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Improvement of the rheological properties of the zirconia/polypropylene system for ceramic injection moulding using coupling agents

M. TAKAHASHI, J. HAYASHI, S. SUZUKI
Ceramics Research Laboratory, Nagoya Institute of Technology, Asahigaoka, Tajimi, Japan
Y. ISHIGURE
Gifu Prefectural Industrial Research Technical Center, Kitaoyobi, Kasamatsu, Japan

In order to improve the rheological properties of the zirconia/polypropylene system for ceramic injection moulding, the zirconia powder was surface-treated with aluminate (A), silane (S) and titanate (T) coupling agents dissolved in toluene. 2% additions of these coupling agents decreased the torque, T_h, for compounding the zirconia filled-polypropylene after 1 h at 180 °C. The surface treatment also reduced the viscosity, η_a, of the compound, the effectiveness of the coupling agents on viscosity reduction being T > S > A. On the contrary, the apparent activation energy, E_a, for flow of the compound increased when fluidity was promoted by surface treatment. Rheological measurements in systems with different titanate concentrations showed that the three parameters, T_h, η_a, and E_a, remained nearly constant for coupling agent additions of over 2%. This critical concentration of 2% showed good correspondence to the optimum concentration evaluated from thermogravimetric analysis of the powders.

1. Introduction

Compounds for ceramic injection moulding are usually prepared by mixing ceramic powder with an organic vehicle (often called binders) such as polymer or wax. A primary requirement in injection moulding is that the compound must have adequate fluidity for moulding. The major factors influencing the fluidity of particle-filled polymer are: (1) the properties of organics involving lubricants and plasticizers in addition to polymers; (2) the powder concentration; (3) the powder characteristics such as particle size, distribution and shape; and (4) the chemistry of the particle–organic interface [1]. However, the powder concentration of the compound can be varied within only a narrow range because of the necessity to obtain a capillary state [2–4].

It is obvious that a moulded body will fail to keep its shape during binder removal if the concentration is lowered too much in order to improve fluidity. Therefore, alteration of organics formulation [5–8] and control of particle size and distribution [1, 9, 10] have been attempted as a means of providing proper fluidity. Unfortunately, changes in the geometrical characteristics of particles are not desirable from the aspect of ceramic design, because they will result in the microstructure of the sintered body being different from that expected from the original geometry. Determination of better organics formulation requires numerous compounding and moulding tests. Also, new formulations will enforce changes in the heating schedule for binder removal. Surface modification of the powder, which will change neither the geometrical characteristics of particles nor the heating schedule, is an attractive method for improving the rheological properties of ceramic/polymer compounds [11–15].

Zirconia powders used for engineering ceramics are usually in the submicrometre range, and have a narrow size distribution. Compounds of such fine zirconia and polyolefin lack appropriate fluidity, which causes considerable difficulty in injection moulding. Coupling agents are therefore potentially effective candidates for improving the fluidity of zirconia/polyolefin compounds through enhancement of the compatibility between powder and polymer [11].

In this study, surface treatment of zirconia powder was carried out using aluminate, silane and titanate for improving the rheology of the zirconia/polypropylene system. Instead of referring to the coupling mechanisms of these agents, the macroscopic changes in mixing torque, apparent viscosity and activation energy for flow have been investigated. The relation between these rheological variables and the concentration of coupling agent has been examined closely in the system treated with titanate. A method for estimating the optimum amount of coupling agent through thermogravimetric analysis has also been described.

2. Experimental procedure

2.1. Materials and surface treatment

Partially stabilized zirconia (PSZ) powder (Y31710)

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was used as the ceramic filler. The mean diameter was 0.292 μm, the specific area 12.3 $\mathrm{m^2\,g^{-1}}$, and the density 6021 $\mathrm{kg\,m^{-3}}$.

