entropy production by irreversible, dissipative processes into account.

The measurements on the SiO$_2$ systems have been performed upon heating (0.3 K/min) with a modulation period of 120 s. In case of the Al$_2$O$_3$ system, we used a cooling rate of -0.3 K/min and a modulation period of 90 s. In between the two measurement series, the sensor plate had to be changed, and the system was completely re-calibrated. Further measurements of the two model systems with identical parameters are on the way. The error bars in Figs. 5–7 were obtained by repeating measurements for the DGEBA-10% Al$_2$O$_3$ system with different sample masses and different cooling and heating rates.

3. Results and discussion

We have studied the complex specific heat capacity for our two model systems as a function of temperature as well as of the mass concentration x of the nanoparticles.

Already during sample preparation it was obvious that the viscosity of the DGEBA-x% Al$_2$O$_3$ system depends significantly stronger on the concentration of the nanoparticles, than it is the case for the DGEBA-x% SiO$_2$ system. Whether these transport properties have any impact on the thermodynamic properties of the nanocomposites of interest will be discussed in the following.

Fig. 2a and b show the specific storage capacities c'_p of DGEBA-x% Al$_2$O$_3$ and DGEBA-x% SiO$_2$ as a function of temperature T for various mass concentrations x of nanoparticles. In the case of DGEBA-x% Al$_2$O$_3$ we observe a continuous shift of the c'_p values with increasing filler content in the glassy and liquid states. This does not hold for the DGEBA-x% SiO$_2$ system. We expect that the scatter of the c'_p values exhibited by the DGEBA-x% SiO$_2$ samples is due to experimental uncertainties. Independently of the chemical composition (Al$_2$O$_3$ and SiO$_2$) and concentration x of nanoparticles the c'_p-curves display a unique glass transition, evidenced by the jump in $c'_p(T)$. At least in the investigated temperature regime no further thermal anomalies exist. As is well known [e.g. 9] the c'_p-jump is indicative for the so-called α-relaxation, which in turn is believed to be responsible for the dynamic glass transition [9].
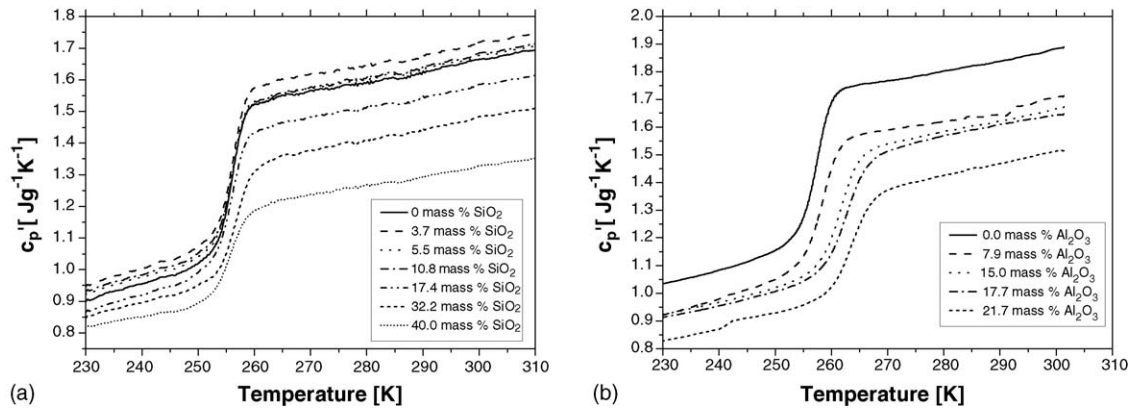

Fig. 1. Structural formula of DGEBA.

Fig. 2. Specific storage heat capacity of (a) DGEBA-x% SiO$_2$ and (b) DGEBA-x% Al$_2$O$_3$ as a function of temperature.

As usual, the 'dynamic glass transition temperatures' T_{Gdyn} correspond to the inflection points of the $c'_p(T)$-curves. Taking into account that neither SiO$_2$ nor Al$_2$O$_3$ is expected to show a phase transition or a glass transition in the temperature regime of interest, we conclude that both nanocomposites behave from the thermodynamic point of view apparently as 'homogeneous glass-forming liquids'. The most prominent feature of the Fig. 2a and b is the different glass transition behaviour displayed, whereas the Al$_2$O$_3$ system shows a significant shift of T_{Gdyn} with mass concentration, T_{Gdyn} of the SiO$_2$ system is almost unaffected by the amount of nanoparticles.

