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Influence of ambient temperature on the rheological properties of alumina tape casting slurry

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Abstract

Pseudoplasticity and viscosity of slurries are two important characteristics which are always monitored to get good and reproducible tape-cast samples. Though it is known that the viscosity of solvents changes with temperature, no work has so far been done to study the viscosity of standard tape casting slurries with ambient temperature (which shows seasonal variation), excepting a few reports on slurries containing powder and dispersant only. In the present work, it has been observed that ambient temperature has a significant effect on the viscosity and shear rate exponent of a typical tape casting slurry containing powder, dispersant, binder and plasticizer. Though the dispersant and plasticizer have important roles to modify the viscosity and shear rate exponent of a tape casting slurry, the binder plays the key role to exhibit the temperature dependence of viscosity and shear rate exponent of the tape casting slurry. The roles of binder, plasticizer and dispersants have been studied to explain the slurry characteristics with temperature. From the present study it can be inferred that the influence of ambient temperature during tape casting should be taken into account to get truly reproducible tape-cast samples.

Keywords: Al_2O_3; Suspensions; Tape casting

1. Introduction

Tape casting is widely used in manufacturing thin sheets of ceramic materials primarily for various electronic applications like multilayered capacitors, ceramic substrates and packages, transducers, actuators, solid-oxide fuel cell etc.[1–5] Tape casting is a well-known process and basically consists of the preparation of a stable slurry of ceramic powder in a nonaqueous or aqueous medium usually by adding dispersants. Also binder and plasticizers are added to confer strength and flexibility to the green tapes. The most important characteristic[6] of a powder suspension for successfully tape casting is its rheological behaviour. The solid loading must be high, but, at the same time, the viscosity must be low enough to facilitate the flowability of the slip through the doctor blade. Pseudoplastic (shear thinning) behaviour is desired,[6] where the viscosity decreases because of the shear force that takes place when the slip passes under the blade. Just beyond the blade no shear force is present and the viscosity increases again preventing sedimentation of the particles and the uniformity of the slip is preserved by reducing the mobility of the constituents. Though it is known that rheological properties are affected by temperature, a little work has been done to understand the variation of rheological properties of tape casting slurry with temperature so as to get reproducible properties of the tape-cast samples even at different ambient temperatures, (e.g., due to seasonal change). There are only a few reports of such study on slurries containing powder and dispersants only. For example, Uematsu et al.[7] studied the sedimentation behaviour and electrophoretic mobility of alumina–water–polyelectrolytic dispersant at 20 and 40 °C. Tomita et al.[8] also studied the effect of temperature on the dispersion characteristics of alumina slurry. Pagnoux et al.[9] evaluated the influence of temperature on the stability of aqueous alumina suspension dispersed with either sodium salt of polymethacrylic acid or Tiron. Yang and Sigmund[10] studied the temperature dependence of relative viscosity of alumina suspension with polyacrylic acid addition.

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In the present work, the rheological properties of alumina tape casting slurries (in a standard nonaqueous medium) throughout the temperature range of −5° to 35 °C have been evaluated. Such understanding is essential to get reproducible properties of the samples tape-cast at different ambient temperatures.

2. Experimental procedure

Alumina (A-16SG) from Alcoa, India was used for the present study. The average particle size of the powder was 0.5 μm as observed from particle size analyzer (Sedigraph, Micromeritics). Suspensions of alumina were prepared using reagent grade solvents consisting of an azeotropic mixture of methyl ethyl ketone (MEK) and ethanol (66:33 by volume). Alumina and the solvent in the weight ratio of 57:43 along with 1–3 wt.% phosphate ester (Emphos PS21-A, Witco Chemicals, USA) were ball milled for 20 h using alumina balls to get the desired suspension.

Electrophoretic mobilities of the particles in the above suspension were studied (after dilution) using a micro-electrophoresis apparatus (Zetameter 3.0+ Zeta-Meter Inc., USA).

For evaluating the sedimentation behaviour, 10 ml of the suspension and 20 ml of the solvent were shaken thoroughly in a 50 ml glass stoppered graduated cylinder. The height of the sediment (initially as a dispersed phase when there was no sedimentation and as a settled mass) was measured after different days standing.

A typical alumina tape casting slurry was made as per the composition given in Table 1. To prepare the tape casting slurry, alumina powder along with the dispersant was ball milled in the solvent for 20 h using alumina balls. Then binder, plasticizer and homogenizer were added to the slurry followed by further milling for 24 h. Slurries were also made without adding binder/plasticizer to understand their impact on rheological characteristics.

