The Effect of Filler Size, Rheology Control Agent Content and Temperature Variation on Viscosity of Epoxy Resin System

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Abstract— In this study, viscosity variation for three different epoxy resin adhesives including three different fillers was determined with increasing the CABOSIL TS 720 content from 1% to 5% and reducing the filler content from 19.9 to 15.9% at the temperatures of 25, 40 60, 70 and 80^{0}C. Variation of viscosity was also determined for SHELL resin system consisting of EPIKOTE® 828 epoxy resin and EPIKURE® 3090 polyamidoamine curing agent. Calcite with having three different particle diameters of 0.7, 0.9 and 10 µm was used as filler. CABOSIL® TS 720 used as rheology control agent was an other filler. Viscosity models were developed with measuring the viscosity by using HA model Brookfield type DV-II+Pro Viscometer with SC4-27 spindle at constant shear rate. It was found that viscosity increased as CABOSIL® TS 720 content increased and viscosity decreased with increasing the temperature. Generally, the adhesive prepared by the calcite with the particle diameter of 0.7 µm gave the lowest viscosity value.

Keywords— Adhesives, epoxy resin, viscosity, fillers, particle size distribution

I. INTRODUCTION

Fluids are generaly separated into two categories known as Newtonian and non-Newtonian. In Newtonian fluids, viscosity does not vary with changing shear rates, whereas, viscosities of non-Newtonian fluids vary at different shear rates. Non-Newtonian fluids are also divided into two groups as time independent non-Newtonian and time dependent non-Newtonian. Time independent non-Newtonian fluids show pseudoplastic, dilatant behaviour when time dependent non-Newtonian fluids represent thixotropic, rheopectic behaviour [1].

Epoxy resins extensively used in coating and adhesive industry demonstrate both thixotropic and rheopectic behaviour together. Viscosity measurement of a thermoset material during processing is very complicated due to kinetic rate of conversion from a liquid to a solid material [2].

Fumed silicas are commonly used in coating and adhesive industry as rheological control agents [3]. CABOSIL® TS 720 treated fumed silica is a very efficient thixotrope for epoxy resin adhesives., giving a stable sag resistance at vertical surfaces without changing other properties such as cure rate or lap shear tensile strengths of adhesives [4].

Temperature, shear rate and loading level of filler are factors influencing the rheology of the epoxy resins and effect of those factors was also studied (5-12). Investigations including epoxy resin and fumed silica were met(14-19).

The rheological properties of composites and the variations during hardening process were explored on literature data (20-21)..Kinetics of the chemical reactions during hardening were also investigated(22-27).

The aim of the study is to investigate rhe variations in the rheological properties of the epoxy resin depending on rheology control agent content, filler size and temperature,

2. EXPERIMENTAL

Fifteen different types of adhesives were prepared with the addition of EPIKOTE® 828 epoxy resin and EPIKURE® 3090 polyamidoamine curing agent with a ratio of 1:1 by weight. CABOSIL® TS 720 rheology control agent was increased from 1 to, 2, 3, 4 and 5% , while one of three fillers (calcite with the mean particle diameter of 0.7 µm, calcite with the average particle diameter of 0.9 µm, calcite with the mean particle diameter of 10 µm) was decreasing from 19.9 to 15.9%. Those adhesives were also mixed by a mechanical stirrer for five minutes approximately to insure the complete mixing. Then, viscosity of the samples was measured by using HA model Brookfield type DV-II + Proviscometer with the usage of complete computer control in terms of ‘’Rheocalc’’ software collecting data automatically. Variation of viscosity was also measured with changing the temperature from 25 to 40, 60, 70 and 80^{0}C by providing temperature control between water jacket of small sample adapter and water bath.