Although the c'_p data for the SiO$_2$ composites depend on the mass concentration x of the nanoparticles, T_{Gdyn} remains unchanged with changing x. As expected, this interpretation is supported by the temperature dependence of the imaginary part of specific heat capacity c''_p (Fig. 3a). The so-called loss curves of SiO$_2$ remain almost centred at $T_{Gdyn} = 256$ K. It is clear-cut that $c''_p(T)$ reflects the dynamics of DGEBA molecules. Thus, this quantity is purely related to the partial phase of DGEBA and an eventual influence of the interfaces of the nanoparticles on the DGEBA molecules. As a matter of fact even the magnitudes of the loss peaks are almost identical. In the case of the Al$_2$O$_3$ composites (Fig. 3b) the shift of T_{Gdyn} to higher temperatures with increasing concentration of the nanoparticles is also supported by the imaginary part c''_p.

The related dynamic glass transition temperatures T_{Gdyn} (evaluated from the position of the peak maximum of c''_p) are shown in Fig. 4. Within the margin of error T_{Gdyn} of the SiO$_2$ composites shows no concentration dependence at all, even though for the highest concentration of $x = 40$%, the peak value of the loss peak is reduced in comparison to those of lower concentrations (Fig. 3a).

This result and the fact that the integrated surface of the loss peaks is independent of the concentration x (Fig. 5) indicate that there are almost no specific interactions between the SiO$_2$-nanoparticles and the DGEBA molecules. The SiO$_2$-nanoparticles just occupy volume and create a large amount of internal surfaces within the DGEBA melt. However, the DGEBA molecules at the interfaces of the SiO$_2$-nanoparticles are expected to be more mobile than the bulk molecules because at these interfaces the constraints due to the mean field of the environment seem to be reduced. Consequently, the size of the nanoparticles and their concentration should influence the average mobility of the DGEBA molecules and in turn the bulk viscosity. In other words, assuming that the DGEBA molecules at the SiO$_2$/DGEBA interfaces are more mobile then in the DGEBA bulk, these interface molecules are expected to decrease the overall viscosity. As a result, in the case of the DGEBA-x% SiO$_2$ system the increase of volume viscosity due to the increasing concentration of nanoparticles is partially compensated by
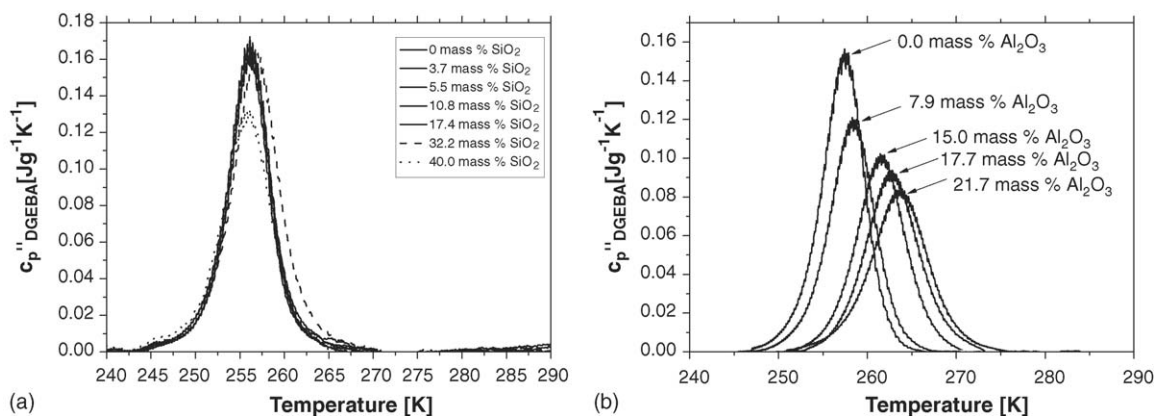