The coupling agents used were acetoalkoxy aluminium diisopropylate (AL-M), *n*-octadecyl trimethoxy silane (AX43-065) and isopropyl triisostearoyl titanate (KR-TTS), denoted A, S and T, respectively. The densities of A, S and T, were 950, 980, and 940 $\mathrm{kg\,m^{-3}}$ at room temperature. The reasons for selecting these coupling agents were; (1) the burned-out ash of A, i.e. Al_2O_3, will not degrade the mechanical properties of the sintered PSZ body (examination of this aspect, however, is beyond the scope of this study), (2) the alkyl chain of S is longer than those of commonly used silanes, and (3) T is known to improve the fluidity in the zirconia/atactic polypropylene system [11] which is similar to the zirconia/polypropylene system.

Using a polyethylene jar charged with zirconia balls of 5 mm diameter, the PSZ powders were ball-milled for 1 h in toluene containing the dissolved coupling agent. The ratio of powder to solvent was 200 g:400 $\mathrm{cm^3}$. The amount of coupling agent was 2% by weight of PSZ powder. Other powders with 0.5%, 1%, and 5% titanate additions were prepared separately. In order to determine the effect of ball milling on the as-received powder, blank powder (i.e. powder without coupling agent additions) was also prepared. The mixed slurries were decanted, and this was followed by vacuum evaporation. After pulverizing the dried cakes to under 250 μm, the powders were further dried for 2 days in an electric oven at 110 °C.

The weight of coupling agent adsorbed on the PSZ powder was evaluated by thermogravimetric analysis (TG) in static air from room temperature to 900 °C at a heating rate of 5 °C $\mathrm{min^{-1}}$.

2.2. Compounding and rheological measurements

The PSZ powders were mixed with polypropylene at 180 °C for 60 min, using a torque rheometer (R-100, Toyo Seiki, Tokyo, Japan) with roller-type blades. The molecular weight of the polypropylene used was 1.90×10^5, and the density 905 $\mathrm{kg\,m^{-3}}$. The properties of the resin and the mixing procedure are detailed elsewhere [2].

The critical powder volume concentration (CPVC), which can be determined from the curve of mixing torque versus oleic acid volume [16], was 59.8% for the as-received PSZ. A simple ceramic/polymer compound without plasticizers or lubricants often loses fluidity when its powder concentration becomes greater than 85% CPVC [17]. Compounds with filler loadings of 45%, 50% (about 85% CPVC) and 55% were prepared.

The flow rate responses to extruding pressures between 1 and 50 MPa were measured using a capillary type viscometer (Flowtester CF-500, Shimazu Corp., Kyoto, Japan) with a capillary of 1 mm diameter and 10 mm long. The apparent viscosity was calculated by Hagen–Poiseuille's equation. The apparent activation energy for flow was calculated using the viscosities at 170, 180, 190, and 200 °C.

3. Results and discussion

3.1. Thermal weight losses of zirconia powders

Fig. 1 shows the TG curves for powders with and without coupling agent addition. The weight loss of the as-received powder was almost equal to that of the ball-milled powder (0%). Moreover, the ball-milled powder had the same specific surface area as the original powder. Therefore, the weight loss of these two powders should be attributed to the desorption of water and –OH groups from the PSZ surface.

The measured weight loss, W_{meas}, increased with increasing titanate concentration (Fig. 2). As summarized in Table I, W_{meas} was smaller than the amount, W_c, of coupling agent added in all cases. The discrepancies between W_{meas} and W_c were caused by evaporation of alcohols which are produced by hydrolysis of the coupling agents. The reactions for the A, S and T can be expressed by

$$\mathrm{X{-}Al{-}(OC_3H_7)_2 + 2H_2O \rightarrow X{-}Al{-}(OH)_2 + 2C_3H_7OH} \quad (1)$$

$$\mathrm{X'{-}Si{-}(OCH_3)_3 + 3H_2O \rightarrow X'{-}Si{-}(OH)_3 + 3CH_3OH} \quad (2)$$

$$\mathrm{X''{-}Ti{-}OC_3H_7 + H_2O \rightarrow X''{-}Ti{-}OH + C_3H_7OH} \quad (3)$$

