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Low-temperature synthesized aluminosilicate glasses

Part II *Rheological transformations during low-temperature cure and high-temperature properties of a model compound*

H. RAHIER, B. VAN MELE*
Department of Physical Chemistry and Polymer Science, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

J. WASTIELS
Department of Civil Engineering, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

The reaction below 100 °C of a dehydroxylated clay (metakaolinite) suspended in an alkaline sodium silicate solution leads to an amorphous aluminosilicate, called in this work "low-temperature inorganic polymer glass " (LTIPG or IPG).
Some rheological transformations during the isothermal hardening process are followed with dynamic mechanical analysis (DMA) and compared with differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC). It can be concluded that the change in storage modulus (DMA) during the formation of the inorganic network can be characterized quantitatively with the evolution of the heat capacity (MDSC), and that the reaction rate is not decreased by the vitrification process. During the first heating after polymerization up to 1000 °C, the material shrinks due to the evaporation of residual water from the reaction mixture as illustrated by thermogravimetric analysis (TGA) and thermomechanical analysis (TMA). The low-temperature synthesized inorganic polymer glass is thermomechanically stable up to a temperature of at least 650 °C. In that temperature zone, the glass transition can be detected with TMA and DMA.

1. Introduction

The aluminosilicate in this work is synthesized at low temperature, starting from a castable suspension. This amorphous aluminosilicate glass is denoted as "low-temperature inorganic polymer glass" (LTIPG or IPG). The material's structure and nomenclature is investigated and justified elsewhere [1].

The two constituents of the reaction mixture are an alkaline silicate solution and a dehydroxylated clay. The rheology of the reaction mixture can be tuned by altering the properties of the two reactants or their mixing ratio (composition). The reaction between the silicate solution and the dehydroxylated clay is exothermic and transforms the reaction mixture from a suspension into solid IPG and a residue, which is mainly water. The processability and the hardening process of this material can be compared to the cure of organic resins.

However, the mechanical and chemical (degradation) stability of IPG is better, especially at elevated temperatures. The fact that the material is inorganic enables its application as a fire-proof material at elevated temperatures, where organic materials become unstable. IPG retains its mechanical properties up to about 650 °C depending on the composition of the initial reaction mixture. The combination of low-temperature production and high-temperature properties makes LTIPG a promising new material in the more general class of inorganic polymers [1–3].

In a previous paper, a few important parameters for establishing the "structure–property" relations of these materials were investigated on a well defined model system [1]. The stoichiometry of the reaction between a specific sodium silicate (composition $SiO_2/Na_2O = 1.4$; $H_2O/Na_2O = 10$; the amount of bound water is indicated by x) and a representative calcined clay (metakaolinite with composition $(Al_2O_3)(SiO_2)_2(H_2O)_{0.05}$) was investigated with differential scanning calorimetry (DSC). The amorphous nature of the material was studied with X-ray diffraction (XRD). The molecular structure of IPG was determined by magic angle spinning nuclear magnetic resonance (MAS NMR).

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* Author to whom correspondence should be addressed.

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It was shown that the overall low-temperature reaction between silicate and metakaolinite could be described by the following reaction equation

$$(Na_2O)(SiO_2)_{1.4}\,(H_2O)_x + (Al_2O_3)(SiO_2)_2\,(H_2O)_{0.05} \xrightarrow{\text{aq.}\,(<100\,^\circ\text{C})} (Na_2O)(Al_2O_3)(SiO_2)_{3.4}\,(H_2O)_z$$

with z the amount of bound water in LTIPG (the approximate value of z is 0.4).

In this paper, these findings will be used to investigate the low-temperature formation behaviour and its influence on some material's properties at elevated temperatures.

With dynamic mechanical analysis (DMA), DSC and modulated differential scanning calorimetry (MDSC), the isothermal hardening process will be observed. MDSC is a new thermal analysis technique with promising capabilities towards polymer characterization [4]. MDSC will be used in this study for the investigation of the vitrification process during isothermal cure. The high-temperature behaviour of the material up to 1000 °C will be studied with thermogravimetric analysis (TGA), thermomechanical analysis (TMA) and DMA.