3. RESULTS AND DISCUSSION

Viscosity variation and thixotropy are very important in the application of epoxy resin adhesives before hardening in spite

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of the fact that the observation of rheopexy during the curing reaction. Application time can be adjusted with respect to the amount of fumed silica known as CABOSIL® TS 720. For this reason, viscosity variation and thixotropic, rheopectic behaviour of epoxy resin adhesives including five different CABOSIL® TS 720 content and calcite with three different particle diameters at the temperatures of 25, 40, 60, 70 and 80^0C were investigated in this study. Thixotropic, rheopectic behaviour and viscosity variation of three compositions were determined by increasing the CABOSIL® TS 720 content from 1% to 2, 3, 4 and 5% and decreasing the filler content from 19.9 % to 18.9, 17.9, 16.9 and 15.9% at equal amount for each temperature in terms of constant shear rate. However, thixotropy was not observed for all compositions, while rheopexy was attained for all compositions because of the curing reaction between epoxy resin and curing agent. Viscosity models depending on time for each adhesive were developed as well and results are given in Tables 1, 2, 3, 4 and 5.

Viscosity variation of three adhesives including calcite with three different particle diameters of 0.7 µm, 0.9 µm and 10 µm at 25^0C was observed for the CABOSIL® TS 720 content of 1, 2, 3, 4 and 5% . Only the composition containing calcite with the particle diameter of 0.9 µm gave thixotropy, while other compositions were demonstrating no thixotropy for the CABOSIL® TS 720 content of 1%. When the CABOSIL® TS 720 content was increased to 2%, lower thixotropy was observed for the compositions having calcite with the particle diameters of 0.7 and 0.9 µm, whereas, thixotropy was not attained for the composition containing calcite with the particle diameter of 10 µm. Thixotropy and rheopexy were obtained for three compositions definitely at the CABOSIL® TS 720 content of 3 and 4%. No thixotropy was followed for two compositions including calcite with the particle diameters of 0.7 µm and 0.9 µm, while other composition including calcite with the particle diameter of 10 µm was representing thixotropy and rheopexy at the CABOSIL® TS 720 content of 5%. This effect is also easily observed from Table 1, therefore, the adhesives containing calcite with the particle diameter of 0.7 and 0.9 µm gave only line equations in viscosity model for CABOSIL® TS 720 content of 1, 2 and 5%, while these adhesives were indicating polynomial equations in viscosity model for CABOSIL® TS 720 content of 3 and 4%. It was generally determined that viscosity and thixotropy increased as CABOSIL® TS 720 content increased. The reason why thixotropy increases with increasing the CABOSIL® TS 720 content is that the process of epoxy hardening is retarded by the presence of filler based on silica with low particle size distribution (5). It acts as curing retardation agent for a while as a consequence of the aggregates between the solid particles and the polymer chain by van der Waals forces(4). In general, higher viscosity values were observed for the adhesives including calcite with the particle diameters of 0.7 µm and 0.9 µm at the temperature of 25^0C for all CABOSIL® TS 720 content except for 4%. The reason for this can be explained in terms of reducing the particle size of the filler. This effect leads to an increase in the number of particles and higher number of smaller particles results in more particle-particle interactions and an increased viscosity (28-33). For this reason, the composition including calcite with the highest particle diameter of 10 µm gave the lowest viscosity for the CABOSIL® TS 720 content of 2, 3 and 5% at the temperature of 25^0C. Since, low filler contents and large particle sizes resulted in low viscosity resin (16-19). Lower particle size effect on viscosity is observed from Figures 1, 2, 3 and Table 1.

Table 1. Viscosity models of SHELL adhesives with respect to CABOSIL TS 720 content and particle diameter at the temperature of 25^0C

CABOSIL TS 720 content (%)	Viscosity variation	Particle diameter (µm)	Viscosity models at the temperature of 25^0C
1	High	0.9	V=8.719t+37085
	Medium	10	V=5.528t+29782
	Low	0.7	V=7.299t+22187
2	High	0.9	V=11.3t+76851
	Medium	0.7	V=8.923t+66873
	Low	10	V=10.17t+48233
3	High	0.7	$V=0.003t^2-1.443t+21390$
	Medium	0.9	$V=0.006t^2-21.14t+16429$
	Low	10	$V=0.013t^2-62.38t+15070$
4	High	10	$V=0.049t^2-251.3t+2E+06$
	Medium	0.9	$V=0.052t^2-394.9t+2E+06$
	Low	0.7	$V=0.027t^2-267.3t+1E+06$
5	High	0.9	V=17194t+3E+07
	Medium	0.7	V=13068t+3E+07
	Low	10	V=1.477t2-10087t+4E+07