Where X(= $(COCH_3CHCO_2C_{18}H_{37})_3$), X′(= $C_{18}H_{37}$) and X″(= $(CO_2C_{17}H_{35})_3$) are the organofunctional groups in the coupling agents. Among the three coupling agents, aluminate digests the greatest quantity of

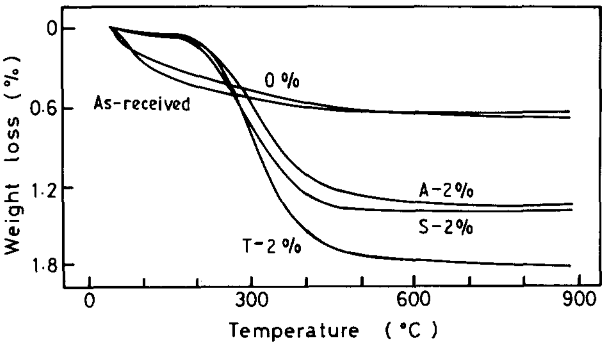

Figure 1 TG curves for PSZ powders with and without coupling agent addition.

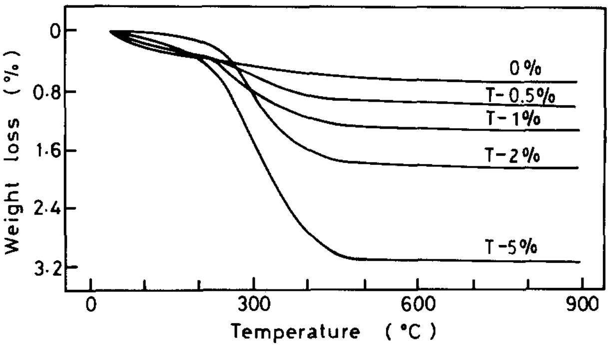

Figure 2 TG curves for PSZ powders treated with different titanate concentrations.

TABLE I Relation between the added amount of coupling agent, W_c, and the measured, W_{meas}, and theoretical, W_{theo}, weight losses of the zirconia powders

Powder	Coupling agent	W_c (wt %)	W_{meas} (wt %)	W_{theo} (wt %)
As-received	–	0	0.64	–
0% (ball-milled)	–	0	0.66	–
A-2%	Aluminate	2.0	1.33	1.34
S-2%	Silane	2.0	1.38	1.30
T-0.5%	Titanate	0.5	0.96	0.47
T-1%	Titanate	1.0	1.29	0.85
T-2%	Titanate	2.0	1.84	1.70
T-5%	Titanate	5.0	3.14	4.65

water for the reaction (Equation 1). Approximately 0.1 g water is necessary for hydrolysis of 1 g aluminate. The as-received PSZ powder contains about 6 mg adsorbed water per gram (Table I). This amount of water should be sufficient to complete the hydrolysis reaction for coupling agent additions of less than 6%.

The hydrolysed coupling agents being adsorbed on the particle surface through certain mechanisms [18–20], representatively through chemical bonding, will be decomposed by heating. Phase diagrams concerned with the $ZrO_2/(Al_2O_3$, SiO_2 or $TiO_2)$ systems suggest that the formation of a new phase or solid solution may occur at relatively high temperatures [21–23]. However, it is reasonable to assume that the product of pyrolysis of each agent exists as a metal oxide at 500 °C where the weight loss approaches a constant value (Fig. 1). On this assumption, the relation between the theoretical weight loss, W_{theo}, and the amount of coupling agent, W_c, can be expressed as

$$W_{theo}(\%) = 100 \times W_c\ (\%) \frac{M_a - M_o}{M_c} \tag{4}$$

Where M_c, M_a, and M_o are the molecular weights of the virgin coupling agent, the hydrolysed coupling agent, and the metal oxide, respectively.