Rheological measurements of the slurries were carried out using a concentric cylinder rotational viscometer (VT500 Haake, Germany, equipped with the sensor system SV1) at different shear rates from 4.45 to 440.6 s^{-1}. The measurements were carried out at five different temperatures from −5, to +35 °C with an interval of 10 °C. At each point the temperatures of the slurry was controlled within ±0.5 °C using a refrigerated bath with circulator (F3-K, Haake, Germany). During measurement, the system was allowed to equilibrate at each temperature for half an hour before evaluating the shear dependent properties. The experimental tests at a particular temperature were performed in 5 min by ascending the shear rate from 4.45 to 440.6 s^{-1} in 10 equal steps. A 20 s equilibration time was given to the system at each shear rate before measurement.

3. Results and discussion

The variation of electrophoretic mobility of alumina suspension with the concentration of dispersant (phosphate ester) is shown in Fig. 1. It is evident from the figure that the optimum dispersion should be obtained at 1.75 wt.% phosphate ester concentration, which corresponds to maximum in electrophoretic mobility or equivalently highest in zeta potential. The sediment heights with days (Fig. 2) indicate that the slurries containing phosphate ester around the optimum concentration (i.e., 1.75 wt.%) remain more or less stable for 5–7 days and then start settling at a fast rate. As expected,[11] the slurry containing no dispersant settled within a day and showed higher sediment (settled mass) volume.

To understand the settling behaviour of phosphate ester containing slurries, we have to first appreciate that phosphate ester acts as an electrostatic[12] dispersant. Phosphate ester ionizes only to a very small extent in the MEK/ethanol solvent.[13] In a nonaqueous system the surfactant adsorbs onto the powder surface as neutral molecules. After adsorption, the surfactant transfers a proton to the powder surface, charging it positively. Some portion of the anion surfactants then desorb, leaving a charged particle. The anion then acts as the electrolyte in the

Table 1
Composition of alumina tape casting slurry

Ingredient	Function	Weight (%)
Al_2O_3 (Alcoa, ACC, India)	Ceramic	59.86
Phosphate Ester (Emphos PS21-A)	Dispersant	1.05 (equivalent to 1.75 wt.% of Al_2O_3)
Methyl Ethyl Ketone (E. Merck India Ltd.) + Ethanol (Bengal Chemicals & Pharmaceuticals Ltd. India.)	Solvent	28.28
Polyvinyl Butyral (Hipol B-30, Hindustan Inks and Resins Ltd. Gujrat, India)	Binder	5.24
Polyethylene Glycol (S. D. Fine-Chem Pvt. Ltd.)	Plasticizer	3.03
Butyl Benzyl Pthalate (Merck - Schuchardt)	Plasticizer	2.09
Cyclohexanone (S. D. Fine-Chem Pvt. Ltd.)	Homogenizer/Skin inhibitant	0.45

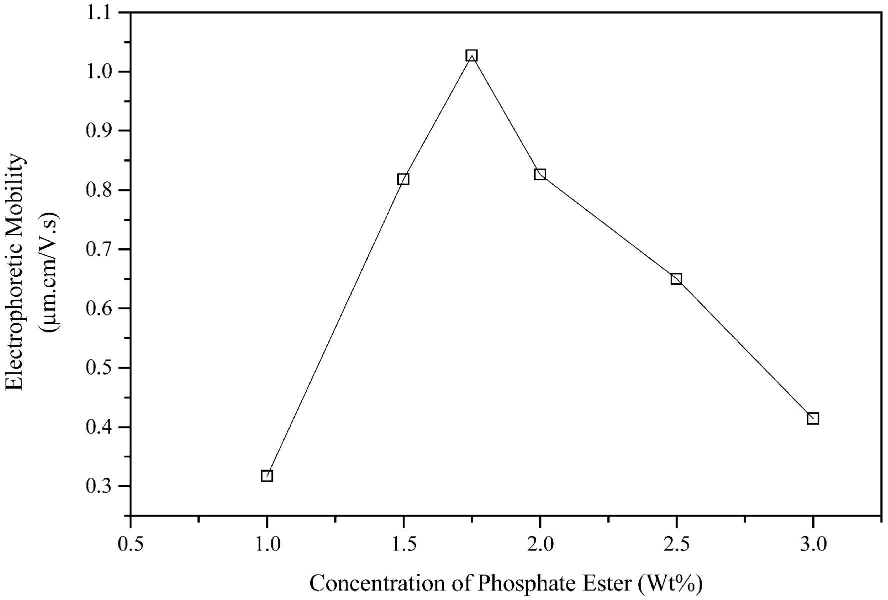

Fig. 1. Variation of electrophoretic mobility of alumina suspension with phosphate ester concentration.

