Development of Viscosity Models with the Variation of Rheology Control Agent Content and Temperature for Two Different Epoxy Resin Adhesives

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Abstract— In this study, variation of viscosity with time for three epoxy compositions used as adhesives including three different fillers was investigated by increasing the CABOSIL TS 720 content from 1 to 2, 3, 4 and 5% and decreasing the filler content as 19.9, 18.9, 17.9, 16.9 and 15.9% at the temperatures of 25, 40, 60, 70 and 80^0C.Variation of viscosity was also determined for two different epoxy systems as DURATEK® and SHELL resin systems consisting of DURATEK® KLM 606 A epoxy resin, DURATEK® KLM 606 B polyamide curing agent and EPIKOTE® 828 epoxy resin, EPIKURE® 3090 polyamidoamine curing agent respectively. Calcite with having three different particle diameters of 0.7, 0.9 and 10 µm , CABOSIL® TS 720 employed as rheology control agent were used as fillers in adhesives. Viscosity was measured by using HA model Brookfield type DV-II+Pro Viscometer with SC4-27 spindle at constant shear rate and viscosity models were developed for both resın systems. It was found that viscosity of DURATEK® resin system was higher than SHELL resin system. Viscosity increased as CABOSIL® TS 720 content increased and viscosity decreased with increasing the temperature. Generally, the composition prepared by the calcite with the particle diameter of 0.7 µm gave the lowest viscosity in both resin systems.

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

I. INTRODUCTION

Fluids including different rheological characteristics can be described by viscometer measurements and they are separated into two categories known as Newtonian and non-Newtonian. Newtonian fluids have the same viscosity at different shear rates, whereas, non-Newtonian fluids have different viscosities at different shear rates. Non-Newtonian fluids also fall into two groups as time independent non-Newtonian and time dependent non-Newtonian. Time independent non-Newtonian and time dependent non-Newtonian fluids show pseudoplastic, dilatant and thixotropic, rheopectic behaviour respectively [1] Pseudoplastic fluid displays a decrease in viscosity with increasing shear rate when dilatant fluid imparts an increase in viscosity with an increase in shear rate. However, a thixotropic fluid undergoes a decrease in viscosity with time, while rheopexy exhibits an increase in fluid viscosity with time as it is sheared at a constant shear rate [1].

Epoxy resins used in coating and adhesive industry also indicate rheopectic behaviour in addition to thixotropy. The development of the viscosity of a thermoset material during processing is complicated because of the kinetic rate of the conversion from a liquid to a solid material [2].

Fumed silicas well-known mineral fillers are commonly employed as rheological control agents in coating and adhesive industry [3]. CABOSIL® TS 720 treated fumed silica is a very efficient thixotrope for epoxy resin adhesives. It offers a stable sag resistance at vertical surfaces, even in high temperature cure systems. This occurs without changing other properties such as cure rate or lap shear tensile strengths of adhesives[4].

There are many factors influencing the rheology of the epoxy resins such as temperature, shear rate and loading level of filler. Effect of those factors was studied [5-12]. Studies related to epoxy resin and fumed silica were met [14-19]. Extensive literature data on the rheological properties of composites and the variations during hardening process were investigated [20, 21]. Also, kinetics of the chemical reactions which take place during hardening were explored [22-25].

The aim of the study is to investigate the variations in the rheological properties of two different epoxy resin adhesives depending on rheology control agent content , temperature and develop viscosity models.

2. EXPERIMENTAL

EPIKOTE® 828 liquid epoxy resin and EPIKURE® 3090 curing agent were provided from SHELL CHEMICAL COMPANY(ENGLAND), when KLM 606 A epoxy resin and KLM 606 B polyamide curing agent were attained from

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DURATEK® COMPANY (TURKEY). Calcite with three different particle diameters of 0.7 μm, 0.9 μm and 10 μm was purchased from ERCIYES MIKRON CORPORATION (TURKEY)[13] and CABOSIL® TS 720 with the average particle diameter of 0.2-0.3 μm was also supplied by CABOT CORPORATION (USA).