At 2% titanate addition, W_{theo} was almost consistent with W_{meas} (Table I). However, W_{theo} was smaller than W_{meas} in powders treated with less than 2% titanate. This result indicates that some sites on the particle surface were left unoccupied by the titanate molecules because of insufficient addition. Desorption of water and hydroxyl groups from the unoccupied sites (0.66% for the powder without addition) will probably cause an apparent increase of W_{meas}. In contrast to the cases of titanate additions of less than 2%, W_{theo} was greater than W_{meas} in powder treated with 5% titanate. If the coupling agent is added over the amount required for a monolayer coverage on the surface, the extra amount will remain in toluene. A large part of such dissolved agent will be removed with the solvent during decantation, resulting in the apparent decrease of W_{meas}. It may be concluded that the concentration at which W_{meas} is equal to W_{theo}, approximates the optimum titanate addition. Actually, mixing tests of powders with distilled water showed that no homogeneous slurry could be obtained for powders treated with 2% and 5% titanate, whereas partially dispersed slurries were obtained for powders treated with 0.5% and 1% titanate.

3.2. Mixing characteristics

A small change in powder concentration will considerably affect the rheological properties of compounds with a high concentration near CPVC. No theoretical interpretations about the volume effect of molecules of coupling agent adsorbed on the surface of particles seem to be available. If the adsorbed molecules are very stiff, they will increase the apparent particle size, and therefore increase the powder concentration. Conversely, the powder concentration should be corrected to a lower one if the adsorbed coupling agent functions as a vehicle. In this study, the volume of adsorbed coupling agent was assumed to act as a vehicle because the rheological improvement by the coupling agent should not be overestimated. The adsorbed volume was derived from the thermal weight loss of the treated PSZ powder divided by the density of the coupling agent before pyrolysis.

Fig. 3 shows the curves of mixing torque versus time in compounds with a corrected powder volume concentration of about 50%. Surface treatment of the PSZ powder with 2% titanate reduced the torque after 1 h (T_h) from 30.2 N m to 7.6 N m. Silane coupling agents have been believed to be effective for the materials containing silicon (for example, silicon and SiO_2), but have rarely been applied to ZrO_2 (certainly, one reason for not attempting application to ZrO_2 is that problems of contamination may arise after pyrolysis of silane). The effect of silane on the reduction of T_h was similar to that of titanate. This may be related to zirconium having the same ion charge number as silicon, and to the somewhat long alkyl group of the AX 43–065 used. In comparison to titanate and silane, aluminate decreased T_h by a smaller extent, although a simple mixing test with water

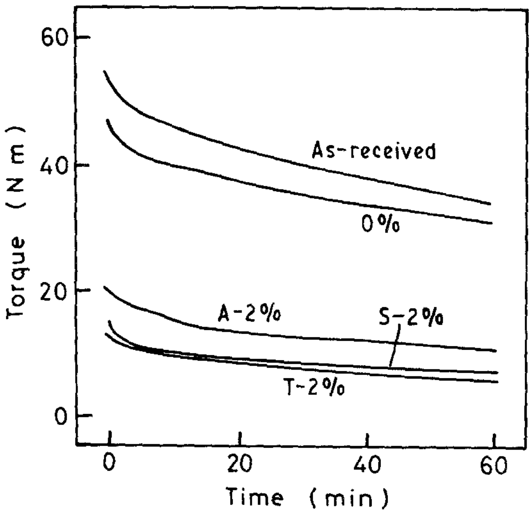

Figure 3 Mixing torque versus time curves at 180 °C in the system with a corrected powder volume concentration of about 50%. The corrected powder volume concentrations are: as-received; 49.7% (50%), 0%; 49.7% (50%), A-2%; 50.4% (55%), S-2%; 49.8% (55%) and T-2%; 48.5% (55%). The values within parentheses are the initial filler loading concentrations.

proved perfect hydrophobicity of the aluminate-treated powder. The weak reduction by the aluminate may be a reflection of its organofunctional group being quite different to those of silane and titanate [11]. Ball-milling of the as-received powder also decreased T_h. Uniaxial compaction tests for the dried PSZ powders showed that the bulk density at 200 MPa was 2% higher in the ball-milled powder than in the as-received powder. Generally, the higher the compaction density becomes, the higher is the fluidity of the compound at the same powder concentration [2]. These two powders had the same specific surface area. The increased compaction density of the ball-milled powder may have resulted from the breakdown of the particle agglomerates existing in the original powder.

