Structure-property relationship of dispersants used in ceramic feedstock development

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Abstract

With respect to polymer-filler composite (feedstock) development for the different variants of powder injection molding the use of dispersants or surfactants is essential for a large filler load and a homogenous feedstock quality. In this paper the influence of a series of citrate derived dispersants on the viscosity of feedstock systems with different binder composition and ceramic fillers will be described. Citrates posses four polar functionalities, which can interact with the hydroxy-groups at the alumina or zirconia surface. The investigated surfactants differ in the extension of the lipophilic end chains (ethyl or butyl) and in the presence of one free hydroxy group, which is masked partially by an acetic acid group. The impact of the dispersant concentration, molecular structure, dipole moment and the used binder composition will be discussed in terms of the resulting composite feedstock flow behaviour, some structure-property relationships can be found.

Keywords: Polymer-ceramic-composites, rheological properties, feedstock development

1. Introduction

Small and microsized ceramic components become more and more important due to their outstanding thermomechanical properties and chemical stability. A low cost part fabrication depends directly on a simple process chain starting from compounding and ending up with the sintered ceramic part. In the recent past different variants of injection molding techniques using reactive resin resins, wax or thermoplastics as binder in the investigated feedstock system have been developed [1-4]. For the realisation of dense ceramic parts using polymer binder-ceramic filler-composites a powder load of at least 50 vol% is necessary, which causes a significant increase of the composite's viscosity [5]. In literature a large number of publications deals with the realisation of feedstock systems with large filler loads, mostly related to wax, paraffin or thermoplastic binders applying different kinds of dispersing agents for a reduction of the feedstock viscosity [6-10]. In 2005 Zürcher and Graule gave a comprehensive overview of the influence of the dispersant structure on the flow behaviour of zirconia/organic solvent/dispersions [11]. Quite recently two papers dealing with the influence of the dispersants' chemical structure on the composites viscosity have been published [12,13].

The low apparent viscosity of reactive resins between 1 and 5 Pa s under ambient conditions allows a rapid composite processing using standard laboratory dissolver stirrers. On a molecular level dispersants designed for the use in polymer matrix materials are either small amphiphilic molecules or oligomers as well as polymers. These molecules adsorb via van-der-Waals-forces or hydrogen-bridge-linkage on the filler’s surface and reduce the interactive forces between the individual filler particles preventing reagglomeration and supporting wetting by the binder.

The surfactant properties of a molecule can be predicted using the hydrophilic-lipophilic-balance value (HLB) introduced by Griffin [14,15] considering the hydrophilic and lipophilic moieties in a dispersant molecule (see Eq. 1). $M_{\text{hydrophilic}}$ is the mass of the hydrophilic groups in the molecule, $M_{\text{tot}}$ the total molecular mass. A HLB value of 0 corresponds to a completely hydrophobic molecule, a value of 20 would correspond to a molecule made up completely of hydrophilic components. Molecules with a HLB-value between 3 and 6 can be used as water in oil emulsifier, between 7 and 9 as surfactant, between 8 and 12 as oil in water emulsifier; molecules with HLB-values larger than 12 behave as a detergent.

$$HLB = 20 \frac{M_{\text{hydrophilic}}}{M_{\text{tot}}}$$ (1)
2. Experimental

2.1. Reactive resin based feedstocks

An unsaturated polyester resin (Roth GmbH) with a polymer content around 65 wt% and styrene as reactive thinner was used as polymer binder. All dispersants, chemically derived from citric acid, were given to the resin before adding the alumina filler (Alcoa CT3000SG, average particle size 0.7 µm, specific surface 6-8 m²/g). Table 1 lists the nomenclature of the investigated dispersants, the Figures 1-4 show the chemical structure (dark balls: oxygen atoms). Basic structural element is the citric acid core, the three carboxylate functionalities are esterified either with an ethyl (TEC, ATEC) or butyl (TBC, ATBC) functionality. Additionally the free hydroxy group (TEC, TBC) is esterified by an acetyl moiety (ATEC, ATBC). All investigated composites consist of 50-x wt% of the polyester resin, x wt% dispersing agent and 50 wt% (22.4 vol%) alumina, the composite without dispersant is named as reference composite. The relatively low filler content enables the use of a cone and plate rheometer (CVO50, Bohlin) avoiding experimental complications like sticking or gap emptying at larger shear rates. All composites were processed using a dissolver stirrer at 1000 rpm for 30 min under ambient conditions. All viscosity measurements were done at 20°C, 40°C and 60°C in the shear rate range between 1 and 100 1/s. The experimental uncertainty of the obtained data is in the range of ± 5%.

