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Effect of fluid-particle-interactions on dispersing nano-particles in epoxy resins using stirred-media-mills and three-roll-mills

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ABSTRACT:

Fibre reinforced composites are indispensable in the field of modern lightweight structures, such as used in aerospace, automotive industry or in wind power plants. Those materials provide high weight savings and increase the efficiency of a structure significantly. Therefore, various efforts are made to continuously improve the quality of the matrix and the fibres. By embedding nanoparticles into the epoxy matrix, the mechanical properties as well as the electrical and thermal characteristics can significantly be improved [1]. In most cases these nano-sized particles are produced as dry powders not

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as single primary particles but rather as particle collectives consisting out of several primary particles. For the application in reinforced composites the particles must be suspended in epoxy resin as separately dispersed primary particles or in a certain aggregate size. Generally, the influencing parameters to break up the aggregates in a dispersion process can be divided into the stress mechanism, the intensity and the frequency of the dispersing machine itself, the properties of the dispersed particles (e.g. the particle-particle-interactions) the properties of the homogenous phase and the particle-resin-interactions. Besides the effect of the chosen dispersing machine the optimization of the dispersing process was investigated by applying modified particle surfaces and varying the fluid properties. The results show that the surface properties of the particles must fit to the epoxy resin properties and the attractive forces between the primary particles must be reduced or the stabilization improved, respectively. An indication for an improved stabilization and adjustment of the particles surface properties to the fluid properties can be obtained by measurements of the contact angle and the rheological properties. Generally, an increase of viscosity and mass fraction of the product leads to a higher energetic efficiency of the dispersion process in the stirred media mill and three-roll-mill.

KEYWORDS: Nano composites, nano particles, mechanical properties, dynamic light scattering, dispersing, formulation

1. INTRODUCTION:

The idea of producing nano-sized particles is to reach certain properties, which are principally determined by the high ratio of surface to volume. This ratio strongly influences characteristics like attractive forces between particles, their sizes themselves or the transparency of the solution. By embedding nanoparticles into the epoxy matrix, the mechanical properties of the composites as well as the electrical and thermal characteristics can significantly be improved. In many cases nano-sized particles are produced by pyrolysis or in precipitation processes, often followed by drying processes. In most cases nano-sized particles are produced not as single primary particles but rather as particle

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collectives consisting out of several primary particles, like agglomerates or more compact aggregates. For most applications, the particles must be available in a liquid as separately dispersed primary particles or in a certain agglomerate size. Generally, the influencing parameters of producing nano-scaled dispersions can be divided into three interacting groups (see Figure 1): The stress mechanism, the stress intensity and the stress frequency as well as the specific energy supply are appointed by the dispersing machine itself. The particle properties on the other hand specify the resistance against fragmentation of aggregates in a dispersing process. Basically this contains the material properties, the surface modification, the porosity, the structure, the particle size distribution and the particle-particle-interactions. Especially for nano-particulate agglomerates and aggregates the particle-particle interactions are very strong and can be described according to the Derjaguin-Landau-Verwey-Overbeek-theory [2]. Additionally the dispersion results are strongly influenced by the formulation. This includes the rheological properties of the liquid phase, the ion concentration, the additives and especially the wetting behaviour.

For the deagglomeration of silicia and alumina nano-particles the selection of the liquid phase and the variation of their rheological properties (i.e. temperature, wetting behaviour) as well as a modification of the particle surface by functional groups can optimize a dispersion process. The modification of the formulation, e. g. the particle-particle-interactions and the stability can strongly influence the dispersing result and is independent on the stress mechanism of the dispersing machine.

2. EXPERIMENTAL SET-UP

2.1 MATERIAL AND ANALYTICAL METHODS:

In the experiments a pyrogenic, hydrophilic alumina Alu C (Aeroxide® Alu C, evonik), a modified hydrophobic alumina (Aeroxide® Alu C 805, evonik), a hydrophilic silicon oxide Aerosil 200 V and a hydrophobic silicon oxide Aerosil R 104 were dispersed in different fluids at various fluid conditions. Alumina Alu C 805 represents a modified alumina Alu C with octylsilane-groups on the particle surface.

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Aerosil R 104 represents a modified Aerosil 200 V with octamethylcyclotetrasiloxane-groups on the particle surface. The particles have a median primary particle size of 13 nm (alumina) and 12 nm (silica). Figure 2 shows a schematic representation of the functional groups of the surface modifications of the different dispersed particles.

As liquid phase fluids of high viscosity like glycerol and two different epoxy resins were used. Glycerol shows a polar behaviour, whereas the epoxy resins show a more non-polar behaviour. Additionally, hardening of the deagglomerated samples for additional scanning electron microscopy (SEM) and measuring the mechanical properties of the enhanced composites, is possible. In order to avoid hardening through high temperatures and long residence times in the dispersing machines, resins of two components like the epoxy resin Araldite LY 556 (CIBA-Geigy) and L135i (Lange + Ritter) were used. As indication of the dispersing result the particle size distributions at different dispersing times were measured via dynamic light scattering (Nanophox, Sympatec GmbH) or rotating disc centrifuge (CPS, cps instruments). In order to determine the particle size distribution correctly, a well stabilized sample is necessary Using dynamic light scattering and the disc centrifuge, the different particle-fluid-systems must be prepared using different solvents, i. e. butanon, butanol or destilled water and different stabilizers (Byk Additives and Instruments). In case of dispersing the unmodified, hydrophilic alumina in glycerol, the particle size was measured in distilled water without using any stabilizer. . For reproducible results each measurement of the particle size was averaged from four single measurements. However, each single measurement includes 100.000 scans and a standard deviation of the median particle size of approximately 3 nanometers could be determined..

The wetting of the particles in the different fluids was detected via sorption measurements in the tensiometer K11 (Krüss GmbH). The contact angle between the particles and the fluid was calculated using the Washburn equation:

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$$\frac{l^2}{t} = \frac{\sigma \cdot r \cdot \cos(\theta)}{2 \cdot \eta} \quad (1)$$

The compression of the bulk commodity has to be well defined to compare the results among each other. Therefore, the nano-sized powders were sieved and compacted in a stamp volumeter. The capillary radius was appointed by a calibration run with an ideal wetting liquid (n-heptane). Afterwards the powders were analyzed with the actual carrier fluid. For reproducible results each measurement of the contact angle was averaged from five individual measurements.

Additionally the apparent viscosities of the suspensions at low shear rates were measured using a rotating viscosimeter (CVO 120 HR, Bohlin Instruments), which are a good measure for the particle-particle interactions in the suspension.

In order to characterise the efficiency of the dispersion SEM analyses were carried out. For this purpose the samples consisting of epoxy resin LY 556 were cured by adding 50% of an anhydride hardener HY 917 related to the mass of the pure epoxy resin.