The effect of titanate amount on T_h is shown in Fig. 4. T_h decreased considerably with increasing titanate additions up to 2%. However, the decrease of T_h was only 2.3 N m for further additions up to 5%. All the compounds in this figure were of the same filler loading of 50%. It can be noticed that the corrected powder concentrations which are shown within brackets decrease by 1.7 vol % when the titanate amount is increased from 1% to 2%, and by 4.0 vol % when the titanate amount is increased from 2% to 5%. Even allowing for the changes in the actual powder concentration, the reduction of T_h between 2% and 5% titanate is much smaller than the one between 1% and 2%. The critical value of 2% is almost coincident with the estimated optimum concentration (cf. Table I). It should be noted that the coupling agent may also have a complementary function as a viscosity modifier of the polymer itself [11]. A 13% titanate addition to polypropylene (PP), equivalent to the titanate concentration in the 2% titanate/PP/PSZ compound, almost doubled the viscosity of the PP at 180 °C. This negative effect may also contribute to the smaller reduction of T_h in the 5% compound which is overtreated by the titanate.

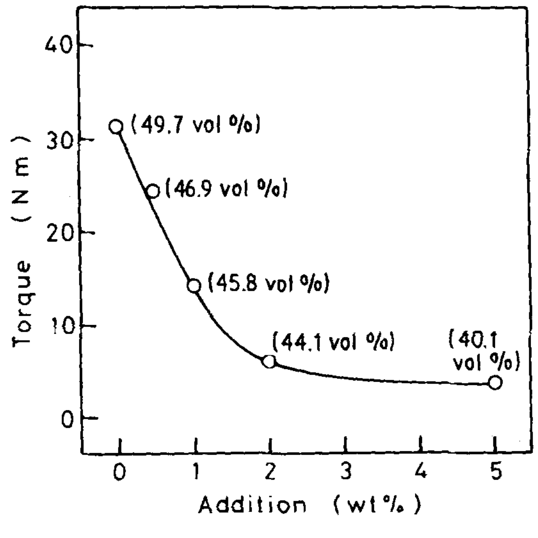

Figure 4 Relation between mixing torque after 1 h and titanate addition in the system with an initial filler loading of 50%. The corrected powder volume concentrations of the compounds are shown in the figure within parentheses.

3.3. Flow characteristics

Fig. 5 shows the effect of the coupling agents on the flow behaviour at 180 °C in compounds having a corrected powder concentration of 50%. The extent of reduction of viscosity at 2% addition was T > S > A. This trend is the same as that observed for mixing torque. Titanate, the most effective agent, reduced the viscosity of the compound without any agent from 520 MPa s to 125 MPa s at a shear rate of $10^3\,s^{-1}$. Ball milling of the as-received powder decreased not only the mixing torque but also the viscosity.

The flow behaviour in all the compounds could be characterized as shear thinning. The intensity of the shear thinning (the slope of the flow curve in other words) was weakened by surface treatment of the PSZ filler. Generally, strong shear thinning will appear when particle-filled polymer has agglomerated particles because of inadequate dispersion [24]. Fig. 5 suggests that dispersion of the PSZ particles in the polypropylene melt was improved to some extent by the use of coupling agents. Somewhat stronger shear thinning appeared in the silane-treated system compared to the titanate-treated system. Consequently, the apparent viscosity became smaller in the former at high shear rates above $5 \times 10^3\,s^{-1}$. Such a tendency was observed even in compounds with lower powder concentrations (Fig. 6).