Fig. 3. Specific loss heat capacity of (a) DGEBA-x% SiO$_2$ and (b) DGEBA-x% Al$_2$O$_3$ as a function of temperature. Index DGEBA indicates that the presented c''_p values are related to the respective DGEBA mass contents in the samples.
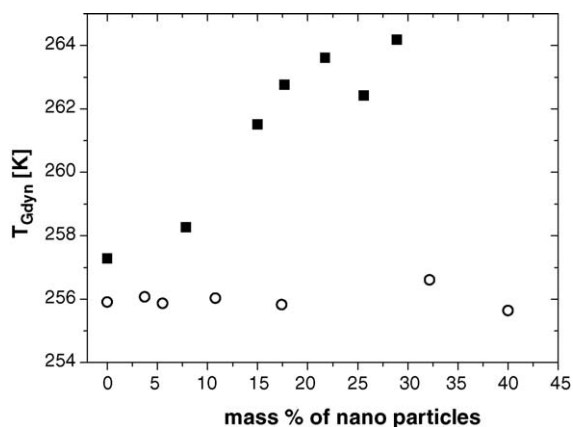
Fig. 4. Dynamic glass transition temperature T_{Gdyn} as a function of mass percentage of nanoparticles. Squares, Al_2O_3; circles, SiO_2.
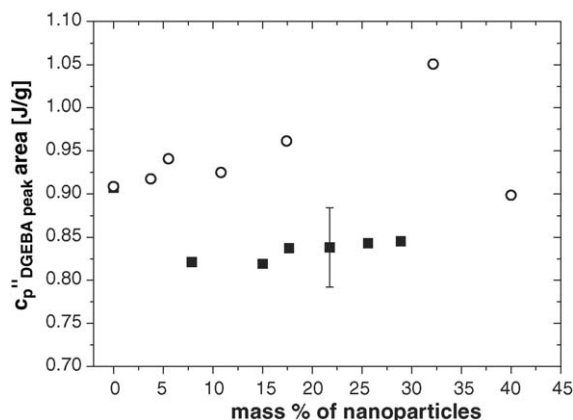

Fig. 6. Linewidth (FWHM) of c_p'' maximum as a function of mass percentage of nanoparticles. Squares, Al_2O_3; circles, SiO_2 (dashed line is just a guidance to the eye).

Fig. 5. Integrated surface of the loss peak as a function of mass percentage of nanoparticles. Squares, Al_2O_3; circles: SiO_2.

the accompanying interface viscosity, which is assumed to be smaller than that of the bulk.

Completely different interaction mechanisms seem to act in the model system DGEBA-x% Al_2O_3. Whereas the apparent fluidity of DGEBA-x% SiO_2 does almost not depend on the concentration x, the viscosity of DGEBA-x% Al_2O_3 increases drastically with increasing concentration of the Al_2O_3-nanoparticles. As a consequence, the dynamic glass transition temperature T_{Gdyn} increases with increasing concentration of nanoparticles (Figs. 2b, 3b and 4). These results indicate the existence of completely different interaction mechanisms at the interfaces between the Al_2O_3-nanoparticles and the DGEBA matrix in the sense that DGEBA molecules undergo at least temporary specific bindings with the surface molecules of the Al_2O_3-nanoparticles. We believe therefore that the hydrodynamic radius of the Al_2O_3 particles is increased as soon these particles are surrounded by the DGEBA matrix.

As a consequence, part of the conformational changes in the DGEBA molecules are hindered which leads to a higher viscosity and to a higher glass transition temperature.

The appearance of nanoparticles in the DGEBA melt ($x = 5$%) immediately reduces the integrated surface of the loss peak (cf. Figs. 3b and 5) by about 10%. Since this reduction seems to
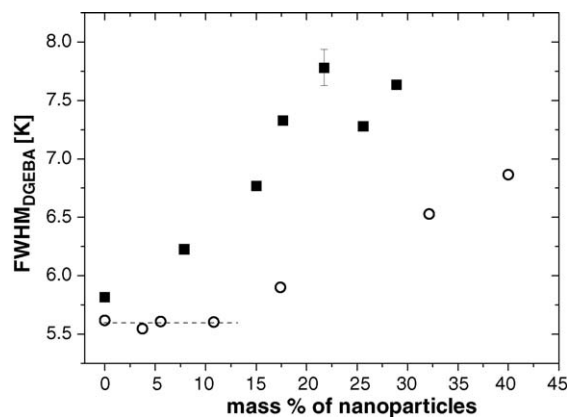
be independent of the percentage of nanoparticles, we assume that it could be due to the dispersion process. During the dispersion process, some of the relaxators could have disappeared by mechanical destruction of DGEBA molecules. Further investigations using different dispersion methods (pearl mills) are on the way.