Thirty different types of adhesives prepared. Fifteen adhesives were obtained as a result of the mixing of DURATEK® KLM 606 A epoxy resin and DURATEK ®KLM 606 B polyamide curing agent with keeping the weight ratio as 1:1. 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%. The other fifteen adhesives were prepared with the addition of EPIKOTE® 828 epoxy resin and EPIKURE® 3090 polyamidoamine curing agent at constant weight ratio of 1:1. CABOSIL® TS 720 was also varied from 1 to 2, 3, 4 and 5%, when one of three fillers explained above was decreased as 19.9, 18.9, 17.9, 16.9 and 15.9%. Those adhesives were stirred by a mechanical mixer at nearly five minutes.

Adhesive sample prepared was poured into aluminium sample cup of the small sample adapter of viscometer. Viscosity of the sample was measured by using HA model Brookfield type DV-II + Proviscometer with the number of SC4-27 spindle. Viscosity was determined by 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, 80^{0}C by providing temperature control between water jacket of small sample adapter and water bath. Measurement of the samples was made at constant shear rate in the viscosity range of 200-80000000 cP.

3. RESULTS AND DISCUSSION

Rheological properties of liquid polymer systems have great industrial importance. Proper rheological control is a significant aspect of formulation technology for adhesives. The most common way to control rheological properties of adhesives is to use ''rheological control agents'' or ''thixotropes'' as additives. One of the best and most popular thixotropes is fumed silica[26]. In this study, CABOSIL® TS 720 treated fumed silica was used as ''rheological control agent''. Measurement of viscosity is an important parameter in the determination of rheological properties [27] .For this reason, viscosity variation of adhesives developed in this study was determined depending on the CABOSIL® TS 720 content, filler particle size and temperature..

Variation of viscosity with time was investigated for DURATEK® and SHELL epoxy resin systems including CABOSIL® TS 720 and calcite with three different particle diameters at the temperatures of 25, 40, 60, 70 and 80^{0}C. Thixotropic and rheopectic behaviour of three adhesives were determined by increasing the CABOSIL® TS 720 content and decreasing the filler content at equal amount for each temperature in terms of constant shear rate. However, thixotropy was not attained for all adhesives, while rheopexy was determined for all adhesive samples due to the curing reaction of epoxy resin and curing agent. For DURATEK® resin system, no viscosity result could be obtained at the CABOSIL® TS 720 content of 5%, whereas, the viscosity result was only obtained for the adhesive containing calcite with the particle diameter of 0.7 μm with the CABOSIL® TS 720 content of 3% and 4% at 25^{0}C and 60, 70, 80^{0}C respectively . Also, no measurement could be made for the adhesive having calcite with the particle diameter of 0.9 μm with the CABOSIL® TS 720 content of only 1% and 1, 3% at 40^{0}C and 80^{0}C respectively. For SHELL resin system, all results were obtained for five CABOSIL® TS 720 content at five temperatures.

Viscosity variation of three adhesives including SHELL resin system, calcite with three different particle diameters of 0.7 μm, 0.9 μm and 10 μm at 25^{0}C is observed for the CABOSIL® TS 720 content of 1, 2, 3, 4 and 5% in Table 1.

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

CABOSIL TS 720 content (%)	Viscosity variation	Particle diameter (μm)	Viscosity models at the temperature of 25^{0}C
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=0.005t^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

Thixotropy effect was only sensible for the adhesive containing calcite with the particle diameter of 0.9 μm, while other adhesive samples gave no thixotropy for the CABOSIL® TS 720 content of 1%. When the CABOSIL® TS 720 content was increased to 2%, lower thixotropy occurred for the adhesives including calcite with the particle diameters of 0.7 and 0.9 μm, whereas, no thixotropy was followed for the adhesive containing calcite with the particle diameters of 10 μm. Thixotropy and rheopexy were observed for three adhesive samples apparently at the CABOSIL® TS 720 content of 3 and 4%. Two adhesives including calcite with the particle diameters of 0.7 μm and 0.9 μm gave no thixotropy, while other adhesive containing calcite with the particle diameter of 10 μm was giving thixotropy and rheopexy at the CABOSIL® TS 720 content of 5%. Also, viscosity models for adhesives prepared with DURATEK® resin system, calcite with three particle diameters of 0.7 μm, 0.9 μm and 10 μm and only one adhesive containing calcite with the particle diameter of 0.7 µm for the CABOSIL TS 720 content of 1 ,2% and 3% at 25^0C are given in Table 2 respectively.