2.2 DISPERSING SYSTEMS:

The efficiency of the dispersing process can be characterized plotting the median particle size versus the specific energy. The specific energy is defined as the quotient of the energy input and the mass of the solid product particles [3,4]:

$$E_m = \int \frac{(P - P_0) \cdot dt}{m_{solid}} = \int \frac{2 \cdot \pi \cdot n \cdot (T - T_0) \cdot dt}{m_{solid}} \quad (2)$$

For the dispersing experiments two dispersing machines with different stress mechanisms, a stirred media mills (Dispermat® SL, VMA Getzmann GmbH) and a three-roll-mill Exakt ES 80 (Exakt

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Vertriebs GmbH) were used. Experiments for dispersing alumina and silica were carried out using the stirred media mill Dispermat® SL (see Figure 3) with a grinding chamber volume of 0.125 l and a separation gap wide of 300 µm at operational temperatures up to 85°C. The small closed grinding chamber, the small dead volume within the pipes as well as the integrated temperature control system makes the mill suitable for problematical and irritant fluids like epoxy resins. An integrated air pressure system helps discharging the grinding chamber.

The stress intensity in a stirred media mill is proportional to the kinetic energy of the grinding media and inversely proportional to the stressed particle mass [5]. Consequently, i in case of stressing single particles at constant operating parameters of the mill the stress intensity is inversely proportional to the third power of the particle size. Besides the particle size, the kinetic energy of the grinding media E_{kin}, strongly influences the stress intensity in stirred media mills and is proportional to the grinding media diameter, d_{GM}, the tip speed, v_t, and the grinding media density, ρ_{GM} (see Eq. 3). Due to frictional losses, energy dissipation, deformation energy and resistance against fluid displacement during the approach of 2 grinding media the stress intensity is not equal but proportional to the kinetic energy of the grinding media:

$$SI \propto \frac{E_{kin}}{m} \propto \frac{E_{kin}}{x^3} \propto \frac{d_{GM}^3 \cdot v_t^2 \cdot \rho_{GM}}{x^3} \qquad (3)$$

Three-roll-mills are frequently used to process high concentrated suspensions. Here the experiments were performed in a three-roll-mill Exakt ES 80 (see Figure 4): The gap width between the first and second rolls is set to 5 µm, while the second gap is set to 10 µm. During the dispersing process the adjacent rollers rotate at different speeds and opposite directions. The dispersing effect results from the high shear stresses generated in the gap between the rolls. The stress intensity can be increased by reducing the width of the gap between the rollers and increasing the rotational speed of the rollers and/or

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the mass concentration of the suspension. Assuming the shear stress acting on particles is only caused by the fluid, the stress intensity is independent on the particle size. This is described by the model of Rumpf and Raasch for high viscous laminar flow as shown in equation 4 [6-8]. For high viscous laminar flow and spherical agglomerates or aggregates, the stress intensity SI is proportional to the shear stress τ and the product of the dynamic viscosity η and the shear rate γ:

$$\mathrm{SI} \propto \tau = 2{,}5 \cdot \gamma \cdot \eta \quad \text{(sphere)} \qquad (4)$$

However, additional stresses can develop due to interactions between the particles by applying shear stress between the surfaces of the rollers. Thus, the total stress intensity might increase with decreasing particle diameter [6-8]. Table 1 shows the operating parameters of the three-roll-mill and the stirred media mill.

Table 1: Constant operating parameters of the three-roll-mill and the stirred media mill

three-roll-mill		
gap 1	g_1	5 µm
gap 2	g_2	10 µm
relative peripheral velocity	v_{rel}	0,186; 0,372 m/s
mass fraction	c_m	0,25
stirred media mill		
diameter of the grinding media	d_{GM}	1,1 mm (ZY 11)
peripheral velocity	v	5,2 m/s
mass fraction	c_m	0,09

3. RESULTS AND DISCUSSION-EFFECT OF FLUID-PARTICLE-INTERACTIONS:

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Besides the mechanism, intensity and frequency of stresses, the particle properties (especially the surface modification) as well as the rheological properties of the liquid phase (like the viscosity as function of the temperature and the wetting behaviour) influence the dispersion result. Especially, dispersing at high solid concentrations in the three-roll-mill strongly depends on the fluid viscosity and the wetting behaviour. At high solid concentrations and viscosities, wall gliding of the suspension can occur at the wall of the rolls depending on the wetting behaviour between the rollers and the liquid phase. In order to verify the influence of the viscosity and wetting behaviour of different fluids, the phenomenon of wall gliding must be eliminated.

Low temperatures and, thus, high viscosities deliver a product of low particle fineness as seen in Figure 5. In this case wall gliding occurred for dispersing alumina in the epoxy resin L135i using a three-roll-mill at high shear rates. The occurrence of wall gliding can be analysed by comparing theoretical values with experimental data: The theoretical shear rate can be calculated with help of the gap size and the peripheral velocity. In case of wall gliding (see Figure 5), the effective shear stress is much lower as the calculated shear rate.

Because of the wall gliding effect the product fineness increases with increasing temperature or decreasing viscosity, respectively. Normally an increase of the temperature and, therewith, a decrease of the viscosity leads to a decrease of the stress intensity acting on the particle surface [6-8] and, thus, to coarser particle sizes. Additionally, the dispersing process gets energetically inefficient.

In order to determine the effect of the wetting behaviour of different fluids and of the attractive and repulsive forces between the primary particles in different fluids on the dispersion process, the viscosity of the fluids should be equal to eliminate viscosity effects. Therefore, the viscosities of the fluids at different temperatures must be measured. Figure 6 shows the dependency of the fluid viscosity at a shear rate of 1000 1/s on the temperature for glycerol, epoxy resin L135i and epoxy resin LY 556. The

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viscosity of all fluids shows Newtonian flow behaviour. Using Figure 6 the operating temperature for further experiments in the three-roll-mill for the different fluids is determined.

In the following the unmodified alumina was dispersed with the three-roll-mill in different fluids at different temperatures but approximately equal fluid viscosity of 0,72 Pas. As shown in Figure 7 the dispersion of the unmodified alumina in glycerol is more efficient than the dispersion in the epoxy resins. Dispersing the unmodified alumina in the epoxy resin L135i requires more specific energy than dispersing it in epoxy resin LY 556 and glycerol to achieve similar product fineness. In accordance with the dispersing experiments the results of the contact angle measurements confirm the tendency of the dispersing experiments: The contact angle of the unmodified alumina in glycerol (60 °C) was determined to approximately 40°, epoxy resin LY 556 (85 °C) was in the range of 80° and epoxy resin L135i (60 °C) shows angels of 90° or higher. Besides the mass fraction of the suspension and viscosity of the solvent, the dispersion efficiency strongly depends on the wetting behaviour of the particles in the different solvents. Figure 8 shows the contact angle of alumina the unmodified alumina in the different solvents.