2. Experimental procedure

2.1 Raw materials and processing

The kaolinite, metakaolinite (Mk) and the sodium silicate solutions (Sil) used are described elsewhere [1]. The DSC, MDSC, and DMA samples for study of the low-temperature reaction are always freshly mixed. LTIPG samples for TGA, TMA, and DMA are obtained by mixing the silicate solution $(Na_2O)\,(SiO_2)_{1.4}(H_2O)_x$ and Mk $(Al_2O_3)\,(SiO_2)_2(H_2O)_{0.05}$ in a one to one ratio [1], and curing this mixture in a closed mould at room temperature for at least two days.

2.2 Analytical techniques

2.2.1 (Modulated) differential scanning calorimetry

Isothermal measurements are performed in a DSC 2920 of TA Instruments, equipped with a temperature modulation MDSC™ and a liquid nitrogen cooling accessory. For DSC reusable high pressure stainless steel sample pans are taken. The sample (about 40 mg) is scanned from 20 °C at 20 °C min^{-1} to the isothermal temperature. For MDSC gold sample pans are used. The sample is scanned as fast as possible (jump) from 20 °C to the isothermal temperature. A period of 80 s and an amplitude of 0.5 °C are chosen.

The purge gas is helium (40 ml min^{-1}). The temperature calibration is performed with indium and zinc, and the enthalpy calibration with indium standards. Water is taken for the c_p calibration. For the calculation of the reaction enthalpy a straight baseline is used.

2.2.2 Thermomechanical and dynamic mechanical analysis

The Perkin Elmer TMA 7 and DMA 7 are used with a quartz expansion probe (diameter 3 mm). The heating and cooling rate is 5 °C min^{-1} for TMA and DMA experiments. The purge gas is He. The applied frequency in all DMA measurements is 1 Hz.

For the study of the isothermal cure from liquid to solid with DMA, the fresh reaction mixture is poured into an open cylindrical container of 10 mm height and covered on the upper surface with a thin rubber seal. In this way, the expansion probe is separated from the reaction mixture by the rubber seal. This experimental set-up influences the measurements, so that before hardening the observed storage modulus is too high and after hardening it is too low. Therefore the measured moduli are to be interpreted in a qualitative rather than in a quantitative way. A static stress of 2.2×10^4 Pa and a dynamic stress of 2×10^4 Pa is used.

For the high-temperature TMA and DMA experiments, cylindrical samples of LTIPG (with a diameter of 6 mm and an approximate height of 10 mm) are investigated from room temperature up to 1000 °C. For TMA experiments a load of 10 mN is used; for DMA experiments the maximum load (2.5×10^5 Pa static stress and 2.3×10^5 Pa dynamic stress) is used.

2.2.3 Thermogravimetric analysis

The thermobalance used is a Perkin Elmer TGA 7. The purge gas is He. The scan rate is 5 °C min^{-1}. The weight loss of LTIPG is measured on a cured sample (approximately 100 mg) with dimensions comparable to those of TMA and DMA samples (see earlier).

3. Results and discussion

3.1 Rheological transformations during low-temperature cure – DMA and DSC study

During polymerization the reaction mixture transforms from a suspension into a solid material. The viscosity and Young's modulus vary over an extremely wide range during cure. The fresh reaction mixture has a low viscosity (about 10 Pa s) that will rise far beyond 10^{12} Pa s while changing to the solid state. In this study we are not interested in the limiting values but in the transition from liquid to solid with intermediate values for viscosity and stiffness. This zone is of great technological importance because it yields information on pot-life, minimum time before unmoulding, and also on the influence of vitrification on the final state of cure. Most rheometers designed to measure liquid properties are only capable of investigating the rheology until the onset of hardening, whereas equipment designed to handle stiff (solid) materials cannot render reliable information on the early stage of the reaction. If the appropriate information is to be gained in one single experiment, the measuring device has to be adapted.