Table 2. Viscosity models of DURATEK 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	10	$V=0.154t^2-23.8t+2E+06$
	Medium	0.9	$V=0.020t^2-42.3t+2E+06$
	Low	0.7	$V=0.090t^2-429.9t+1E+06$
2	High	10	V=17507t+4E+07
	Medium	0.9	V=31536t+3E+07
	Low	0.7	$V=1.021t^2-6945.6t+2E+07$
3	Low	0.7	$V=70629t^2-2E+06t+6E+07$

Thixotropy was attained in three adhesives for the CABOSIL TS 720 content of 1%. When the CABOSIL® TS 720 content was varied to 2%, no thixotropy was determined for two adhesives containing calcite with the particle diameters of 0.9 µm and 10 µm, however, thixotropy increased for other adhesive having calcite with the particle diameter of 0.7 µm. No measurement was obtained for the adhsives including calcite with the particle diameters of 0.9 µm and 10µm, whereas, thixotropy decreased a lot according to the CABOSIL® TS 720 content of 1 and 2% for the adhesive containing calcite with the particle diameter of 0.7 µm at the CABOSIL® TS 720 content of 3%. It was found that viscosity and thixotropy generally increased as CABOSIL® TS 720 content increased in both resin types.

Comparison of viscosity models for adhesives prepared with SHELL resin found in Table 1 showed that the adhesives containing calcite with the particle diameter of 0.7 and 0.9 µm gave only line equations for CABOSIL® TS 720 content of 1, 2 and 5%, while these adhesives were indicating polynomial equations for CABOSIL® TS 720 content of 3 and 4%. When the viscosity variation of DURATEK and SHELL resin systems were compared, higher viscosity values were observed for both resin types including calcite with the particle diameter 0.9 µm at the temperature of 25^0C with CABOSIL® TS 720 content of 2%. Results are given in Figures 1 and 2. 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 [28-34].

Variation in viscosity of adhesives including SHELL resin system, calcite with three particle diameters of 0.7 µm, 0.9 µm and 10 µm at the temperature of 40^0C is demonstrated in Table 3 with changing the CABOSIL® TS 720 content from 1 to 5% .

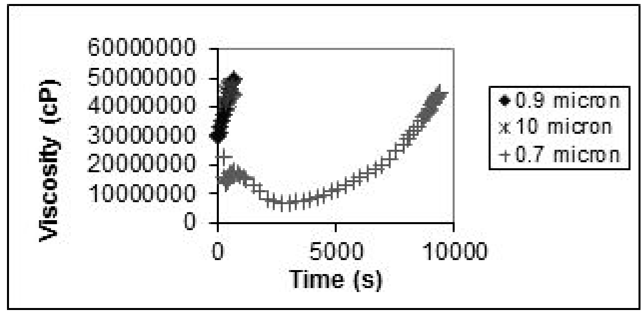

Figure 1 Viscosity variation of DURATEK adhesive according to three different fillers for CABOSIL TS 720 content of 2 % at the temperature of 25^0C

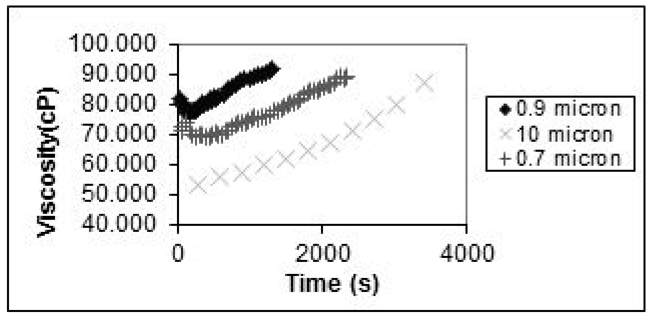

Figure 2 Viscosity variation of SHELL adhesive according to three different fillers for CABOSIL TS 720 content of 2 % at the temperature of 25^0C

Although, thixotropy effect was small for three adhesives at the CABOSIL® TS 720 content of 1%, it increased with an increase in CABOSIL®TS 720 content untill 4 %. When the CABOSIL® TS 720 content was increased to 5%, viscosity increased first, then, thixotropy occurred higher than at the CABOSIL® TS 720 content of 4% for two adhesive samples including calcite with the particle diameters of 0.9 µm and 10 µm. However, other adhesive containing calcite with the particle diameter of 0.7 µm gave lower thixotropy than at the CABOSIL® TS 720 content of 4%.