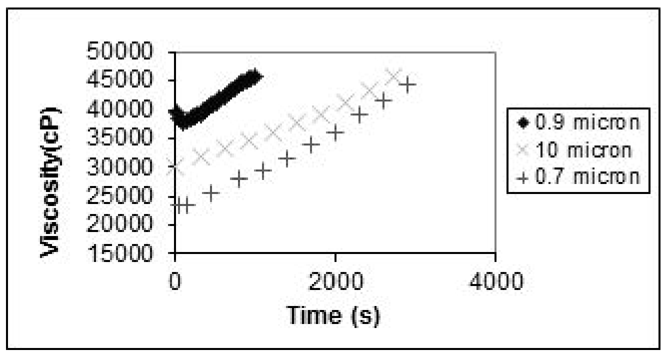

Figure 1 Viscosity variation of SHELL adhesive according to three different fillers for CABOSIL TS 720 content of 1% at the temperature of 25^0C

Viscosity variation of three compositions including SHELL resin system, calcite with three different particle diameters of 0.7 µm, 0.9 µm and 10 µm at 40^0C was detected for the CABOSIL® TS 720 content of 1, 2, 3, 4 and 5%. Even though, a little bit effect of thixotropy was observed for three compositions at the CABOSIL® TS 720 content of 1%, a rise in thixotropy was attained with an increase in CABOSIL® TS 720 content until 4 %. When the CABOSIL® TS 720 content was increased to 5%, viscosity increased and higher

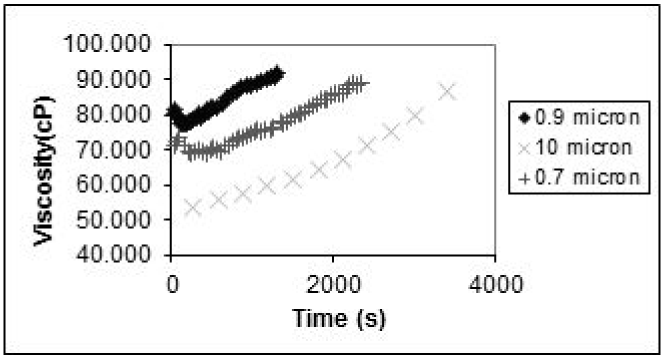

Figure 2 Viscosity alteration of SHELL adhesive including three different fillers for CABOSIL TS 720 content of 2 % at the temperature of 25^0C

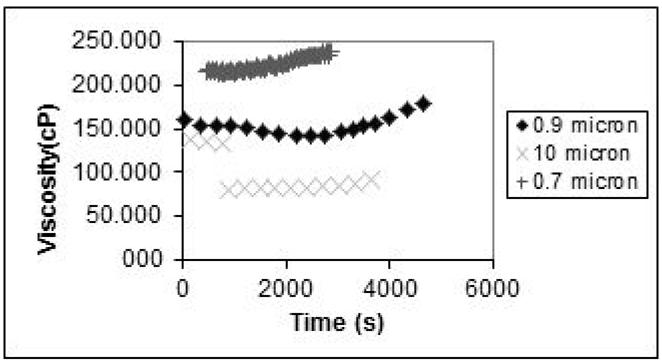

Figure 3 Viscosity variation of SHELL adhesive with respect to three different fillers for CABOSIL TS 720 content of 3 % at the temperature of 25^0C

thixotropy was obtained than at the CABOSIL® TS 720 content of 4% for two compositions including calcite with the particle diameters of 0.9 µm and 10 µm. However, other composition containing calcite with the particle diameter of 0.7 µm indicated lower thixotropy than at the CABOSIL® TS 720 content of 4%. Results showed that viscosity and thixotropy generally increased with increasing the CABOSIL® TS 720 content. Although, the adhesive with having the particle diameter of 0.9 µm gave the highest viscosity at the temperature of 40^0C for the CABOSIL® TS 720 content of 1, 2 and 3% , the lowest viscosity values were observed for the CABOSIL® TS 720 content of 4 and 5% at the same temperature. This effect may be expressed owing to the influence of particle size distribution between silica and calcite with reducing the calcite amount and increasing the CABOSIL® TS 720 content(28-32). Effect of CABOSIL® TS 720 content on viscosity and thixotropy is given in Figures 4, 5, 6, 7, 8 and Table 2.