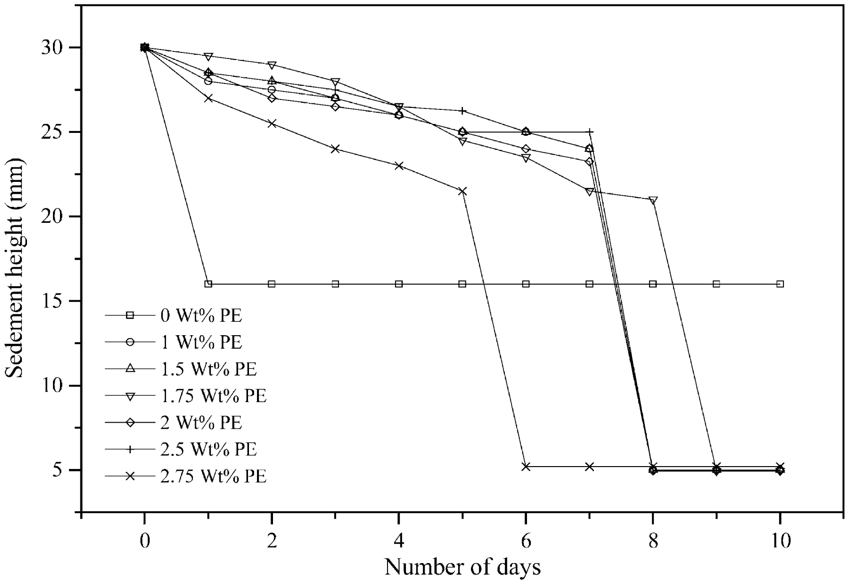

Fig. 2. Variation of sediment height with days for alumina suspensions containing different amounts of phosphate ester.

double layer. However, steric effect[14] due to phosphate ester can also help in dispersion. Generally, suspensions contain a mixture of particles of different shapes and sizes. In such cases, it has been observed[15] that larger spheres attract each other if they get close enough (given sufficient time and considering Brownian motion) such that there is no room for a smaller sphere to fit between them. This is because of the fact that moving the larger spheres together increases the available volume for and hence the entropy of the smaller spheres. Once some particles are close together, either depletion flocculation or bridging flocculation should take place depending on the concentration of the free polymers[16] (here, long chain phosphate ester molecules). Such flocculated particles start settling and once settling starts, it leads to a chain reaction because each particle(s) drags fluid along with it, which then drags on other particles[17] resulting in fast settling of the particles in the slurry.

Fig. 3 depicts the variation of the viscosity of a slurry (containing powder, solvent and 1.75 wt.% phosphate ester and at a temperature of 25 °C) with shear rate. As evident from the figure, the slurry shows strong shear thinning (pseudoplastic) behaviour and can be fitted by power law model[18] (Hershel–Buckey relation[19] with zero yield stress) given by:

$$\tau = \mathrm{k}\dot{\gamma}^{\mathrm{n}} \tag{1}$$

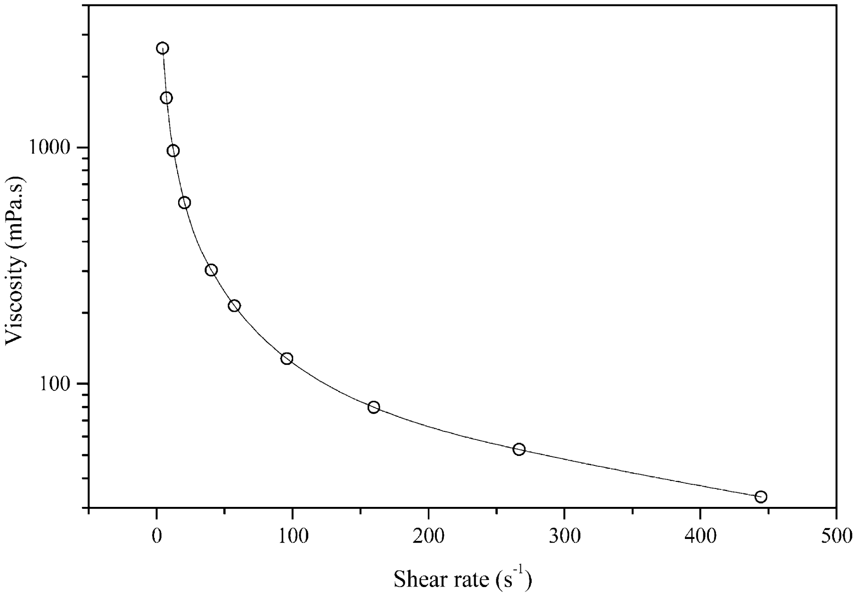

Fig. 3. Variation of viscosity (at 25 °C) of the slurry (containing powder, solvent and 1.75 wt.% phosphate ester) with shear rate.

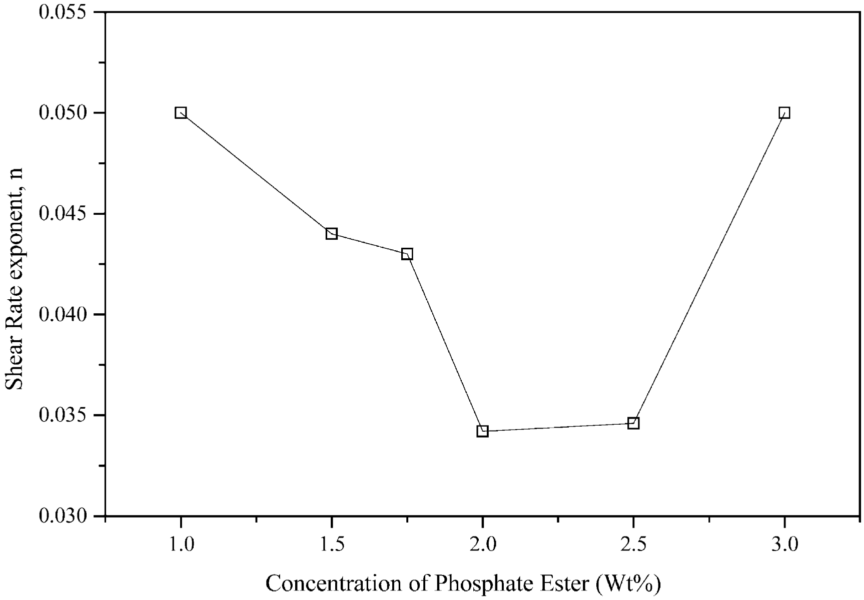

Fig. 4. Variation of shear rate exponent (at 25 °C) of the slurry containing (powder and solvent) with phosphate ester concentration.

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, k is the shear rate factor (also called consistency coefficient) and n is the shear rate exponent (also called flow behaviour index). The shear rate exponent value $n < 1$ is attributed to shear thinning in particle loaded systems and the greater the divergence from Newtonian behaviour, the lower is the value of n. Normally, at low shear rates, the suspension structure is close to equilibrium because the thermal motion dominates over the viscous force (first Newtonian region).[20] At high shear rates, the viscous forces affect the suspension structure and shear thinning occurs due to progressive breakdown of particulate network or agglomerate (floc) structure. At very high shear rates, viscous forces dominate and normally a plateau in viscosity is observed (second Newtonian region)[20] indicating completely hydrodynamically (arising from the shear field) controlled structure.[21]

Fig. 4 shows the variation of shear rate exponent of the slurry (containing powder and solvent and at 25 °C) with the concentration of phosphate ester. Weakly flocculated structure[22] shows strong shear thinning tendency (or in other words low shear rate exponent). Here (Fig. 4), as expected the shear rate exponent, is low (i.e., high shear thinning) around the dispersant concentration of 2.0–2.5 wt.%, where weakly flocculated structure is formed as the dispersant concentration is