Viscosity variation of two adhesives including DURATEK® resin system, calcite with the particle diameters of 0.7 µm and 10 µm for the CABOSIL® TS 720 content of 1% at the temperature of 40^0C is shown in Table 4. No measurement was observed in the adhesive containing calcite with the particle diameters of 0.9 µm, while thixotropy was attaining in the adhesive samples having calcite with the particle diameters of 0.7 and 10 µm at the CABOSIL® TS 720 content of 1%. When the CABOSIL®TS 720 content was increased to 2% , thixotropy increased a lot for the adhesives including calcite with the particle diameters of 0.9 µm and 10 µm, whereas, no thixotropy occurred for the adhesive containing calcite with the particle diameter of 0.7 µm. No thixotropy and very little thixotropy were attained for the adhesive samples including calcite with the particle diameters of 10 µm and 0.7 µm respectively at the CABOSIL® TS 720 content of 3%, while other adhesive having calcite with the particle diameter of 0.9 µm was giving a rise in viscosity first and then a rise in thixotropy with respect to the CABOSIL®

Table 3. 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	$V=7.336t^2-25520t+3E+07$

Table 4. Viscosity models of DURATEK 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	10	$V=4.963t^2+20.65t+35069$
	Low	0.7	$V=15.45t^2-1001.5t+50420$
2	High	0.9	$V=0.205t^2-204.8t+4E+06$
	Medium	0.7	$V=30192t-5E+06$
	Low	10	$V=0.329t^2-1270t+5E+06$
3	High	10	$V=27682t+5E+07$
	Medium	0.7	$V=44.23t^2-63101t+5E+07$
	Low	0.9	$V=1.336t^2-2488.6t+2E+07$

TS 720 content of 2%. Evaluation of the results illustrated that thixotropy and viscosity increased as CABOSIL® TS 720 content increased in both resin systems.

Models developed in the determination of viscosity for adhesives including SHELL resin system, calcite with three particle diameters of 0.7 µm, 0.9 µm and 10 µm at the temperature of 60^0C are shown in Table 5 with varying CABOSIL® TS 720 content from 1 to 5%. Viscosity variation of three adhesive samples including DURATEK® resin system, calcite with three particle diameters of 0.7 µm, 0.9 µm , 10 µm and only calcite with the particle diameter of 0.7 µm is demonstrated for the CABOSIL® TS 720 content of 1, 2 ,3% and 4% at 60^0C respectively in Table 6. Three adhesives gave thixotropy for the CABOSIL® TS 720 content of 1% and thixotropy increased in three adhesive samples when CABOSIL® TS 720 content was increased to 2%. No thixotropy was determined for the adhesive having calcite with the particle diameter of 10 µm at the CABOSIL® TS 720 content of 3%, however, a rise in viscosity first, then, higher thixotropy occurred before the curing reaction for two adhesives including calcite with the particle diameter of 0.7 µm and 0.9µm. When CABOSIL® TS 720 content was increased to 4%, measurement giving lower thixotropy than at the CABOSIL® TS 720 content of 3% was only attained for the adhesive containing calcite with the particle diameter of 0.7µm.

Although, a reduction in viscosity due to temperature rise was sensible in both resin types at the temperature of 60^0C than at 25 and 40^0C, rise in viscosity and thixotropy with respect to CABOSIL® TS 720 content was observed from Figures 3,4 and 5,6 for SHELL and DURATEK resin systems respectively. Results demonstrated that DURATEK resin gave higher viscosity and higher thixotropy values than SHELL resin system.

Table 5. Viscosity models of SHELL adhesives with respect to CABOSIL TS 720 content and particle diameter at the temperature of 60^0C

Cabosil TS 720 content (%)	Viscosity variation	Particle diameter (µm)	Viscosity models at the temperature of 60^0C
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	$V=0.528t^2-816.6t+41246$

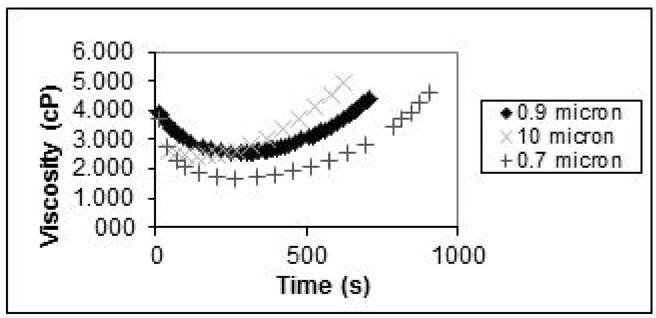

Figure 3 Variation of viscosity for SHELL resin according to three different fillers with CABOSIL® TS 720 content of 1 % at the temperature of 60^0C