Table 2. Viscosity models of SHELL adhesives with respect to CABOSIL TS 720 content and particle diameter at the temperature of 40^0C

Cabosil TS 720 content(%)	Viscosity variation	Particle diameter(µm)	Viscosity models at the temperature of 40^0C
1	High	0.9	$V=0.004t^2-0.199t+7723$
	Medium	10	$V=0.003t^2-3.822t+7029$
	Low	0.7	$V=0.003t^2-2.17t+5733$
2	High	0.9	$V=0.004t^2-1.645t+15358$
	Medium	10	$V=0.005t^2-5.078t+13203$
	Low	0.7	$V=0.006t^2-6.124t+11064$
3	High	0.9	$V=0.009t^2-13.85t+35083$
	Medium	10	$V=0.008t^2-14.46t+31403$
	Low	0.7	$V=0.01t^2-17.87t+26091$
4	High	10	$V=0.042t^2-126.7t+19752$
	Medium	0.7	$V=0.049t^2-154t+20406$
	Low	0.9	$V=0.028t^2-79.3t+12364$
5	High	10	$V=5.786t^2-28214t+6E+07$
	Medium	0.7	$V=5.64t^2-11989t+3E+07$
	Low	0.9	$V=7.336t^2-25520t+3E+07$

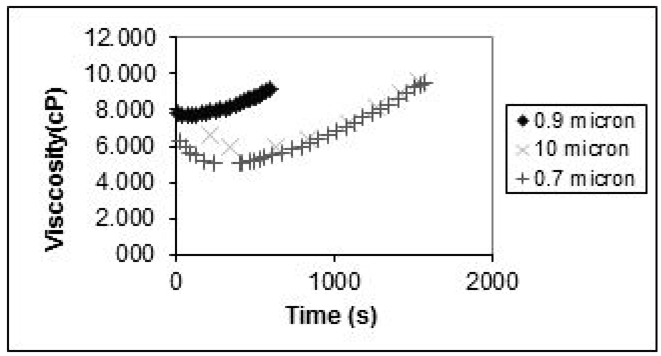

Figure 4 Viscosity alteration of SHELL adhesive according to three different fillers for CABOSIL TS 720 content of 1 % at the temperature of 40^0C

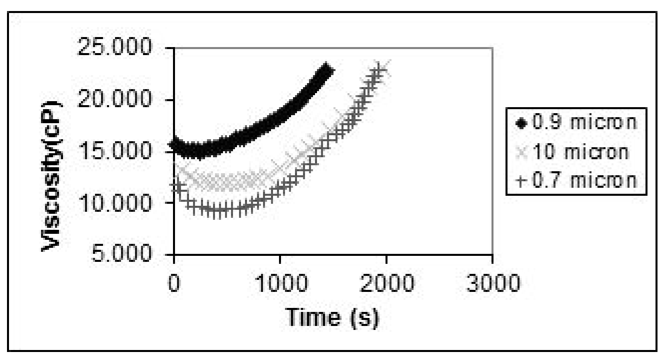

Figure 5 Viscosity variation of SHELL adhesive having three different fillers for CABOSIL TS 720 content of 2 % at the temperature of 40^0C

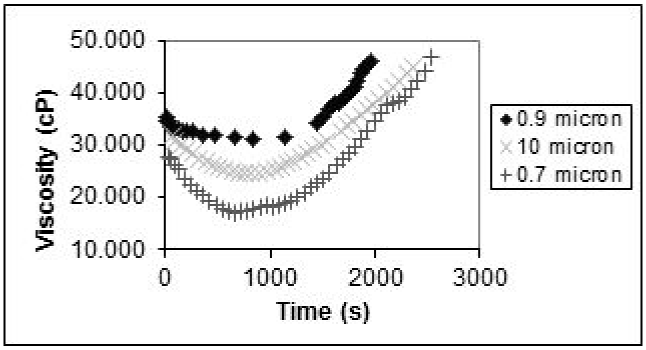

Figure 6 Variation of viscosity for SHELL adhesive including three different fillers with CABOSIL TS 720 content of 3% at the temperature of 40^{0}C