The effect of titanate concentration on the flow behaviour is shown in Fig. 7. Although the viscosity decreased with increasing titanate concentration, the decrease was not so great between 2% and 5%. The intensity of shear thinning also decreased with increasing titanate concentration up to 2%, but increased slightly between 2% and 5%. The explanation offered for the change of mixing torque in Fig. 4 can also be applied to such saturation of viscosity reduction and shear thinning intensity.

Fig. 8 shows the effect of temperature on the flow curves. In all compounds, the slopes of the flow curves were hardly affected by temperature. The activation energy for flow, E_a, obtained at a shear rate of $10^3\,s^{-1}$ is summarized in Table II. E_a was in the order

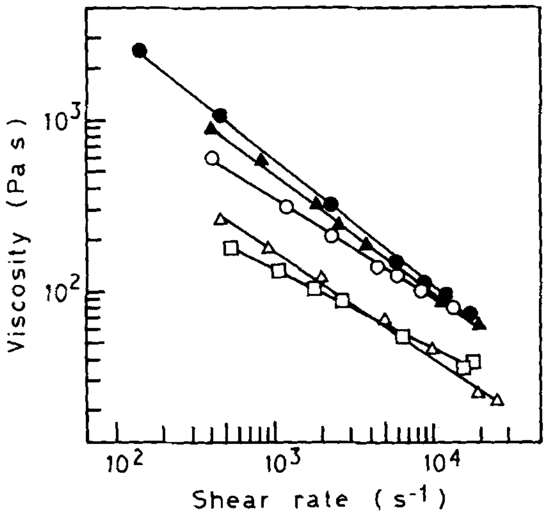

Figure 5 Curves of apparent viscosity versus shear rate at 180 °C for the same compounds as those in Fig. 3. (●) As-received, (▲) 0%, (○) A-2%, (△) S-2%, (□) T-2%.

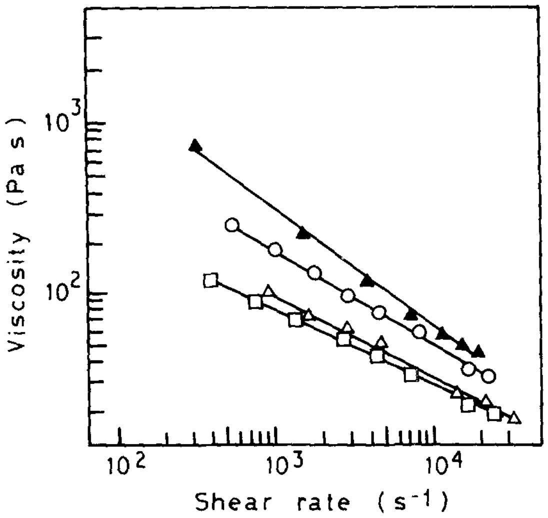

Figure 6 Curves of apparent viscosity versus shear rate at 180 °C in compounds with a corrected powder volume concentration of about 45% (cf. Table II). (▲) 0%, (○) A-2%, (△) S-2%, (□) T-2%.

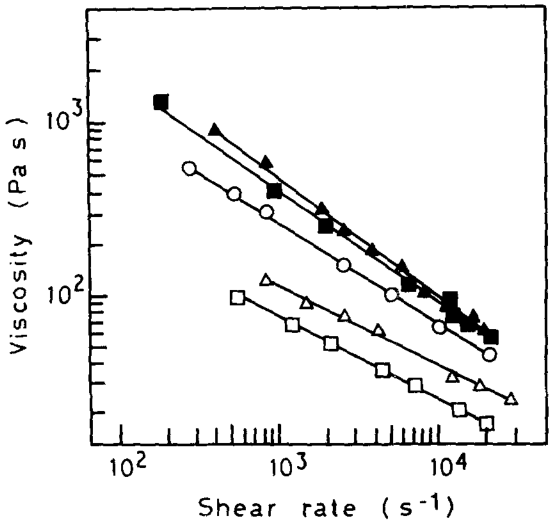

Figure 7 Curves of apparent viscosity and shear rate at 180 °C in compounds with a filler loading concentration of 50%, illustrating the effect of titanate concentration. (▲) 0%, (■) T-0.5%, (○) T-1%, (△) T-2%, (□) T-5% (cf. Table II).