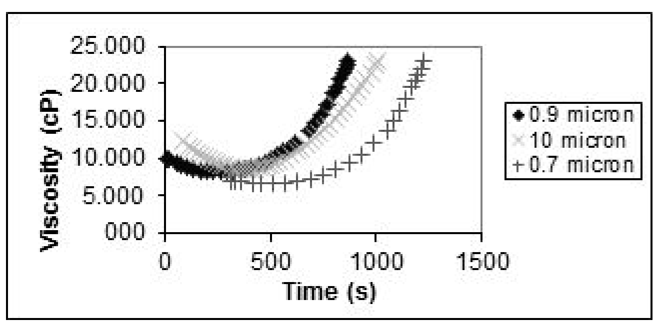

Figure 4 Variation of viscosity for SHELL resin according to three different fillers with CABOSIL® TS 720 content of 3 % at the temperature of 60^0C

Alteration of viscosity for three adhesives including SHELL resin system, calcite with three particle diameters of 0.7 µm, 0.9 µm and 10 µm at the temperature of 70^{0}C is illustrated with the CABOSIL® TS 720 content of 1, 2, 3, 4 and 5% in

Table 6. Viscosity models of DURATEK adhesives with respect to CABOSIL TS 720 content and particle diameter at the temperature of 60^{0}C

Cabosil TS 720 content (%)	Viscosity variation	Particle diameter (µm)	Viscosity models at the temperature of 60^{0}C
1	High	0.9	$V=0.136t^2-37.58t+21919$
	Medium	10	$V=0.062t^2-33.53t+17074$
	Low	0.7	$V=0.121t^2-64.48t+17983$
2	High	0.9	$V=0.630t^2-261.2t+223397$
	Medium	10	$V=0.504t^2-303.1t+216735$
	Low	0.7	$V=0.981t^2-859.1t+310905$
3	High	10	$V=35641t+2E+07$
	Medium	0.9	$V=-22.56t^2+44648t+2E+07$
	Low	0.7	$V=32t^2-29471t+3E+07$
4	Low	0.7	$V=5105t^2-249050t+4E+07$

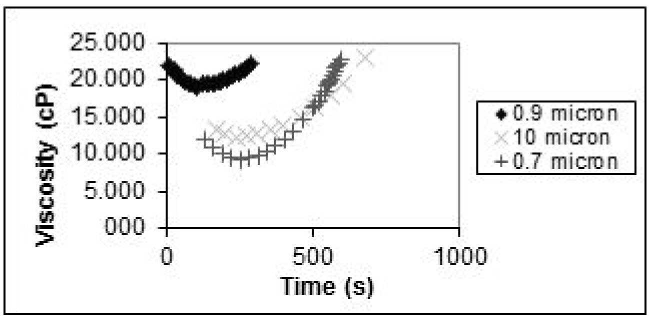

Figure 5 Alteration of viscosity for DURATEK resin including three different fillers with the CABOSIL® TS 720 content of 1 % at the temperature of 60^{0}C

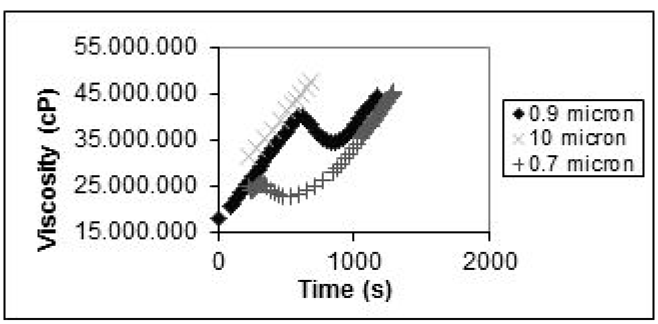

Figure 6 Alteration of viscosity for DURATEK resin including three different fillers with the CABOSIL® TS 720 content of 3% at the temperature of 60^{0}C