Figure 9 shows the effect of different surface modifications (unmodified alumina and modified alumina, unmodified silica and modified silica) on the dispersing result achieved in the three-roll-mill using epoxy resin LY 556. Different surface modifications have an influence on the particle-particle interactions and the wetting behaviour. Figure 2 shows a schematic representation of the functional groups of the surface modifications of the different particles. In case of the modified silica, the octamethylcyclotetrasiloxane-groups on the particle surface represent a good adjustment to the epoxy resin and the attractive forces between the primary particles are relatively low. Compared to the modified silica the attractive interaction forces of the unmodified silica are even lower. However, the affinity of the unmodified silica to the epoxy resins is comparatively bad. Comparing the two hydrophilic versions the unmodified silica and unmodified alumina, lower repulsive electrostatically

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interaction forces can be found for the unmodified silica. This can be a consequence of the hydrophobic siloxan groups (see Figure 2) on the particle surface of the unmodified silica. Additionally, zeta potential measurements in distilled water were performed using a DT 1200 (Dispersing Technology). The zeta potential of the unmodified silica can be found within the range of -18 and -30 whereas the zeta potential of the unmodified alumina shows values around 50. Concluding, the dispersion process of the modified silica in epoxy resin LY 556 is more efficient and leads to smaller median particle sizes as the unmodified silica.

In case of the unmodified and modified alumina (Figure 9), the adjustment of the surface modification to the epoxy resin is not optimal. The major difference in this case are the lower attractive forces of the unmodified alumina through positive charges on the particle surface compared to high attractive van der waals forces of the modified alumina through the long hydrophobic octylsilane-groups (see Figure 2). For this reason the dispersion process of the unmodified alumina in epoxy resin LY 556 is more efficient and leads to smaller median particle sizes than the one of the modified alumina. These considerations can be confirmed by viscosity measurements of the different particle-fluid-systems at low shear rates (see Figure 10). The values of the dynamic viscosity at low shear rates give an indication for the particle-particle interactions. In case of hydrophobic alumina (modified) and silica (modified) the viscosity at low shear rates is much higher as the viscosity of the referring hydrophilic particles. The explanation is similar as the one given above. Attractive interactions between hydrophobic particles cause high viscosities at low shear rates. Strong repulsive electro statically interactions can especially be remarked in case of the unmodified alumina. Comparing the modified silica with the unmodified, the modified silica again delivers higher particle-particle interactions. On the other hand, the octamethylcyclotetrasiloxane-groups represent a better adjustment to the epoxy matrix. In this case the adjustment to the matrix has more influence on the dispersion and is more efficient [9-11].

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For comparison Figure 11 shows the dispersing of aluminia and silica with a hydrophilic as well as hydrophobic surface in epoxy resin LY 556 using a stirred media mill. Here the dependency of the product fineness on the specific energy is shown. Generally, the dispersion of the two different alumina particles shows similar behaviour for the stirred media mill (Figure 11) and the three-roll mill (Figure 9). As seen before the adjustment of the surface modifications of both alumina particles to epoxy resin is not optimal. The difference are the lower attractive van der waals interaction forces and high repulsive electrostatical interaction forces of the unmodified alumina with positive charges on the particle surface compared to higher attractive van der waals forces of the modified alumina with the long hydrophobic octylsilane-groups. For this reason the dispersion process of the unmodified alumina in epoxy resin LY 556 is more efficient and leads to smaller median particle sizes than the one with the modified alumina. Anyway, Figure 11 shows higher fluctuations of the median particle size in the stirred media mill during the dispersion process as found for the three-roll-mill. The basic problem of operating the stirred media mill Dispermat Sl is the exact tempering of suspension during the experiments. This leads to fluctuating temperature values in the range of 5°C and, thus, to a fluctuating median particle size. Especially for dispersing the modified alumina, the tempering of the suspension is difficult and leads to different particle sizes especially for small specific energies. Generally, the dispersion processes in a stirred media mill and the three-roll-mill differ due to the different stress mechanism of the dispersing machine. Moreover, the particles - grinding media - interactions change the dispersing behaviour in a stirred media mill. Especially dispersing silica particles in the stirred media mill results in a differing dispersion process. Figure 11 shows an unexpected dispersing behaviour for the unmodified silica. Dispersing the unmodified silica in the stirred media mill gets more efficient at high specific energies compared to dispersing the modified silica.

Figure 12 shows the SEM pictures of the hardened samples of the unmodified silica (a), modified silica (b), unmodified alumina (c) and modified alumina (d) in epoxy resin LY 556.

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The hydrophilic particle-epoxy resin LY 556-systems of the unmodified alumina (c) and silica (a) after curing leads to a homogenous distribution of the particles within the matrix. The hydrophobic particle-epoxy resin-systems, especially the one containing the modified alumina (d), are reagglomerated. For alumina the unmodified alumina (c) there are many small particles below 50 nm and a few large aggregates. The SEM pictures prove the efficient dispersing of the unmodified alumina obtained by the dispersing experiments. Additionally, the determined median particle sizes for silica are similar to those ones measured via dynamic light scattering.

For an increase of the Young's modulus of composites a high solid content of nanparticles in the matrix are advantageous. Thus, test specimen for the measurement of the mechanical properties were produced using suspensions, which were manufactured using the three-roll-mill with high solids concentrations and with small small particle sizes. Due to the strong agglomeration of the modified alumina during the curing process only mechanical tests of the unmodified alumina are carried out. Figure 13 shows the percentaged change in the Young's modulus, the fracture strength and the fracture strain of the tested alumina epoxy resin composites in comparison to the values of the pure epoxy resin. The Young's modulus was measured via the DIN EN ISO 527-2 using a standard material testing machine. With increasing alumina solid content the Young's modulus and the fracture strength rise, while the fracture strain decreases. At high solid contents the ceramic nanoparticles lead to an embrittlement of the elastic resin matrix. Similar results were shown for alumina- and silica- epoxy composites by Moloney using particles in the micrometer range [12]. Ng shows, that the Young's modulus of nanostructured titania-epoxy composites measured by indentation experiments increases with increasing solid content [13].