The DMA used in this work is designed for the investigation of solid materials, so special arrangements for measuring low-viscosity liquids have to be made. The commercially available "cup and plate" accessory uses a large plate "floating" on the low-viscosity liquid by the application of very low stresses, the disadvantages being that (i) the floating is disturbed by the increasing stress needed to measure the rising E' of the curing material; (ii) the maximum stress will not allow to follow the cure till vitrification (maximum $E' = 10^7$ Pa, limited by the maximum applicable force); (iii) water will evaporate from the reaction mixture altering its composition, reaction kinetics and rheology, and (iv) the curing sample will glue the measuring cup and plate together. These problems are solved here by applying a thin rubber seal between the surface of the reaction mixture and the expansion probe (small contact surface; see also section 2.2). With this experimental set-up, the time interval of the interesting rheological transformations can be characterized quantitatively. The disadvantage of this adapted measuring device is that the calculated DMA values (E', E'' and tan δ) and especially their limiting values are influenced and can only be interpreted qualitatively.

Fig. 1 illustrates how the sample set-up affects the characterization of an isothermal cure at 40 °C and which significant information is gained. In the early stage of the reaction, the observed loss modulus is smaller than the storage modulus. This is not expected for the liquid reaction mixture, but the rubber seal determines the rheological response of the sample under these conditions. No information on the rheology of the reacting system is obtained as long as the modulus of the reaction mixture is small and negligible compared to that of the rubber seal.

After 50 min of isothermal reaction, the modulus of elasticity E' starts to increase sharply due to the vitrification of the sample by formation of a network. The loss modulus E'' and tan δ go through a maximum. The glass transition temperature, which is − 50 °C at the beginning of the reaction [1], meets the isothermal cure temperature (vitrification) and the material becomes glassy. This cure rheology is comparable to that of organic resins: they transform also from a viscous liquid into an energy elastic solid, sometimes via a gel phase. A major difference lies in the fact that the final glass transition temperature of organic polymer networks hardly exceeds the isothermal cure temperature, whereas the glass transition of this IPG can reach a temperature hundreds of degrees higher than the cure temperature, as will be illustrated in section 3.3. The DMA measurement shows that the vitrification process during LTIPG formation can be followed, and for purposes of comparison the onset of vitrification will be defined here as the onset of the observed rise in E'. The observed upper value of E' is again limited due to the rubber seal in the sample set-up, but the real Young's modulus of LTIPG at this stage of the reaction is above 1 GPa if the rubber seal is removed (see also Fig. 6 later on). So, compared to the sol–gel method [5], a material with high storage modulus and high mechanical strength [1] is obtained at environmental conditions in one single step without the necessity for additional drying and sintering.

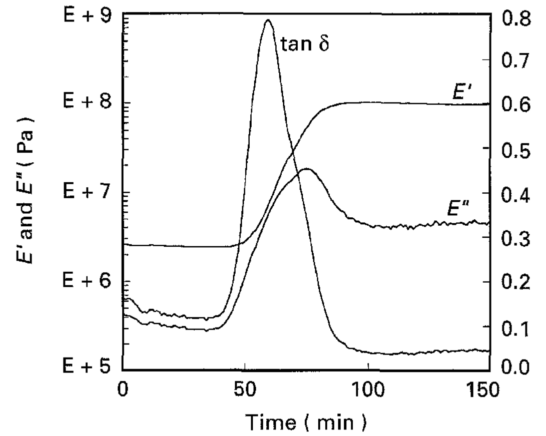

Figure 1 DMA thermogram (storage modulus E', loss modulus E'' and tan δ) of an isothermal cure of the reaction mixture at 40 °C.

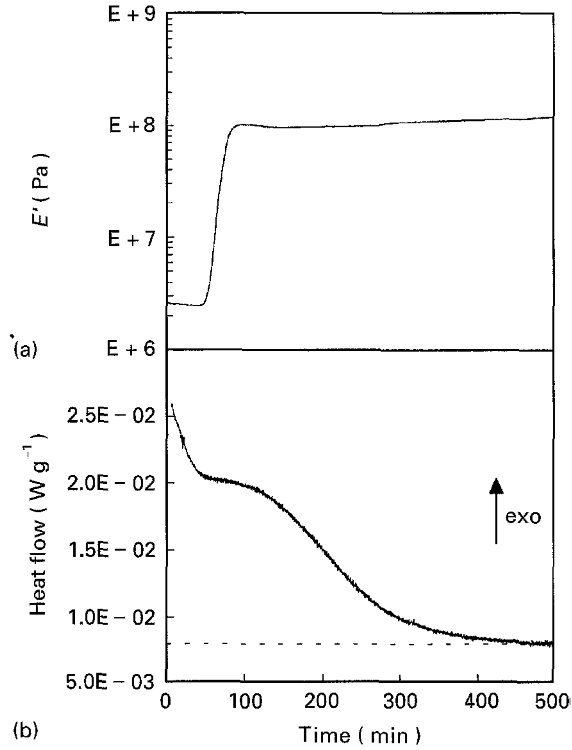

Figure 2 Isothermal cure of the reaction mixture at 40 °C: (a) DMA thermogram with storage modulus E'; (b) DSC thermogram; the dashed line represents the base line.