Table 7. Thixotropy occurred in three adhesives for the CABOSIL® TS 720 content of 1%. When the CABOSIL® TS 720 content was varied to 2%, thixotropy of two adhesive samples having calcite with the particle diameters of 0.7 µm and 10 µm increased and other adhesive containing calcite with the particle diameter of 0.9 µm had no variation in thixotropy nearly. While thixotropy was getting higher for the adhesives 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 attained for the adhesive sample having calcite with the particle diameter of 0.7 µm. When the CABOSIL® TS 720 content was varied to 4%, thixotropy increased for the adhesives ontaining calcite with the particle diameters of 0.7 µm and 10 µm, whereas, nearly constant and lower viscosity was observed in the adhesive including calcite with the particle diameter of 0.9 µm with respect to other adhesive samples. Thixotropy was also getting higher for three adhesives, while CABOSIL® TS 720 content was increased to 5%.

Table 7. Viscosity models of SHELL adhesives with respect to CABOSIL TS 720 content and particle diameter at the temperature of 70^{0}C

Cabosil TS 720 content(%)	Viscosity variation	Particle diameter (µm)	Viscosity models at the temperature of 70^{0}C
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	$V=2.437t^2-2550t+84978$

Variation in viscosity of three adhesive samples including DURATEK® resin system, calcite with three particle diameters of 0.7 µm, 0.9 µm , 10 µm and only calcite with the particle diameter of 0.7 µm is shown for the CABOSIL® TS 720 content of 1, 2 , 3% and 4% at the temperature of 70^{0}C respectively in Table 8. Although, higher thixotropic measurements were not obtained, results attained were definite for three adhesives at the CABOSIL® TS 720 content of 1%. Thixotropy decreased for the adhesive sample including calcite with the particle diameter of 10 µm when CABOSIL® TS 720 content was increased to 2%, whereas, thixotropy of the adhesive containing calcite with the particle diameter of 0.9 µm increased, other adhesive having calcite with the particle diameter of 0.7 µm gave a rise in viscosity first, then, almost the same thixotropy with respect to the CABOSIL® TS 720 content of 1% before curing. A little bit thixotropy was only determined for the adhesive having calcite with the particle diameter of 0.7 µm, whereas, rheopexy was observed in three adhesive samples, when CABOSIL® TS 720 content was increased to 3%. The measurement could only be obtained for the adhesive including calcite with the particle diameter of 0.7 µm at the CABOSIL® TS 720 content of 4%. A little thixotropy similar to the thixotropy obtained at the CABOSIL® TS 720 content of 3% was attained. It was found that temperature effect was more sensible on the results attained for both resin types in addition to the effect of CABOSIL® TS 720 and filler content.

Viscosity models of adhesives including SHELL resin system, calcite with three particle diameters of 0.7 µm, 0.9 µm and 10 µm at the temperature of 80^{0}C are also observed with varying the CABOSIL® TS 720 content from 1 to 5% in Table 9. Three adhesives gave thixotropy for the CABOSIL® TS 720 content of 1%. When the CABOSIL® TS 720 content was varied to 2%, thixotropy increased according to the CABOSIL® TS 720 content of 1% for two adhesive samples

Table 8. Viscosity models of DURATEK 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	$V=0.17t^2-21.05t+16801$
	Medium	10	$V=0.139t^2-49.52t+13631$
	Low	0.7	$V=0.255t^2-119.8t+21504$
2	High	10	$V=410t^2-62640t+6E+06$
	Medium	0.9	$V=21.38t^2-10746t+4E+06$
	Low	0.7	$V=23.62t^2-9651.4t+2E+06$
3	High	10	$V=38131t+3E+07$
	Medium	0.9	$V=40028t+9E+06$
	Low	0.7	$V=39023t+2E+06$
4	Low	0.7	$V=220658t+3E+07$

Table 9. 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	$V=2197t^2-1262t+9E+06$
	Low	0.7	$V=3634t^2-32200t+2E+07$