4. CONCLUSION:

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Fibre reinforced composites are indispensable in the field of modern lightweight structures, such as used in aerospace, automotive industry or in wind power plants. Those materials provide high weight savings and significantly increase the efficiency of a structure. By embedding nanoparticles into the epoxy matrix, the mechanical properties as well as the electrical and thermal characteristics can significantly be improved. Besides the characteristics of the dispersing device, the formulation of the suspension significantly influences the energy efficiency and the obtained product fineness of the dispersing process. Besides the mechanism, the intensity and the frequency of the stress transferred by the dispersing machines, the surface modification, the fluid properties and at least the stabilization method have a great influence on the energy efficiency and the obtained product fineness of the dispersing process. Generally, an increase of the viscosity and mass fraction of the product leads to an increase of the energetically efficiency of the dispersion process in the stirred media mill and three-roll-mill. In the three-roll-mill the effect of wall gliding of the suspension between the rolls leads to lower stress intensities and thus to coarser product quality. An optimization of the dispersing process can be achieved if the surface properties are adapted to the fluid properties. Additionally, the attractive forces between the primary particles have to be reduced or stabilized. The level of optimization can be indicated by measuring the contact angle and the rheological properties. For dispersing the same particle-liquid system in a stirred media mill instead of in a three-roll-mill the dispersion result can differ strongly. This is related to the different stress mechanisms and additional particle-grinding media interactions.

With increasing alumina solid content in the cured alumina epoxy resin composites the Young's modulus and the fracture strength rise, while the fracture strain decreases. At high solid contents the ceramic nanoparticles lead to an embrittlement of the elastic resin matrix.

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SYMBOL INDEX

c_m	[-]	mass fraction
d_{GM}	[mm]	grinding media diameter
E_m	[kJ/kg]	mass specific energy
g	[µm]	gap range between the rollers
L	[m]	wetting level
m_{solid}	[kg]	mass of the solid
P	[W]	power input
P0	[W]	ideal power
r	[µm]	capillary radius
t	[s]	dispersing time
T	[Nm]	torque
T_0	[Nm]	ideal torque
T	[°C1]	temperature
v	[m/s]	tip speed
$\dot{\gamma}$	[1/s]	shear rate
η	[Pa s]	dynamic viscosity
σ	[N/m]	surface tension
Θ	[°]	contact angle

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Figure 1: Influencing factors on the dispersing result

Figure 2: Schematic representation of the functional groups of the surface modification of the different nanoparticles used in the investigation

Figure 3: Schematic representation of the laboratory mill Dispermat® SL

Figure 4: Schematic representation of the Exakt ES 80

Figure 5: Product fineness as function of the specific energy for dispersing nano-sized alumina in the three-roll-mill at different temperatures (particle sizes measured by disc centrifuge)

Figure 6: Dependency of the fluid viscosity on the temperature for glycerol, epoxy resin L135i and epoxy resin LY 556 (Bohlin CVO 120)

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Figure 7: Dependency of the product fineness on the specific energy for dispersing of nano-particulate alumina in the three-roll-mill using different fluids (particle sizes measured by dynamic light scattering)

Figure 8: Contact angle of the unmodified alumina in the different solvents

Figure 9: Dependency of the product fineness on the specific energy for dispersing of the modified and unmodified alumina as well as for the modified and unmodified silica in the three-roll-mill in epoxy resin LY 556 (particle sizes measured by dynamic light scattering)

Figure 10: Dependency of the dynamic viscosity on the shear rate for dispersing of the modified and unmodified alumina as well as for the modified and unmodified silica in epoxy resin LY 556 (9 wt%)

Figure 11: Dependency of the product fineness on the specific energy for dispersing of the modified and unmodified alumina as well as for the modified and unmodified silica in stirred media mill Dispermat SL in epoxy resin LY 556 (particle sizes measured by dynamic light scattering)

Figure 12: SEM picture of the unmodified silica (a), modified silica (b), unmodified alumina (c) and modified alumina (d) in cured epoxy resin LY 556.