2.2. Thermoplastic based feedstocks

All dispersants were added to a feedstock consisting of a polyethylene/wax based binder and 50 vol% zirconia (Tosoh TZ-3YS-E, data sheet: average particle size 0.45 µm, specific surface area 6 m²/g); the flow behaviour was determined using torque measurement during compounding. The set temperature was 125°C, the kneader blades rotation speed was 30 rpm. Due to experimental reasons only a fixed dispersant concentration of 2.2 wt% was applied.

3. Results and Discussion

3.1. Reactive resin based feedstocks

The Figures 5-8 show the viscosities of the reference composite and of the dispersant containing composites (Figure 5: 2 wt% TEC, Figure 6: 1.0 wt% ATEC, Figure 7: 2 wt% TBC, Figure 8: 2 wt% ATBC) at 20°C and 60°C. In most of the cases a viscosity reduction relative to the reference composite can be observed. The strongest impact can be detected using TEC (Figure 5) and ATBC (Figure 8). The addition of TBC reduces the viscosity slightly (Figure 7), whereas ATEC does not alter the viscosity (Figure 6). The addition of dispersants does not change the principal flow behaviour significantly. At 60°C and low shear rates, with exception of TEC, all dispersants cause a slight viscosity increase in comparison to the reference composite. At the lower measuring temperature this effect can only be observed in case of ATEC. Depending on the chemical
structure the most suitable dispersant concentration for an effective viscosity reduction can be different. Figure 9 shows the dispersant concentration dependent composite viscosity (T= 20°C, shear rate 100 1/s). With exception of ATEC the strongest viscosity reduction occurs at a dispersant amount of 2 wt%, in case of ATEC at 1 wt%. ATEC and TBC show the smallest influence on the viscosity under the given conditions, TEC and ATBC the strongest. Table 2 summarizes the impact of the different dispersants on the composite viscosity at all measured temperatures, listed as percentage amount of the reference composite. TEC and ATBC show the strongest viscosity reduction effect, which changes with increasing temperature, which was observed earlier using different other types of surfactants [12,13]. The addition of ATEC and TBC induces a different behaviour; the influence on the viscosity is smaller. Using ATEC at 40°C even a slight viscosity increase can be seen.

3.2. Thermoplastic based feedstocks

With respect to feedstock development for micro powder injection molding the citrate based dispersants have been added to polyethylene/wax/ZrO$_2$ feedstocks. The mixtures were homogenized using a laboratory compounder with simultaneous torque measurement (Figure 10). The feedstock without dispersant shows a torque increase within the first 15 minutes followed by a slight and continuous descent down to a value of 45 Nm indicating the end of the compounding process. The dispersant addition causes, with exception of TBC, a significant increase of the initial torque. In case of TEC the large torque value remains constant (78 Nm), whereas the torque of feedstocks, containing ATEC (48 Nm) and ATBC (50 Nm), return to a value, which is similar to the reference feedstock. TBC delivers an intermediate impact on the torque (63 Nm). But in all cases the torque values are larger than in the reference feedstock. Only one positive side effect can be observed: The addition of dispersant reduces the torque fluctuation yielding a more homogenous feedstock.

3.3. Correlation with molecular properties

A correlation of the dispersant’s molecular properties with the obtained results using the polyester resin or the polyethylene based feedstocks seems to be difficult. In a rough approximation the surface chemistry of the alumina and the zirconia should be similar, that means in both cases the hydroxy-functionalities interact with the hydrophilic molecular moieties. Table 3 lists the calculated molecular properties like dipole moment and
Different feedstock systems can be observed. The binder system has to be considered. Hence, depending on the interaction of the dispersants with the inorganic filler, which is dominated by the presence of hydrophobic groups, as well as with the organic matrix, which is affected by the polarity and the size of the lipophilic moieties, has to be considered. Partially destroyed in the compounding process progression. These aspects explain the viscosity reduction effect in the polyester based compositions and the torque increase in the polyethylene/wax based feedstocks. A further differentiation within the applied citrate derived dispersants is difficult because the interaction of the molecules with the ceramic as well as with the used binder system has to be considered. The HLB-values of TBC and ATBC are significantly smaller than the TEC and ATEC values. A clear correlation of the HLB-values with dispersant via the free hydroxy group, which will be partially destroyed in the compounding process progression. The authors gratefully acknowledge the financial support by the European Commission within the 4M-Network of Excellence and the Deutsche Forschungsgemeinschaft DFG (SFB 499) as well as Morflex Inc. for the provision of dispersant samples.

**Acknowledgements**

**References**