T > S > A for compounds with 2% additions. E_a showed a negative correlation with the mixing torque, T_h, after 1 h and with the viscosity at a shear rate, η_a, of $10^3\,s^{-1}$, i.e. the lower T_h or η_a became, the higher was the activation energy.

E_a increased with increasing titanate addition (Table II). However, the change between 2% and 5% was much smaller than the change between 1% and 2%. Again, the critical value of 2% was coincident with the optimum titanate concentration estimated from TG (cf. Table I).

Compatibility with polypropylene is enhanced when the surface of the PSZ particles is covered by the molecules of coupling agent. As a result, it is quite probable that the interaction near the surface will gradually shift from powder–polymer to coupling agent–polymer or polymer–polymer. If such a change of interaction actually occurs, E_a of the compound fully treated with the coupling agent will approach that of the polymer. To verify this assumption, the activation energy of polypropylene without the PSZ filler was measured, and the value obtained was 45.8 kJ mol^{-1} which is close to 40.6 kJ mol^{-1} for the compound treated with 5% titanate. The same activation energy as that of the polymer melt indicates an ideal flow around particles although the flow behaviour near the particle surface still remains obscure in terms of fluid mechanics.

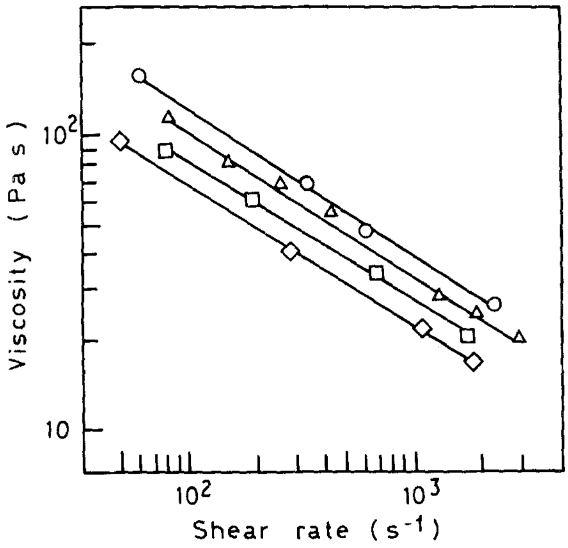

Figure 8 Effect of temperature on the flow characteristics of T-2% compounds with a filler loading concentration of 50%. (○) 170 °C, (△) 180 °C, (□) 190 °C, (◇) 200 °C.

TABLE II The apparent activation energy for flow calculated at a shear rate of $10^3\,s^{-1}$

Compound	Loading filler concentration (%)	Corrected filler concentration (%)	Activation energy (kJ mol^{-1})
Polypropylene	0	0	45.8
0%	45.0	44.7	15.8
A-2%	50.0	45.8	22.1
S-2%	50.0	45.6	33.5
T-0.5%	50.0	46.9	17.9
T-1%	50.0	45.8	20.0
T-2%	50.0	44.1	39.8
T-5%	50.0	40.1	40.6

4. Conclusions

The effects of the aluminate (A), silane (S) and titanate (T) coupling agents on the rheology of zirconia/polypropylene compounds were investigated experimentally. It was found that there is an intimate relation between the mixing torque after 1 h, T_h, the apparent viscosity, η_a, and the activation energy for flow, E_a, calculated at a shear rate of $10^3\,s^{-1}$. All coupling agents reduced both T_h and η_a, and their effectiveness on torque and viscosity reduction was in the order T > S > A > in compounds with 2% additions. On the other hand, the surface treatment increased E_a in the order T > S > A. Measurements made using compounds treated with different titanate concentrations showed that there is a critical concentration above which the rheological parameters such as T_h, η_a, and E_a do not change any further. This critical concentration was coincident with the optimum concentration estimated through thermogravimetric analysis.

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