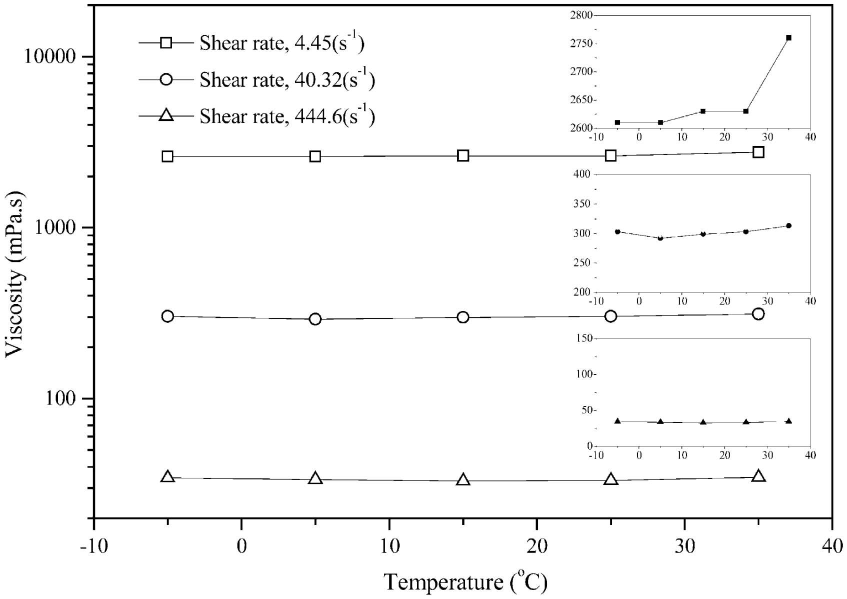

Fig. 5. Viscosity vs. temperature behaviour of the slurry containing powder, solvent and 1.75 wt.% phosphate ester (Insets show the zoomed view).

slightly off from the optimum concentration (maximum in electrophoretic mobility). Much above or below the optimum dispersant concentration the flocs should be more rigid (due to bridging or depletion flocculation) leading to relative low shear thinning.

A typical trend of viscosity vs temperature for the same slurry (containing 1.75 wt.% phosphate ester) at different shear rates has been depicted in Fig. 5. To understand the behaviour of the slurry with temperature, we have to consider the following points. Firstly, the effect of temperature on the viscosity (η) of the solvent ususally follows an Arrhenius type of relationship[19] given by:

$$\eta = \mathrm{A}e^{-\mathrm{B}/T} \tag{2}$$

where A and B are constants and T is the temperature.

Secondly, the flow properties of suspensions depend upon the degree of agglomeration as a result of the dynamic equilibrium between the hydrodynamic force and interactive force between the particles. The maximum hydrodynamic force[23] (F_H) between two touching spheres can be described as

$$F_\mathrm{H} \sim 6.12\pi\eta \mathrm{R}^2\dot{\gamma} \tag{3}$$

where η is the solvent viscosity, R is the radius of flow unit and $\dot{\gamma}$ is the shear rate. It has been observed that at a given shear rate, an increase in temperature results[5] in the reduction of hydrodynamic force (arising from the shear field), which, in turn, could stabilize more agglomerates.

Thirdly, adsorption/desorption of dispersant (phosphate ester) on the powder (Al_2O_3) is a dynamic process. Desorption is facilitated by increasing the temperature and the higher the temperature, the higher is the concentration of dispersant needed to disperse the slurry.[8]

And fourthly, it is known that[6,16] osmotic pressure differences between the bulk solution and the solution in the gap between the particles with attached polymer species can cause depletion stabilization. Interestingly, osmotic pressure (Π) is directly proportional to temperature as given below:[24]

$$\Pi = M\mathrm{R}T \tag{4}$$

where M is the concentration of the solution, R is the gas constant and T is the temperature. Hence, higher osmotic pressure at elevated temperature may enhance depletion stabilization. The interplay of all the above factors dictates the viscosity vs. temperature behaviour of a slurry.

In our case, we have to first note that the variation of viscosity[25] of ethanol and MEK is less than 1 mPa.s in the temperature range of interest (−5 to 35 °C) and can be ignored for the present discussion. It has been observed (Fig. 5) that at high shear rates, the low temperature and room temperature viscosity values are nearly the same, whereas, at low shear rate, the room temperature viscosity of the slurry is higher than the low temperature viscosity. As discussed earlier, an increase in temperature may lead to desorption of the dispersant, resulting in increased slurry viscosity due to formation of more agglomerates. However, at higher shear rates, agglomerates break down resulting in more or less unchanged slurry viscosity with temperature. The character of the flocs probably does not change with temperature as is evident from the near horizontal shear rate exponent vs. temperature curve of Fig. 6.