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Figure 1

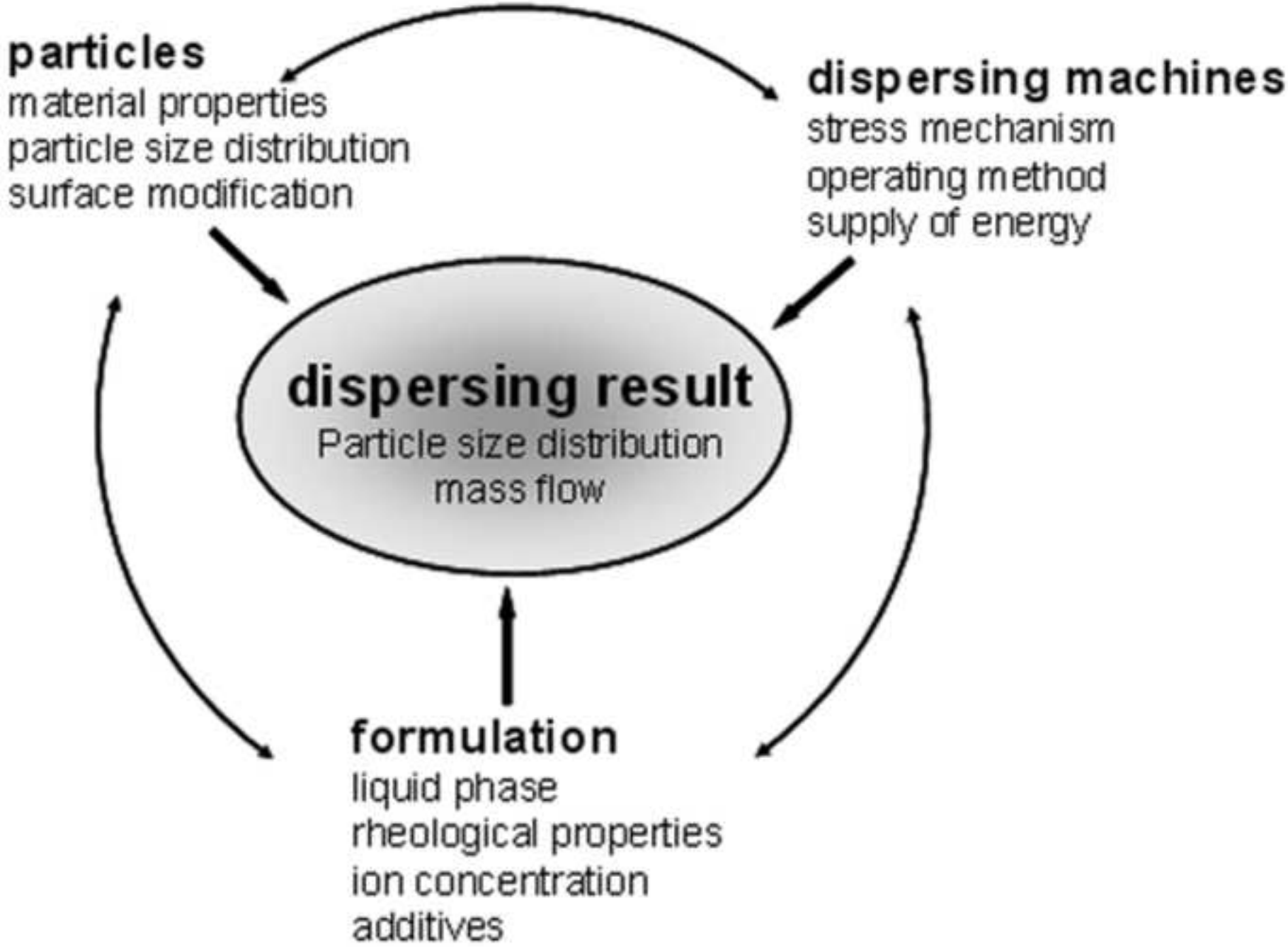

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Figure 2