For the final material properties it is important to know how the reaction conversion is related to the vitrification process. Fig. 2 compares the DSC and DMA curves of an isothermal cure at 40 °C. At the onset of vitrification (defined as onset in E' or 57 min at 40 °C; Fig. 2(a)) the isothermal reaction conversion measured with DSC is 25% (Fig. 2(b)). This value is calculated as a partial reaction enthalpy against the "total" reaction enthalpy at 500 min (ΔH_r(iso) $= -180\ \mathrm{J\,g^{-1}}$). Note that the latter value is not corresponding with "full cure" after non-isothermal cure conditions (ΔH_r(non-iso) $= -230\ \mathrm{J\,g^{-1}}$) [1], but should rather be considered as a reference at 40 °C. The conversion reaches 40% when the rise in Young's modulus flattens off (after 92 min at 40 °C). It seems that the modulus (or at least a large fraction) builds up in a conversion range of less than 15% and at an almost constant reaction rate as deduced from the constant heat flow in that particular time interval (compare Fig. 2(a) and (b)). Moreover, the DSC signal of Fig. 2(b) proves that after vitrification a large part of the reaction enthalpy (at least 60%) is still evolved at a comparable reaction rate. This probably means that a significant part of the IPG-structure is built up in the vitrified state, and is therefore not able to relax to equilibrium in the applied reaction conditions.

3.2 The vitrification process during low-temperature cure – MDSC study

Modulated differential scanning calorimetry is a recently introduced extension of classical differential scanning calorimetry offering new possibilities for material characterization by thermal analysis. The additional benefits include the disentanglement of overlapping thermal events, and an improved resolution and sensitivity [4]. In MDSC a sinusoidal temperature variation is superimposed on the conventional DSC temperature program. Using a discrete Fourier transform calculation procedure, the cyclic component is continuously subtracted from the measured modulated temperature input and the modulated heat flow response. The resulting "total or underlying heat flow" and temperature signals reconstitute the conventional DSC thermogram in a quantitative manner. Two additional signals are also calculated: (i) the heat capacity c_p from the ratio of the modulated heat flow amplitude divided by the modulated heating rate amplitude, and the related "reversing heat flow" as the heat capacity multiplied by the average heating rate; (ii) the "non-reversing heat flow" by subtracting the reversing heat flow from the total heat flow.

This procedure offers for example the opportunity to separate the exothermic reaction enthalpy from the heat capacity evolution during isothermal cure. An illustration is given in Fig. 3 for an isothermal cure at 40 °C of LTIPG (same reaction conditions as in section 3.1, Fig. 2). The "total or underlying heat flow" of Fig. 3(b) is totally comparable with the conventional DSC picture of Fig. 2(b), and coincides with the "non-reversing heat flow" in this case. Indeed, in isothermal conditions the "reversing heat flow" signal equals zero. More important is the simultaneous information from the heat capacity curve during isothermal cure (Fig. 3(a)) which is not available in the conventional DSC experiment. At the beginning of the reaction c_p stays almost constant, but starts to decrease at the onset of vitrification as defined by DMA in Fig. 2(a). The observed heat capacity variation Δc_p of about $0.3\ \mathrm{J g^{-1} {}^\circ C^{-1}}$ is caused by the vitrification process during isothermal cure and not by the chemical reaction itself since this effect is mostly of negligible importance, as demonstrated by the constant c_p for example (Fig. 3(a)) with a maximum conversion rate at the beginning of the reaction (Fig. 3(b)). As the reaction proceeds, the glass transition temperature of the reacting system increases to meet the isothermal cure temperature and this phenomenon is seen by a negative heat capacity variation as a function of cure time. In the case of organic thermosetting systems, the vitrification process quenches the reaction by diffusion effects and the rate drops dramatically as can be seen from the "non-reversing heat flow"; the variation of c_p thus occurs at the end of the reaction exotherm. This is obviously not the case for LTIPG formation because the observed variation of c_p (and thus vitrification) is not changing the reaction rate in a significant way (compare the signals of Fig. 3(a) and (b)). The decrease in rate is mainly caused here by the increasing conversion as a function of reaction time, suggesting that vitrification is not a physical barrier towards a very high final glass transition temperature (see section 3.3).