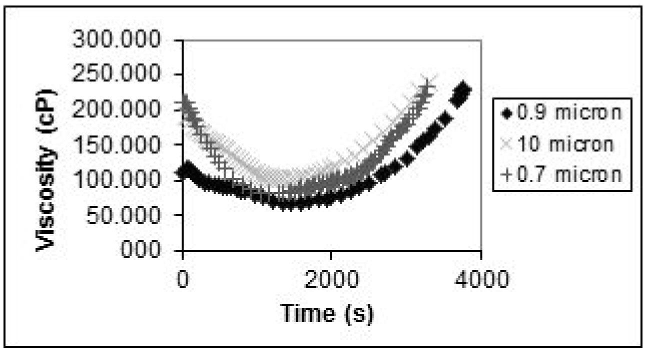

Figure 7 Alteration of viscosity for SHELL adhesive containing three different fillers for CABOSIL TS 720 content of 4 % at the temperature of 40^{0}C

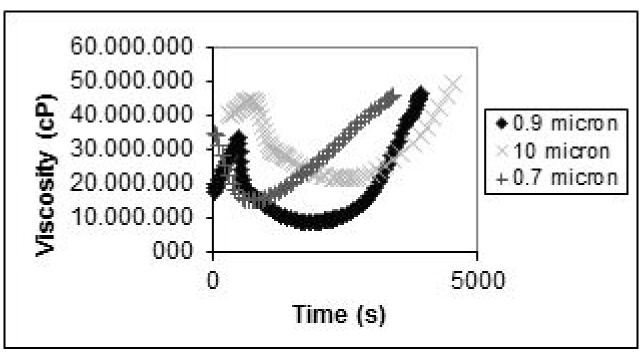

Figure 8 Viscosity variation of SHELL adhesive with respect to three different fillers for CABOSIL TS 720 content of 5 % at the temperature of 40^{0}C

Viscosity variation of three compositions including calcite with three different particle diameters of 0.7 µm, 0.9 µm and 10 µm at 60^{0}C was determined for the CABOSIL® TS 720 content of 1, 2, 3, 4 and 5% and results are represented in Table 3.

Table 3. Viscosity models of SHELL adhesives with respect to CABOSIL TS 720 content and particle diameter at the temperature of 60^{0}C

CabosilTS 720 content(%)	Viscosity variation	Particle diameter(µm)	Viscosity models at the temperature of 60°C
1	High	10	$V=0.01t^2-3.142t+2698$
	Medium	0.9	$V=0.012t^2-7.619t+3775$
	Low	0.7	$V=0.009t^2-7.245t+3019$
2	High	10	$V=0.072t^2-41.06t+14474$
	Medium	0.7	$V=0.029t^2-22.98t+7753$
	Low	0.9	$V=0.027t^2-19.63t+5260$
3	High	0.9	$V=0.039t^2-21.49t+10693$
	Medium	10	$V=0.037t^2-28.43t+14179$
	Low	0.7	$V=0.034t^2-36.9t+16012$
4	High	10	$V=0.087t^2-85.98t+41568$
	Medium	0.9	$V=0.066t^2-51.91t+25708$
	Low	0.7	$V=0.066t^2-66.9t+31144$
5	High	10	$V=0.934t^2-1150t+48303$
	Medium	0.9	$V=0.628t^2-720.4t+34171$
	Low	0.7	$V=0.528t^2-816.6t+41246$

Thixotropy also increased with increasing the CABOSIL® TS 720 content from 1 to 2, 3, 4 and 5% for three compositions. However, viscosity decreases as temperature increases (15) and viscosity increases with increasing the CABOSIL® TS 720 content (4), whereas, particle size distribution of fillers is an important parameter on viscosity as well. This effect is apparently determined from the viscosity results obtained. Even though, lower viscosity values were attained than the temperatures of 25 and 40^{0}C, the highest viscosity values varied between the adhesives containing calcite having the particle diameter of 0.9 and 10 µm owing to the particle size distribution of silica and calcite depending on the content(28-32). The effect of temperature on viscosity is indicated in Figures 3, 6 and 9.