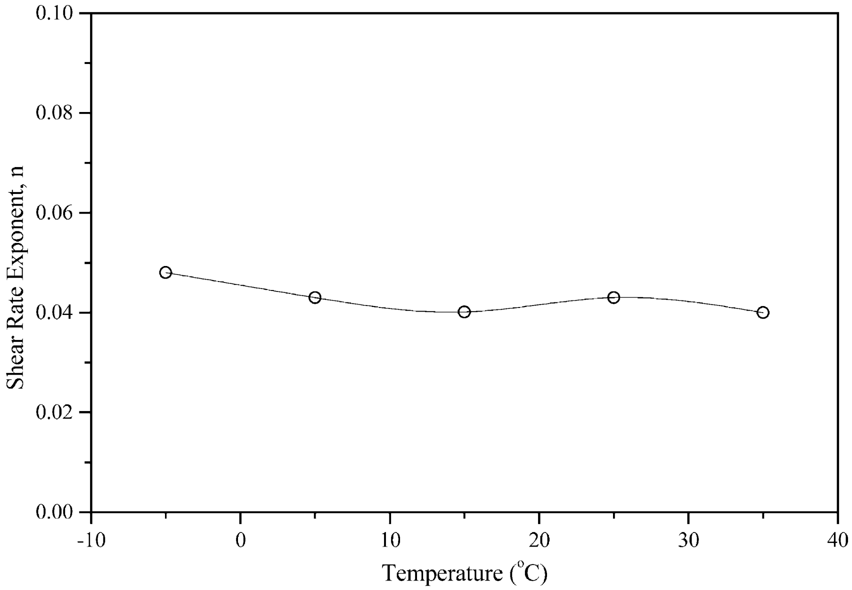

Fig. 6. Variation of shear rate exponent with temperature of the slurry containing powder, solvent and 1.75 wt.% phosphate ester.

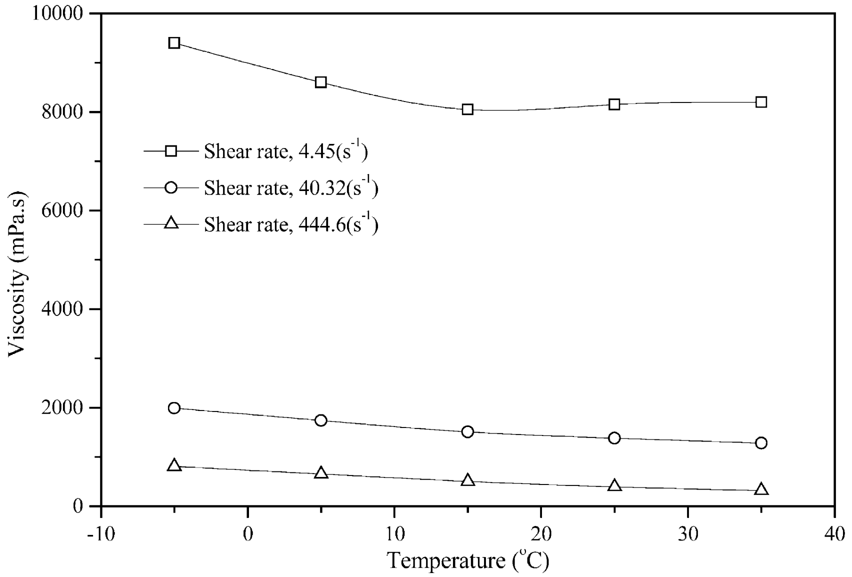

Fig. 7. Viscosity vs. temperature behaviour (at three different shear rates) of a typical tape casting slurry of composition given in Table 1.

Fig. 7 depicts the viscosity vs. temperature curve (at three different shear rates) of a typical tape casting slurry of composition given in Table 1. In contrast to the behaviour of the slurry containing the powder and the dispersant only (Fig. 5), the tape casting slurry shows: (a) lower shear thinning, which is also evident from the values of shear rate exponents (Fig. 8) and (b) an appreciable decrease in viscosity with temperature (around 35–60% from −5 to 35 °C) specifically at the moderate shear rate (which is important for tape casting) and at high shear rate. Also the temperature has a prominent effect on shear rate exponent for the tape casting slurry (Fig. 8). To understand such behaviour which is of utmost importance for reproducible tape casting, we studied the viscosity vs. temperature behaviour of tape casting slurries excluding (a) binder in the first case and (b) plasticiser in the second case.