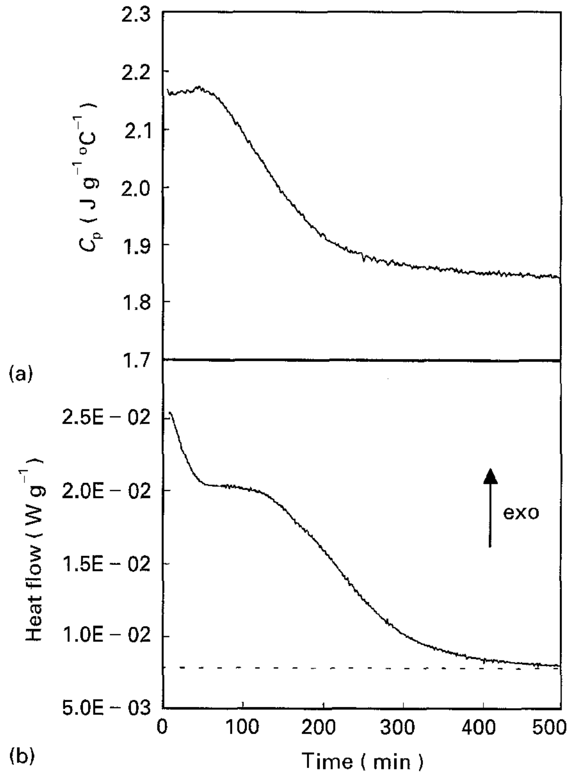

Figure 3 MDSC experiment of an isothermal cure of the reaction mixture at 40 °C: (a) heat capacity; (b) "total" or "non-reversing" heat flow; the dashed line represents the base line.

Note that the increasing storage modulus E' (Fig. 2(a)) levels off earlier than the decreasing heat capacity (Fig. 3(a)) due to the special DMA sample set-up (see also sections 2 and 3.1). MDSC offers the possibility of characterizing the vitrification to a greater extent and without compromises concerning the experimental set-up. So, for the study of LTIPG production, it can be concluded that MDSC provides in one experiment the same information about vitrification, and even in a more quantitative way, as a combined DMA and conventional DSC experiment.

The rheological transformations during low-temperature synthesis discussed in this and the previous section are of major importance for the thermomechanical behaviour and the high-temperature properties in general of IPG.

3.3 High-temperature properties of the inorganic polymer glass – TGA, TMA and DMA study

During the first heating up to 250 °C after polymerization, the LTIPG material shrinks about 5% in the

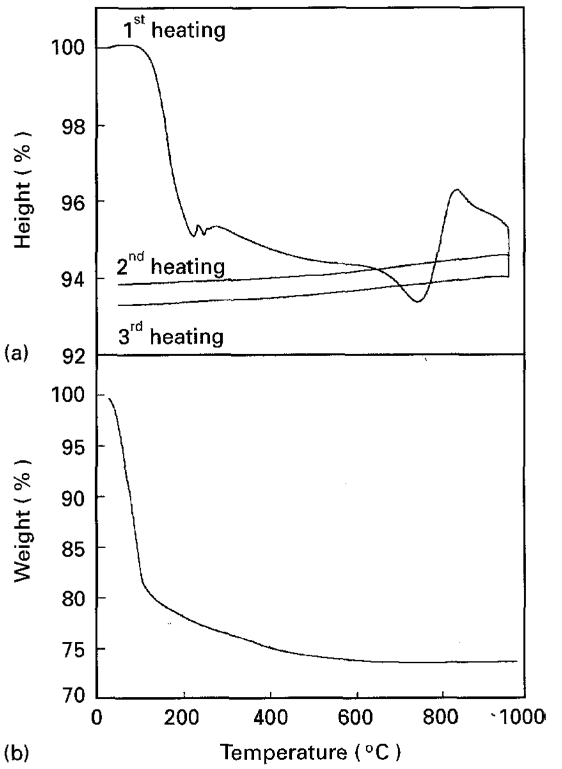

Figure 4 High-temperature behaviour up to 1000 °C of a low-temperature cured IPG: (a) TMA thermogram of first, second and third heating after cure; (b) TGA thermogram of first heating after cure.