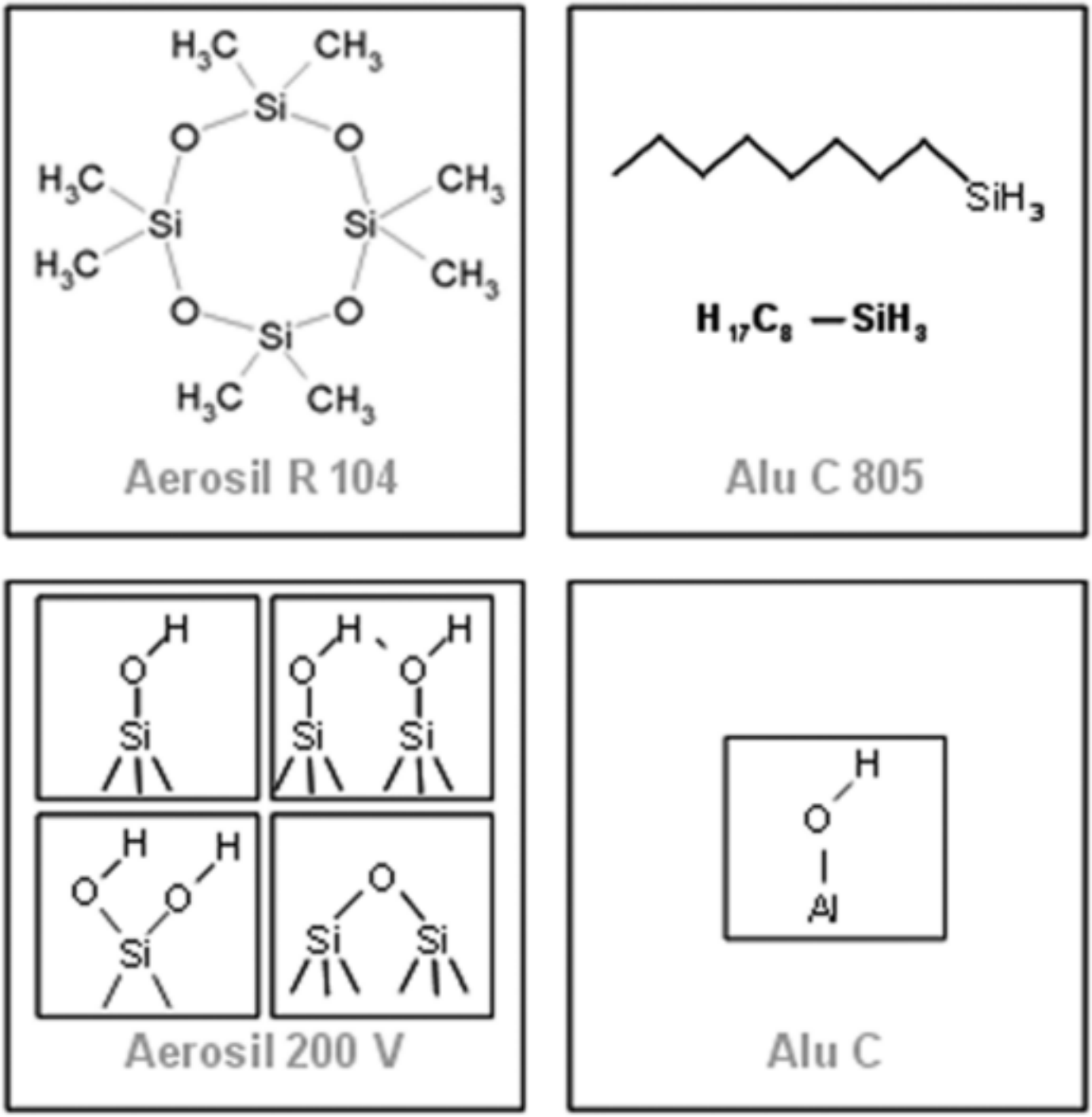

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Figure 3

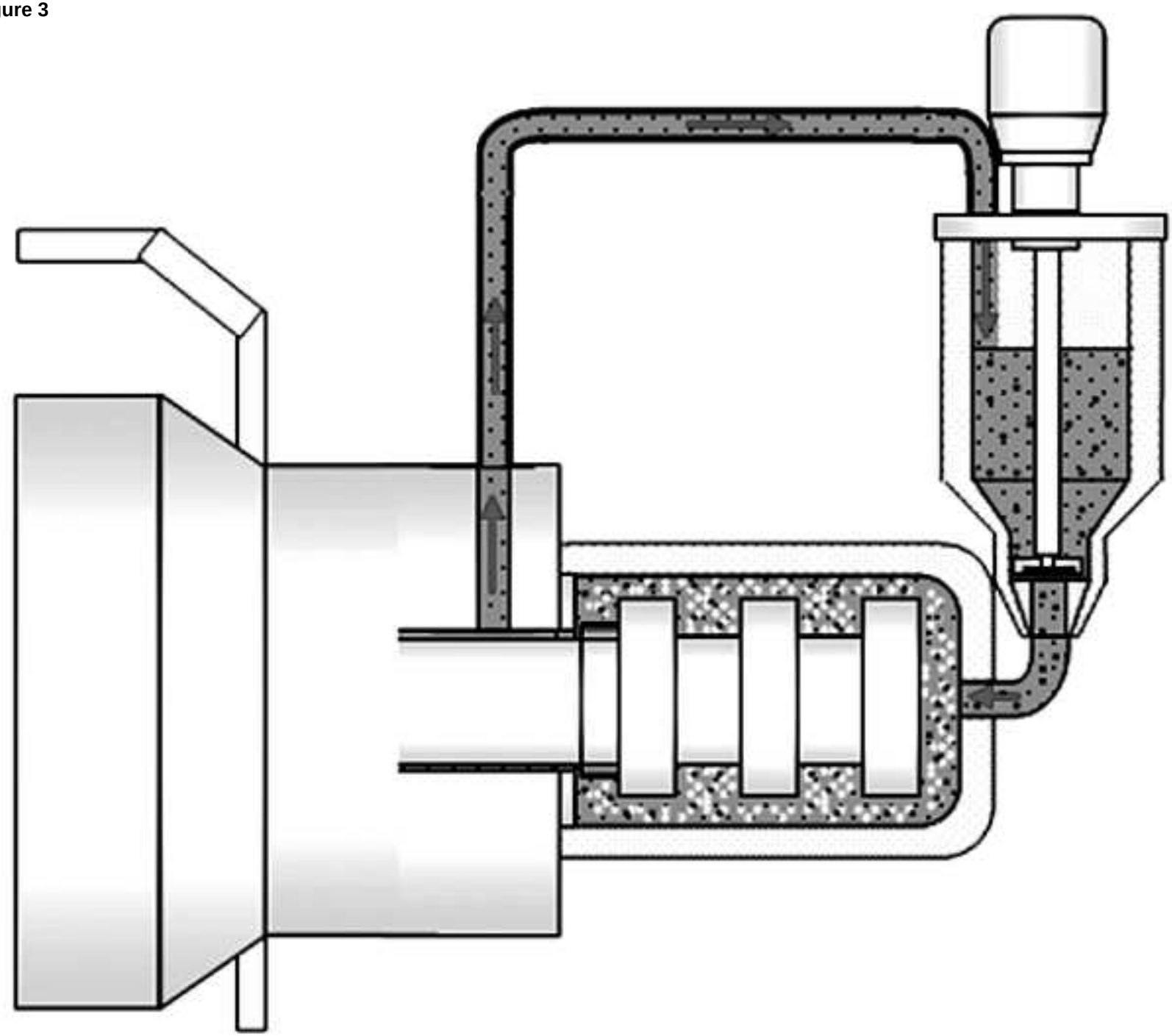