containing calcite with the particle diameters of 0.7 µm and 0.9 µm, whereas, no thixotropy was determined for other adhesive having with the particle diameter of 10 µm. Thixotropy increased with the CABOSIL® TS 720 content of 3% for the adhesive containing calcite with the particle diameter of 0.7 µm according to the CABOSIL® TS 720 content of 2%, while thixotropy decreased for the adhesive having calcite with the particle diameter of 0.9 µm and no thixotropy was followed for the adhesive including calcite with the particle diameter of 10 µm. Thixotropy increased for three adhesive samples, when the CABOSIL® TS 720 content was increased to 4%. Lower thixotropy, then, an increase in viscosity were observed for three adhesives with the CABOSIL® TS 720 content of 5%. Alteration in viscosity of adhesives including DURATEK® resin system, calcite with the particle diameters of 0.7 µm , 10 µm and calcite with three particle diameters of 0.7 µm, 0.9 µm , 10 µm and calcite with the particle diameter of 0.7 µm is represented for the CABOSIL® TS 720 content of 1 , 3 % and 2 % and 4% respectively at the temperature of 80^0C in Table 10. A little bit thixotropy was determined for the adhesives containing calcite with the particle diameters of 0.7 µm and 10 µm, whereas, no measurement could be determined for the adhesive sample having calcite with the particle diameter of 0.9 µm at the CABOSIL® TS 720 content of 1%. A rise in viscosity first, then, thixotropy occurred for the adhesives including calcite with the particle diameters of 0.7 and 10

Table 10. Viscosity models of DURATEK 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	0.7	$V=1.21t^2+152.1t+2673.9$
	Low	10	$V=32.08t^2-2571.4t+56570$
2	High	10	$V=3.66t^2-441.32t+173806$
	Medium	0.9	$V=4.76t^2-1308.4t+191195$
	Low	0.7	$V=3.34t^2-1332.6t+225218$
3	High	10	$V=3887.3t^2-72327t+4E+07$
	Low	0.7	$V=5197.4t^2+15978t+1E+07$
4	Low	0.7	$V=87216t+4E+07$

µm, whereas thixotropy increased in three adhesives at the CABOSIL® TS 720 content of 2%. Thixotropy decreased in the compositions including calcite with the particle diameters of 0.7 µm and 10 µm at the CABOSIL® TS 720 content of 3%, whereas, no measurement could be determined for the adhesive sample having calcite with the particle diameter of 0.9 µm. The measurement could only be attained for the adhesive containing calcite with the particle diameter of 0.7 µm at the CABOSIL® TS 720 content of 4%. However, it was determined that thixotropy decreased when it was compared with the CABOSIL® TS 720 content of 3%. Results obtained showed that temperature was highly effective on viscosity than the effect of fillers and CABOSIL® TS 720 content for both resin types.

Effect of temperature on both resin types and three different fillers is illustrated in Figures 7, 8, 9 and 10. When the effect of temperature on both type of adhesives including three different fillers was considered, it was found that thixotropy effect of fillers decreased with increasing temperature in DURATEK adhesives,. even though, thixotropy of three fillers increased as temperature increased in SHELL adhesives as it is observed from Figures 7, 8, 9 and 10.. This result can be expressed with the disparity of temperature effect on the interaction between fillers and resin systems.

In spite of the fact that thixotropy increased with increasing the CABOSIL® TS 720 content, thixotropy effect of the CABOSIL® TS 720 at 4-5% was not totally observed

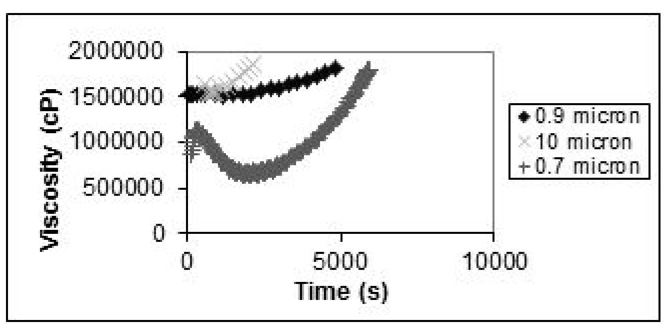

Figure 7 Variation of viscosity for DURATEK resin including three different fillers with the CABOSIL® TS 720 content of 1 % at the temperature of 25^0C

in DURATEK® resin system because of the high viscosity of system remained in unmeasurable range of the viscometer. However, thixotropic effect of adhesives including

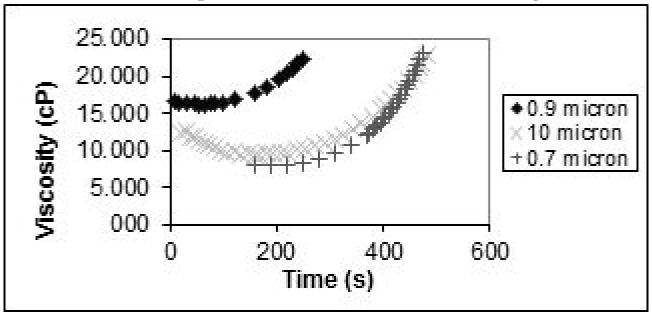

Figure 8 Variation of viscosity for DURATEK resin including three different fillers with the CABOSIL® TS 720 content of 1 % at the temperature of 70^0C