measurement direction (see TMA thermogram of Fig. 4(a)), explained by a simultaneous weight loss of water (see TGA thermogram of Fig. 4(b)). Most of the water is evaporated below 250 °C, where the most important shrinkage ceases too. However, the evaporation of water starts at room temperature whereas the observed shrinkage is retarded. This can be explained by the fact that different types of water are present: free water at the surface and in large pores, in combination with water that swells the network (adsorbed water and/or water in small pores [5]) and bound water probably in the form of Si–OH groups [1]. The free water will evaporate readily (mostly below 100 °C), but this will have no large influence on the dimensional stability of the material. On the contrary, the other types of water will cause the material to shrink, e.g. by desorption of water out of the small pores below 250 °C. The same holds for water formed out of Si–OH groups, evaporating at a still higher temperature (above 250 °C; see TGA procedure for bound water content [1]) and also causing structural changes on a molecular scale.

At much higher temperatures (700 °C and higher) the material shrinks further and immediately expands again. The depth of the minimum and the height of the maximum expansion are not reproducible. This phenomenon does not correspond any longer with a distinct weight loss. At still higher temperatures, the sample height decreases again. During a subsequent cooling or reheating no such shrinkage nor expansion is seen anymore (see Fig. 4(a); second and third heating).

The linear thermal expansion coefficient of LTIPG after a first heating is close to $10^{-5}\,°C^{-1}$ at room temperature and increases to $2\times10^{-5}\,°C^{-1}$ above 650 °C (see slope of enlarged second heating TMA expansion curve of Fig. 5), which is in agreement with literature values for ceramic materials [5, 6].

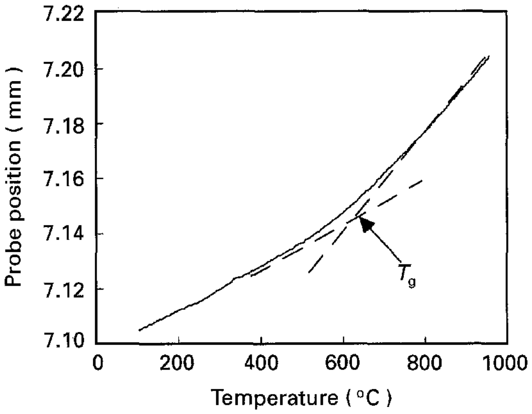

Figure 5 Thermal expansion up to 1000 °C of LTIPG in second heating.

Although difficult to determine, the change in slope of the expansion curve is an indication for a glass transition (T_g) in this temperature range. The calculated onset by linear extrapolation of the change in expansion coefficient suggests T_g at about 650 °C. The position of T_g in the first heating is probably not constant and in any case masked by water evaporation.

A confirmation for the existence and the position of T_g is given in high-temperature DMA experiments. In Fig. 6 (2nd heating) the storage modulus E' remains almost constant and higher than 1 GPa up to temperatures of at least 700 °C, while the loss modulus E'' and tan δ go through a maximum at about 750 °C and 850 °C, respectively. The maximum in E'' is also used to define T_g. Note that by using an expansion probe (see section 2.2), the "parallel plate" measuring mode does not permit measurement of E' values much above 1 GPa meaning that E' below 700 °C is probably underestimated.