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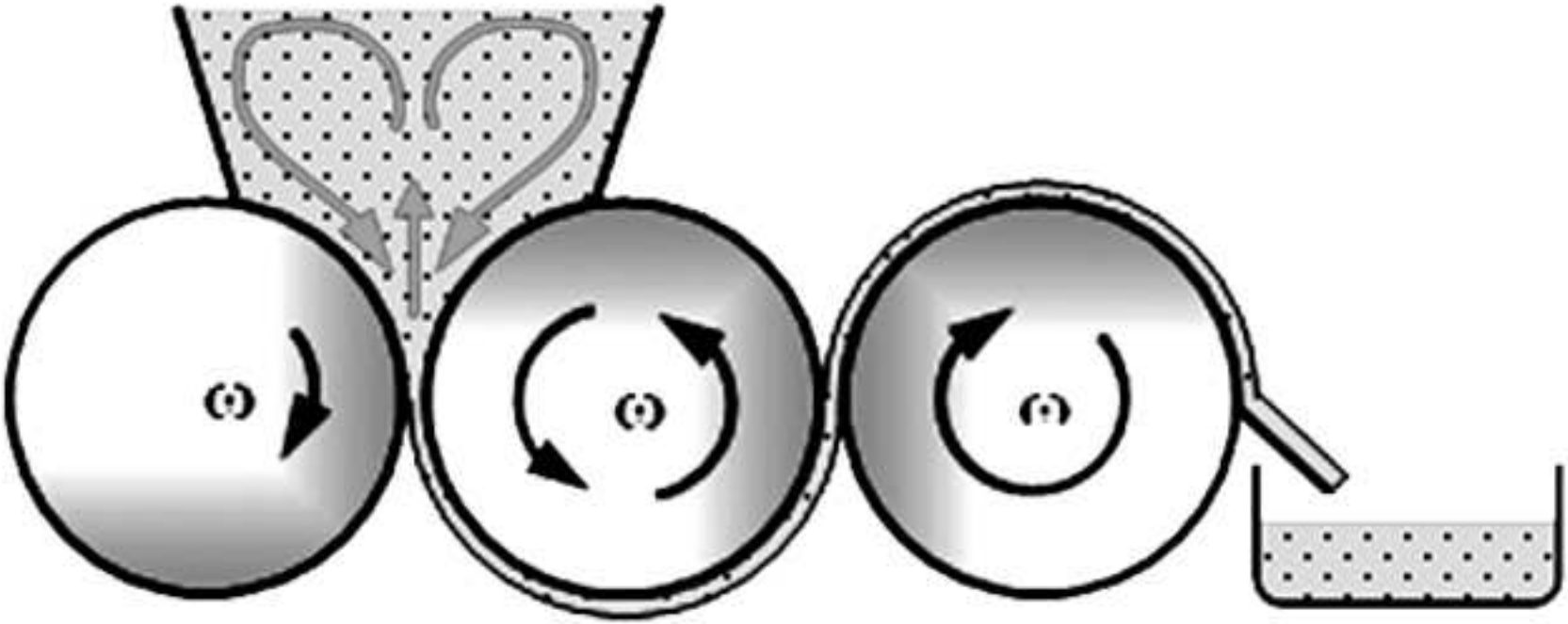
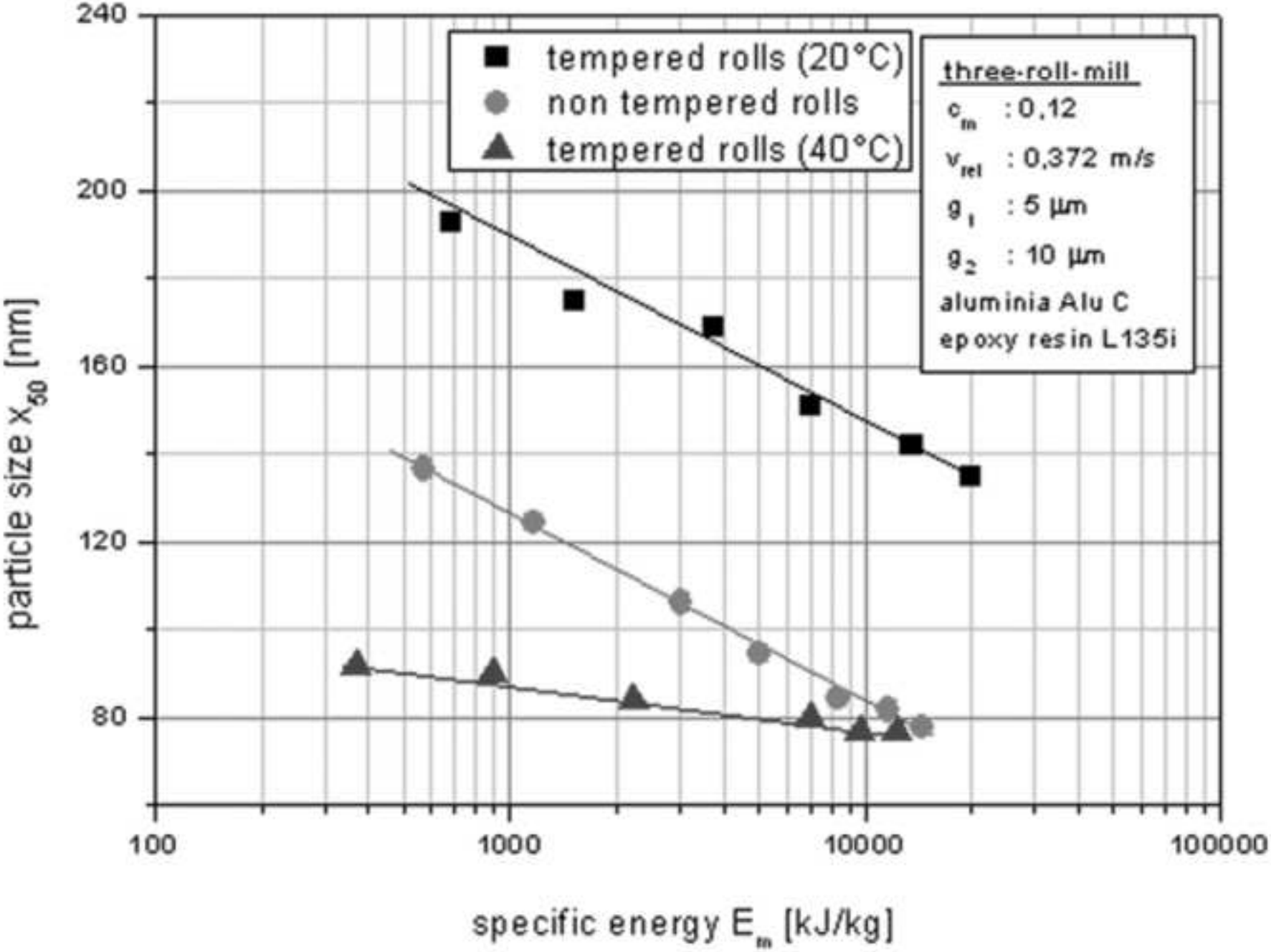
Figure 4