Fig. 9 shows the viscosity temperature characteristics of the slurry without binder. It is evident from the figure that the viscosity of the slurry without binder is temperature independent (for medium and high shear rates) in contrast to that with the binder (Fig. 7). At low shear rate, the complex nature of the variation of viscosity, albeit low, may be accounted for by considering the delicate interplay of the different factors described earlier. However, it is evident from Fig. 10 that at medium and high shear rates, the viscosity of the slurry containing the binder (but without any plasticizer) decreases

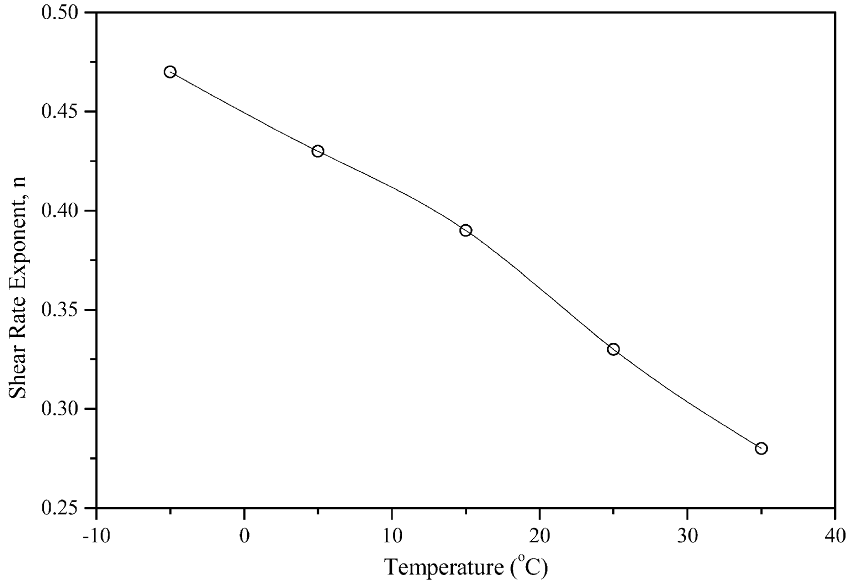

Fig. 8. Variation of shear rate exponent of the typical tape casting slurry (composition given in Table 1) with temperature.

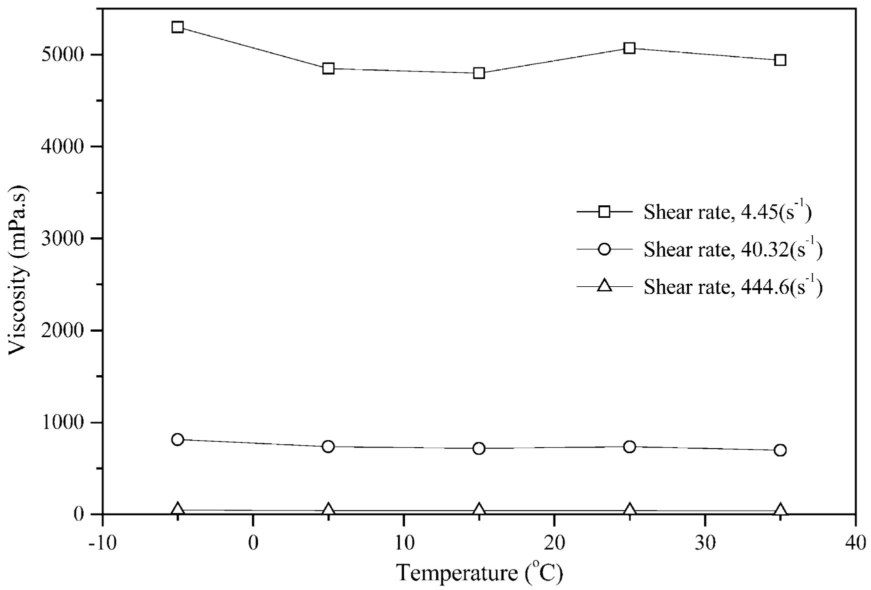

Fig. 9. Viscosity vs. temperature behaviour of the typical tape casting slurry excluding binder only.

with temperature. Hence, it can be concluded that the binder (PVB) plays a key role in generating the typical viscosity vs. temperature profile of the slurry. To understand the role of the binder in imparting temperature dependence of slurry viscosity it is to be appreciated that vinyls have flexible backbones because of the rotatable carbon–carbon bonds and these can lead to a molecule with a coiled and curving configuration.[26] Thus the spatial length of the molecule may be much smaller than the actual length of the molecule backbone. The time-average volume of the binder molecule can be distorted by shear force in the liquid.[26] The molecules tend to line up in a manner that reduces the resistance to flow (pseudoplasticity). Higher, temperature can make the backbones more flexible (easy rotation of carbon–carbon bonds) and can help aligning the molecules (more so at high shear rates) resulting in lowering of the viscosity with temperature. However, plasticizer like PEG has a tendency to form organic bridges between the particles,[6] which are disrupted at high shear rates. This is corroborated in Fig. 11, where the slurry containing the plasticizer (i.e., the typical tape casting slurry without the binder) shows the highest shear thinning (lowest shear rate exponent) behaviour.