According to published glass transition temperatures for aluminosilicates determined by a calorimetric procedure [7], a T_g value in the range of 700 to 800 °C is expected for IPG of this work. The T_g value measured in this work with TMA should be closer to the calorimetric determination than the T_g value measured with DMA. However, it is pointed out that small changes in the ratio Na_2O/Al_2O_3 or in the water content have large effects on T_g [5, 7]. The constituents Si, Al, and Na play a different role in the thermorheological behaviour of the glass [5]. SiO_2 is a network former and is in fact the basis of the glass network. Na_2O is a network modifier and lowers T_g (as does H_2O) and the viscosity in the melt. Al_2O_3 can act as network former or modifier. Al_2O_3 broadens the temperature working range by keeping the viscosity high above T_g. This particular rheological behaviour is related to the fact that structural differences of aluminosilicates below and above T_g are small [8]. Therefore, for aluminosilicates the change in properties between the solid material (below T_g) and

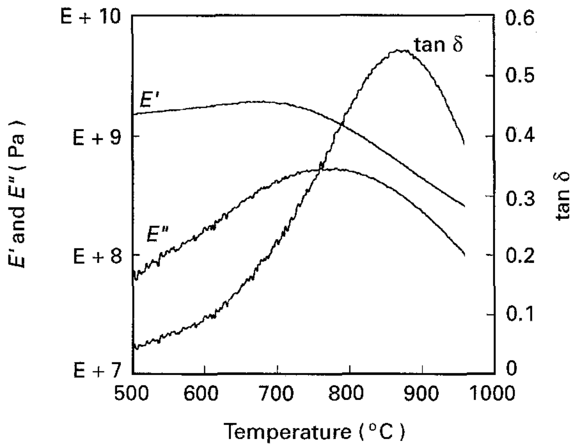

Figure 6 DMA thermogram up to 1000 °C (storage modulus E', loss modulus E'' and tan δ) of LTIPG in second heating.

the weakened material (beyond T_g) is expected to be small [9]. The small change in expansion coefficient and storage modulus E' by passing T_g is thus not surprising.

The shrinkage of the sample above 650 °C observed with TMA (Fig. 4(a)) in the first heating is probably due to the way of low-temperature processing. It was already concluded that a large part of the structure should not be able to relax during low temperature cure. As a result, residual stresses remain in the material. Upon heating the material will relax and shrink when the glass transition region is reached. The same effects are observed during sintering of a dried gel obtained by the sol–gel technique and in organic glasses after e.g. a quench cooling and subsequent heating.

The final expansion in Fig. 4(a) could be explained by a sintering effect above T_g. Gases in the pores will be entrapped by a skin effect of the sintering material. These gases build up an internal pressure by the rising temperature and force the weakening specimen to expand substantially. The shrinkage that immediately follows this expansion is due to flow. This is illustrated by the decreasing sample height as a function of time at the maximum temperature and between each subsequent heating. The second and third reheating curves are parallel (the thermal expansion coefficient is not changed) indicating that the material's structure has not changed and that this final shrinkage is due to flow. The sample is also visibly deformed after the high-temperature experiment. This flow behaviour is not possible with organic networks. To understand the phenomenon of glass transition in three-dimensional oxide networks one has to realize that different molecular events are involved such as bond rupture [9, 10]. This mechanism can lead to molecular rearrangements and crystallization [5].

The previous TGA, TMA and DMA results confirm the statements of sections 3.1 and 3.2 and emphasize the strong link between the low-temperature production route of LTIPG and its high-temperature behaviour. The short range symmetry around the quadrupolar Al nucleus observed with ^{27}Al nuclear magnetic resonance spectroscopy is probably a result of the low-temperature reaction mechanism too, and thus not an equilibrium state [1, 11].

4. Conclusions

It is demonstrated that a "ceramic-like" material (LTIPG) can easily be obtained at ambient temperature, starting from an aqueous silicate and a dehydroxylated clay. The chemorheological transformation during the reaction is comparable to that of organic thermosets. The most important difference is that the glass transition temperature of LTIPG rises far above the cure temperature.

During the first heating after polymerization, LTIPG will shrink due to the evaporation of water. The glass transition temperature of LTIPG is at least 650 °C and probably higher.

The high temperature behaviour of LTIPG is strongly influenced by the cure at environmental conditions building up the molecular structure.

Therefore, LTIPG materials synthesized from silicate solutions with other Na/Si ratios and with another cation will be studied in the future. It is expected that the Si/Al ratio of LTIPG depends on this Na/Si ratio. Since T_g depends on the Si/Al ratio and on the involved cation it is likely that inorganic polymer glasses could be synthesized according to the proposed low-temperature route with a tuneable T_g, even within a range of a few hundreds of degrees.

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