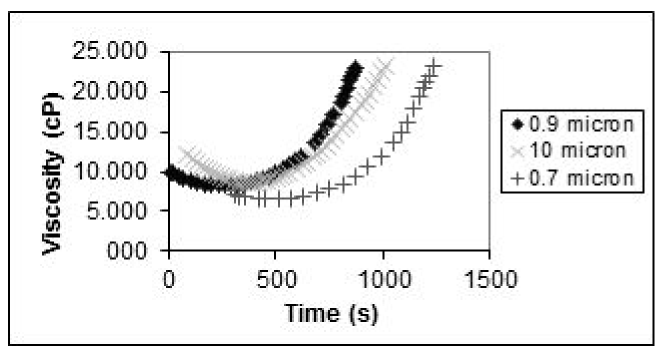

Figure 9 Variation of viscosity for SHELL adhesive including three different fillers with CABOSIL TS 720 content of 3 % at the temperature of 60^{0}C

Viscosity variation of three compositions including calcite with three different particle diameters of 0.7 µm, 0.9 µm and 10 µm at 70^{0}C was observed for the CABOSIL® TS 720 content of 1, 2, 3, 4 and 5% and the viscosity models developed are shown in Table 4.

Table 4. Viscosity models of SHELL adhesives with respect to CABOSIL TS 720 content and particle diameter at the temperature of 70^0C

Cabosil TS 720 content(%)	Viscosity variation	Particle diameter (µm)	Viscosity models at the temperature of 70^0C
1	High	0.9	$V=0.02t^2-7.581t+2518$
	Medium	10	$V=0.019t^2-8.597t+2531$
	Low	0.7	$V=0.022t^2-10t+2246$
2	High	0.9	$V=0.044t^2-15.84t+4399$
	Medium	10	$V=0.043t^2-24.19t+6332$
	Low	0.7	$V=0.016t^2-8.041t+2451$
3	High	0.9	$V=0.139t^2-54.3t+11962$
	Medium	10	$V=0.122t^2-73.41t+18818$
	Low	0.7	$V=0.081t^2-46.2t+11570$
4	High	0.9	$V=0.763t^2-367.76t+44308$
	Medium	10	$V=0.785t^2-640.8t+19118$
	Low	0.7	$V=0.795t^2-721.2t+20705$
5	High	0.9	$V=1.516t^2-1074t+30990$
	Medium	10	$V=1.090t^2-1147t+53046$
	Low	0.7	$V=2.437t^2-2550t+84978$

Thixotropy was attained in three compositions for the CABOSIL® TS 720 content of 1%.When the CABOSIL® TS 720 content was varied to 2%, thixotropy was followed for two compositions having calcite with the particle diameters of 0.7 µm and 10 µm and other composition containing calcite with the particle diameter of 0.9 µm demonstrated no thixotropy nearly. Thixotropy increased for the compositions including calcite with the particle diameters of 0.9 µm and 10 µm at the CABOSIL® TS 720 content of 3%, almost no variation was observed for the composition having calcite with the particle diameter of 0.7 µm. When the CABOSIL® TS 720 content was increased to 4%, thixotropy increased for the compositions containing calcite with the particle diameters of 0.7 µm and 10 µm, whereas, nearly constant and lower viscosity was obtained in the composition including calcite with the particle diameter of 0.9 µm with respect to other compositions. Thixotropy also increased for three compositions, while CABOSIL® TS 720 content was varied to 5%. It was observed that viscosity and thixotropy generally increased with an increase in CABOSIL® TS 720 content. However, the lowest and the highest viscosity having adhesives were found as calcite with the particle diameter of 0.7 µm and calcite with the particle diameter of 0.9 µm respectively. This order was not affected by particle size distribution of silica and calcite with increasing the CABOSIL® TS 720 and decreasing the calcite content at the temperature of 70^0C.

Viscosity variation of three compositions including SHELL resin system, calcite with three different particle diameters of 0.7 µm, 0.9 µm and 10 µm at 80^0C was detected for the CABOSIL® TS 720 content of 1, 2, 3, 4 and 5% and viscosity variation is explained with models given in Table 5.