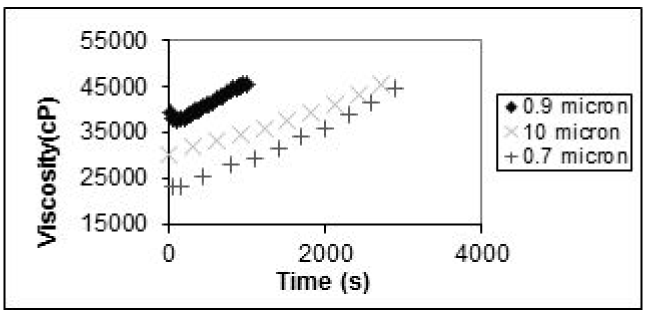

Figure 9 Alteration of viscosity for SHELL resin including three different fillers with the CABOSIL® TS 720 content of 1 % at the temperature of 25^0C

CABOSIL® TS 720 content of 1-3 % in DURATEK® resin system nearly at all temperatures was found longer than SHELL resin system due to higher sensitivity and higher activation energy of DURATEK® resin. Since, EPIKOTE®828 epoxy resin gave lower thixotropy owing to the higher rate of degree of cure at lower temperatures, higher reactivity and epoxy content [35].

Rheopexy decreased in SHELL and DURATEK® resin systems at higher temperatures due to lower curing time.

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

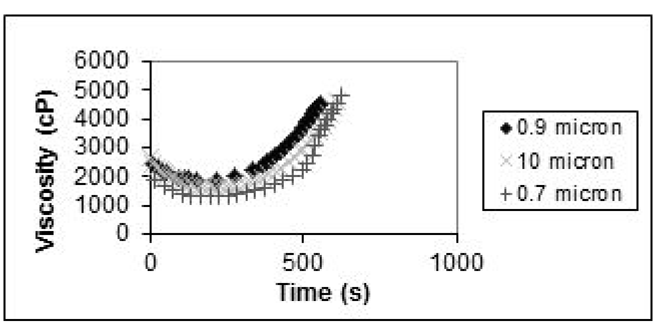

Figure 10 Alteration of viscosity for SHELL resin including three different fillers with the CABOSIL® TS 720 content of 1 % at the temperature of 70^0C

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].

When the viscosity variation results obtained from SHELL and DURATEK® resin adhesives including three different fillers were compared at 25, 40, 60, 70 and 80^0C for the CABOSIL® TS 720 content of 1, 2, 3, 4 and 5%, it was observed that higher viscosity results were obtained for DURATEK® resin system. However, viscosity decreased as temperature increasesd[15] and viscosity increased with increasing the CABOSIL® TS 720 content in both resin types.

Calcite having particle diameter of 0.9 µm known as coated calcite with fatty acids and calcite with the particle diameter of 10 µm gave especially higher viscosity results at the temperatures of 60, 70 and 80^0C. Even though, viscosity decreasing effect of coated calcite is known from literature [36], this unexpected result can be explained in terms of an increase in resin-filler interaction by fatty acids [37]. Higher viscosity result of calcite with the particle diameter of 10 µm can be expressed by means of viscosity reduction in adhesives with an increase in temperature as well. This effect led to more interaction between resin and filler and an increased viscosity.

In general, the lowest viscosity results both in SHELL and DURATEK® resin systems were attained for the adhesive including calcite with the particle diameter of 0.7 µm The reason for this can be explained in terms of good packing effect of ultrafine particle diameter for the filler.

The best results both in viscosity and thixotropy were attained by SHELL resin system 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

DURATEK® resin system had higher viscosity than SHELL resin system. Viscosity decreased as temperature increased and viscosity increased with increasing the CABOSIL® TS 720 content for both resin systems.

Rheopexy decreased in SHELL and DURATEK® resin systems at higher temperatures due to lower curing time.

In general, the lowest viscosity results both in SHELL and DURATEK® resin systems were attained for the adhesive including calcite with the particle diameter of 0.7 µm

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