The different interface interactions in our two model nanocomposites are elucidated furthermore by comparing how the width (Fig. 6) and height (Fig. 7) of the loss peaks as well as the c_p' step height (Fig. 8) do evolve as a function of mass concentration x of the two types of nanoparticles. An increasing line width for the DGEBA-x% Al_2O_3 system with x is accompanied by a decreasing height of the loss peaks. This suggests, that the distribution of the α-relaxation time is broadened with an increasing content of Al_2O_3 particles. In accordance with the discussion given above, this effect is much less pronounced for the DGEBA-x% SiO_2 system. In both systems, the relaxation strength (Fig. 8) does not change dramatically. A detailed comparison between $\Delta c_{pDGEBA}'$ and the properties of the imaginary part of the specific heat capacity are problematic as long as the form of the underlying distribution function of relaxators is unknown.
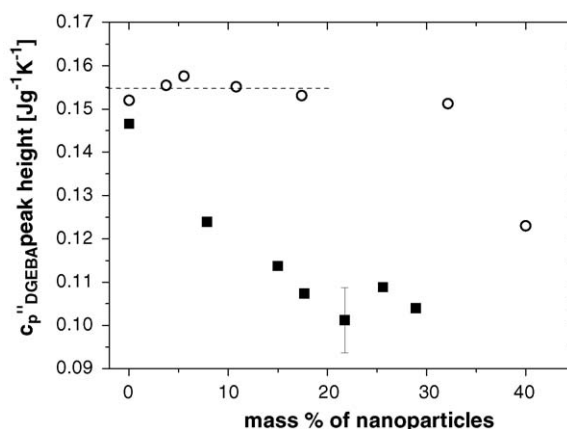

Fig. 7. Height of c_p'' maximum as a function of mass percentage of nanoparticles. Squares, Al_2O_3; circles, SiO_2 (dashed line is just a guidance to the eye).
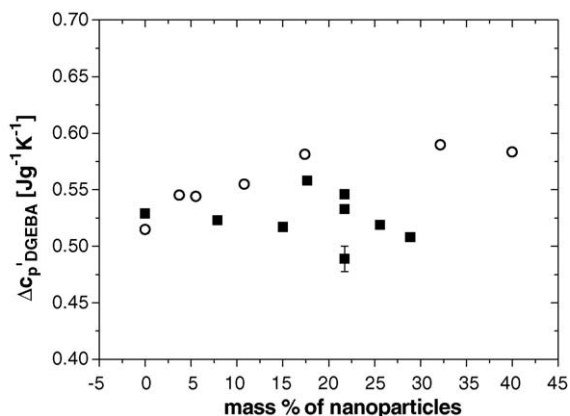
Fig. 8. Height of c_p' step as a function of mass percentage of nanoparticles. Values are related to the respective DGEBA mass contents in the samples. Squares, Al_2O_3; circles, SiO_2.

4. Conclusions

Temperature and concentration dependence of the dynamic specific heat capacity has proven that organic molecules may interact in a very selective manner and with very different strengths with the surface molecules of inorganic nanoparticles embedded in the organic matrix. In the case of the DGEBA-x% Al_2O_3 system the interactions between the nanoparticles and the matrix molecules have an influence on the α-relaxation process responsible for the glass transition of the matrix. In contrast, the interactions between SiO_2-nanoparticles and DGEBA molecules rather appear to be neutral with regard to the glass transition dynamics of the oligomer matrix. Both nanocomposites appear as homogeneous glass-forming liquids. It is evident that only calorimetric data are not sufficient to elucidate the local mechanism of interaction of nanocomposites and their relevance for the interesting phenomenological properties. Additional investigations with optical (TEM, refractive index measurements), electrical (dielectric spectroscopy) and acoustic (Brillouin scattering) methods are therefore under way.

Acknowledgment

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