Three compositions showed thixotropy for the CABOSIL® TS 720 content of 1%. When the CABOSIL® TS 720 content was increased to 2%, thixotropy rise was followed with respect to the CABOSIL® TS 720 content of 1% for two compositions containing calcite with the particle diameters of 0.7 µm and 0.9 µm, whereas, no thixotropy was observed for the the composition having with the particle diameter of 10 µm.

Table 5. Viscosity models of SHELL adhesives with respect to CABOSIL TS 720 content and particle diameter at the temperature of 80^0C

Cabosil TS 720 content (%)	Viscosity variation	Particle diameter (µm)	Viscosity models at the temperature of 80^0C
1	High	0.9	$V=0.043t^2-14.36t+3122$
	Medium	10	$V=0.035t^2-14.4t+2699$
	Low	0.7	$V=0.031t^2-11.44t+2080$
2	High	10	$V=0.164t^2-24.44t+3219$
	Medium	0.9	$V=0.049t^2-16.12t+3133$
	Low	0.7	$V=0.038t^2-16.89t+3315$
3	High	10	$V=5.37t^2-66.61t+4814$
	Medium	0.9	$V=0.106t^2-31.28t+6583$
	Low	0.7	$V=0.08t^2-41.13t+8173$
4	High	10	$V=1.727t^2-1002t+22118$
	Medium	0.9	$V=0.833t^2-539.1t+16440$
	Low	0.7	$V=1.884t^2-1427t+30929$
5	High	10	$V=43.13t^2-29158t+3E+07$
	Medium	0.9	$V=21.97t^2-1262t+9E+06$
	Low	0.7	$V=36.34t^2-32200t+2E+07$

An increase in thixotropy was detected with the CABOSIL® TS 720 content of 3% according to the CABOSIL® TS 720 content of 2% for the composition containing calcite with the particle diameter of 0.7 µm, while thixotropy was decreasing for the composition having calcite with the particle diameter of 0.9 µm and no thixotropy was attained for the composition including calcite with the particle diameter of 10 µm. Thixotropy increased for three compositions, when the CABOSIL® TS 720 content was varied to 4%. Lower thixotropy, then, an increase in viscosity was obtained for three compositions with the CABOSIL® TS 720 content of 5%. Results demonstrated that viscosity and thixotropy generally increased with an increase in CABOSIL® TS 720 content, effect of temperature was also sensible.

It was found that the adhesive containing calcite with the particle diameter of 0.7 µm had the lowest viscosity for CABOSIL® TS 720 content of 1, 2, 3, 4 and 5% at the temperatures of 60, 70 and 80^0C. The reason of this can be explained by means of higher particle packing effect of a polydisperse composition with a broad size distribution than a monodisperse composition besides having the effect of decreasing the viscosity because of the temperature rise(28-32). However, the adhesive including calcite with having the particle diameter of 0.9 µm had generally lower viscosity values than the adhesive with the particle diameter of 10 µm for the CABOSIL® TS 720 content of 1, 2, 3, 4 and 5% at the temperatures of 60 and 80^0C. The calcite with the particle diameter of 0.9 µm is known as coated calcite and surface of calcite is treated with fatty acids. For this reason, particle-particle interactions reduced and viscosity decreased in addition to the high temperature effect(33).

In general, results attained from experimental calculations showed that viscosity and thixotropy increased as CABOSIL® TS 720 content increased(4) and thixotropy decreased with increasing the temperature (14). Even though, a decrease in thixotropy was obtained with an increase in temperature for epoxy resin adhesives, rheopexy also decreased at the temperature of 80^0C due to high reaction rate.

In spite of very complex viscosity variation was observed due to curing reaction, the best results both in viscosity and thixotropy were obtained at the temperatures of 40^0C, 60^0C and 70^0C with the CABOSIL® TS 720 content of 4 and 5% for calcite with the particle diameter of 0.7 µm.

4. CONCLUSION

Viscosity decreased as temperature increased and viscosity increased with increasing the CABOSIL® TS 720 content.

Rheopexy and thixotropy also decreased as temperature increased.

The best results both in viscosity and thixotropy were attained at the temperatures of 40^0C, 60^0C and 70^0C with the CABOSIL® TS 720 content of 4 and 5% for calcite with the particle diameter of 0.7 µm.

It was deducted that particle size, particle size distribution and temperature data were significant with developing adhesives having specific rheological properties.

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