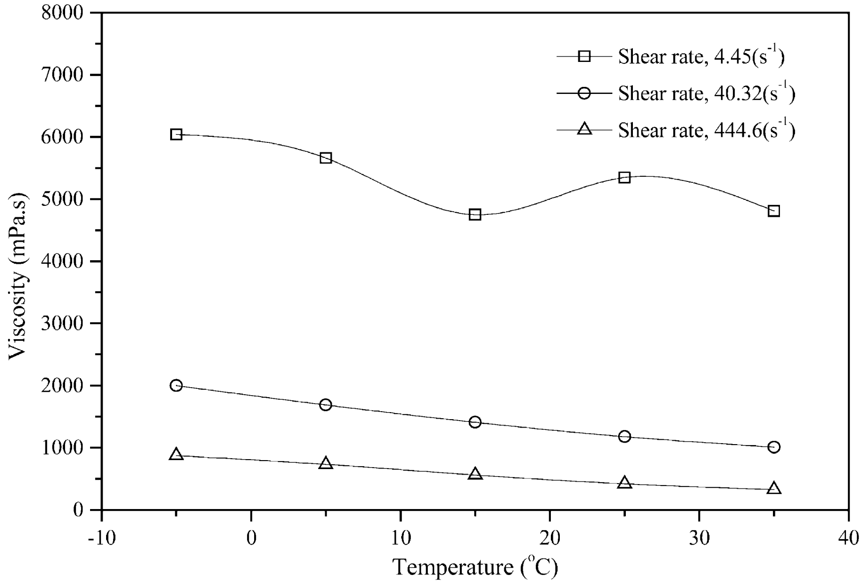

Fig. 10. Viscosity vs. temperature behaviour of the typical tape casting slurry excluding plasticizer only.

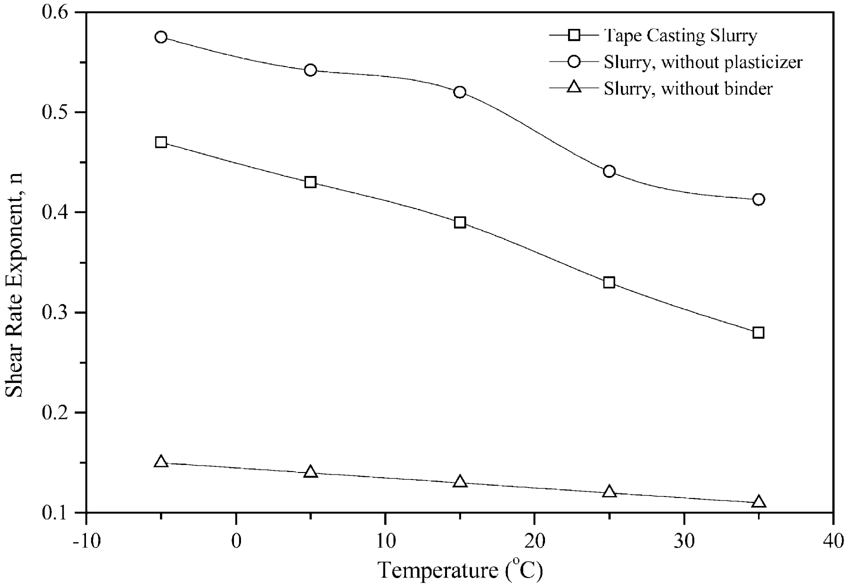

Fig. 11. Shear rate exponent vs. temperature curves of typical tape casting slurry, slurry without plasticizer and slurry without binder.

4. Conclusions

(a) It has been observed that two important characteristics of tape casting slurry, namely, viscosity and shear rate exponent show significant temperature dependence around the ambient temperature.

(b) Though the dispersant and plasticizer have definite roles in modifying the viscosity and shear rate exponents of the slurry, the binder (PVB) plays the key role in imparting the temperature dependent behaviour of tape casting slurry.

(c) It is essential to consider the importance of monitoring the ambient temperature during tape casting to get truly reproducible tape-cast samples as can be inferred from the present study.

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