ACCEPT

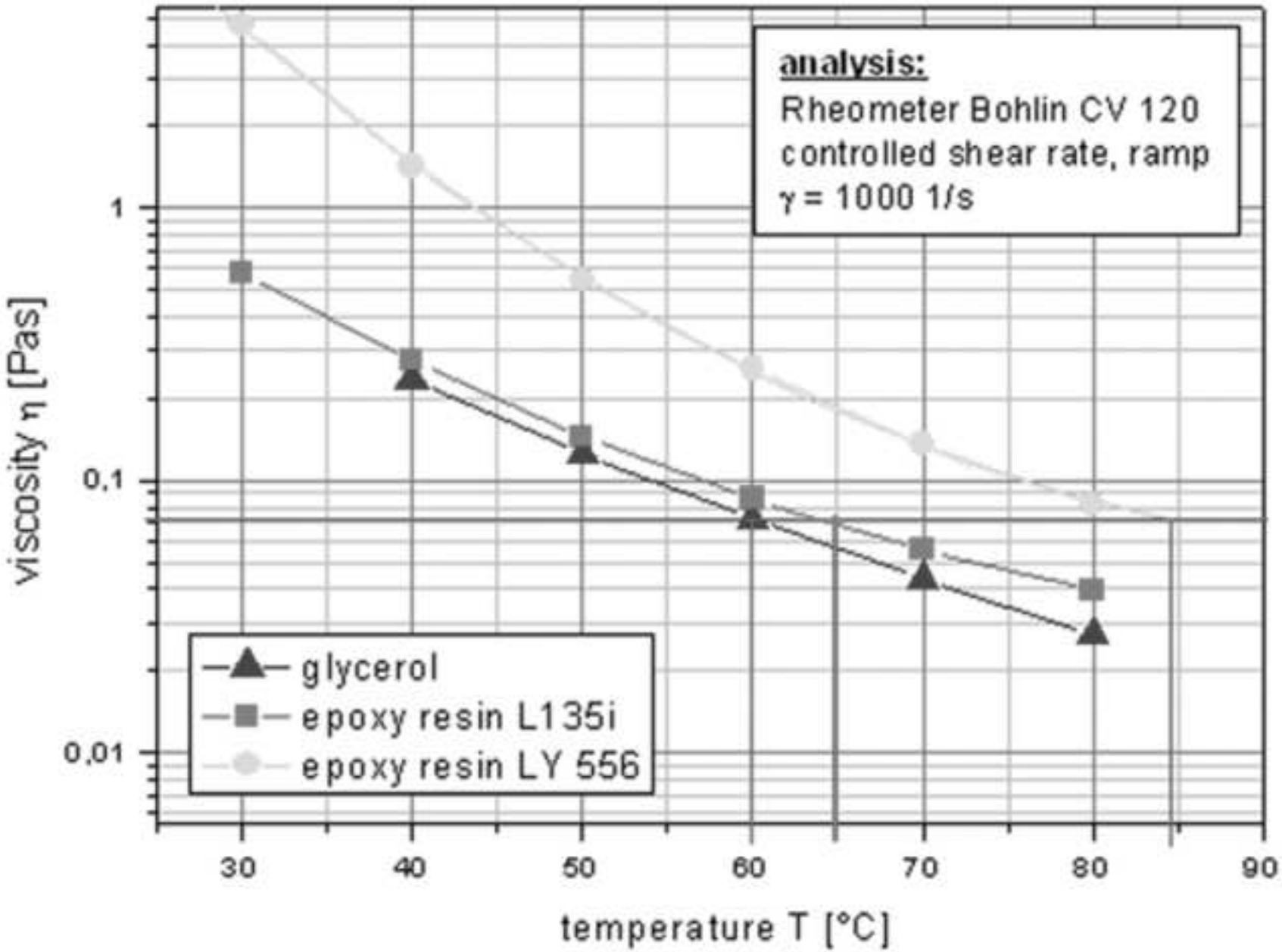
ACCEPTED MANUSCRIPT

Figure 5



ACCEPTED MANUSCRIPT

Figure 6



ACCEPTED MANUSCRIPT

Figure 7

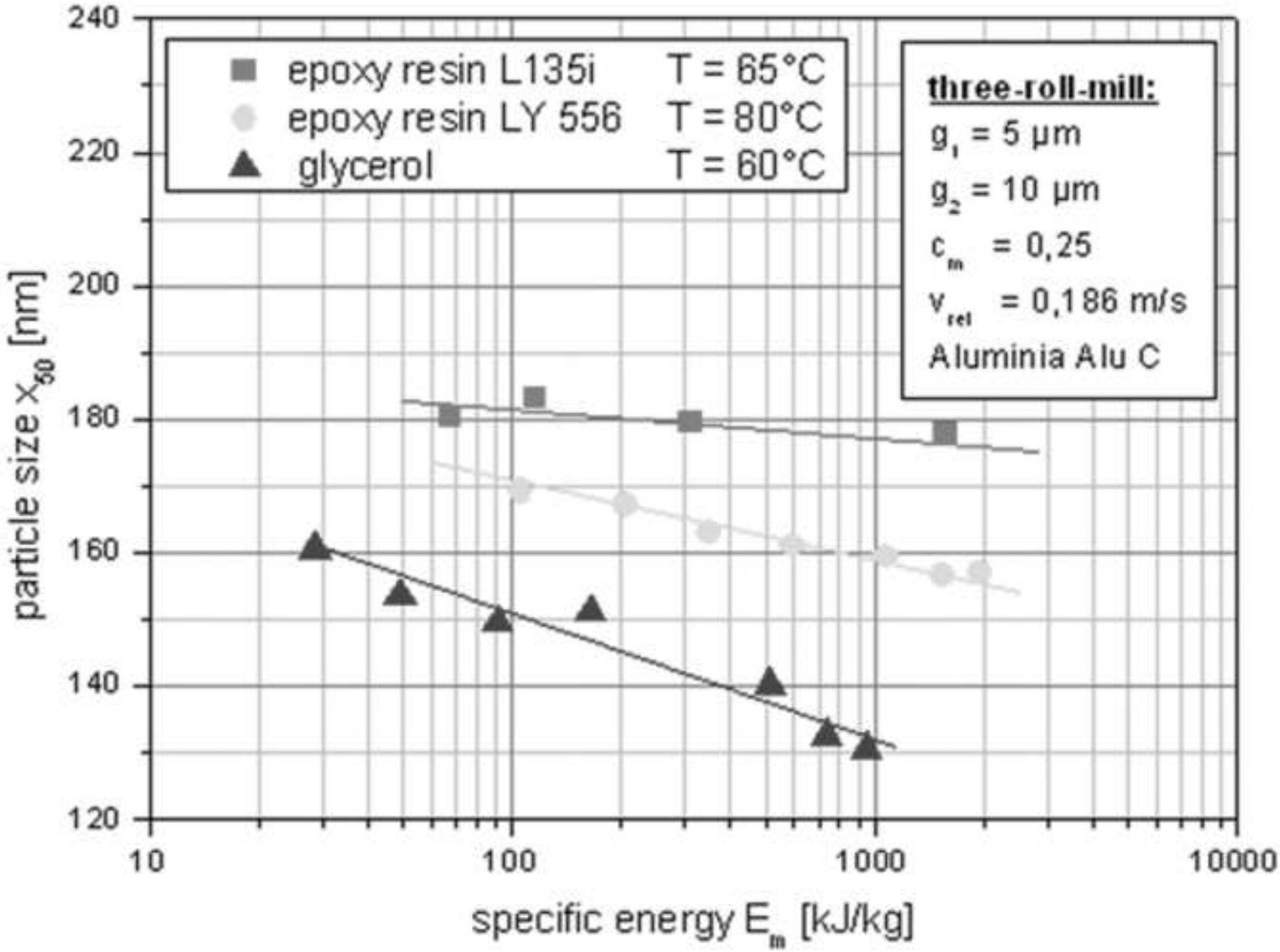


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Figure 8

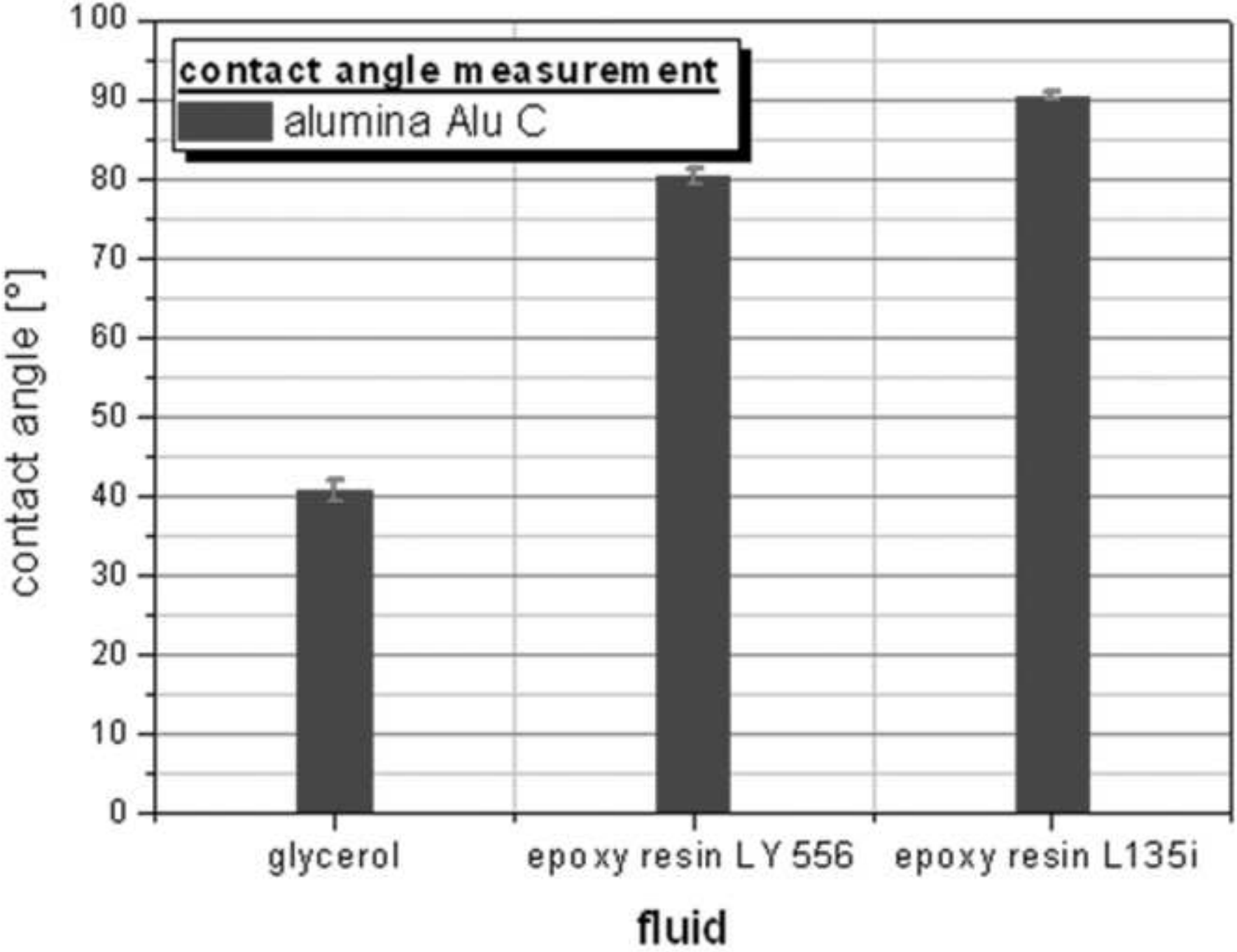

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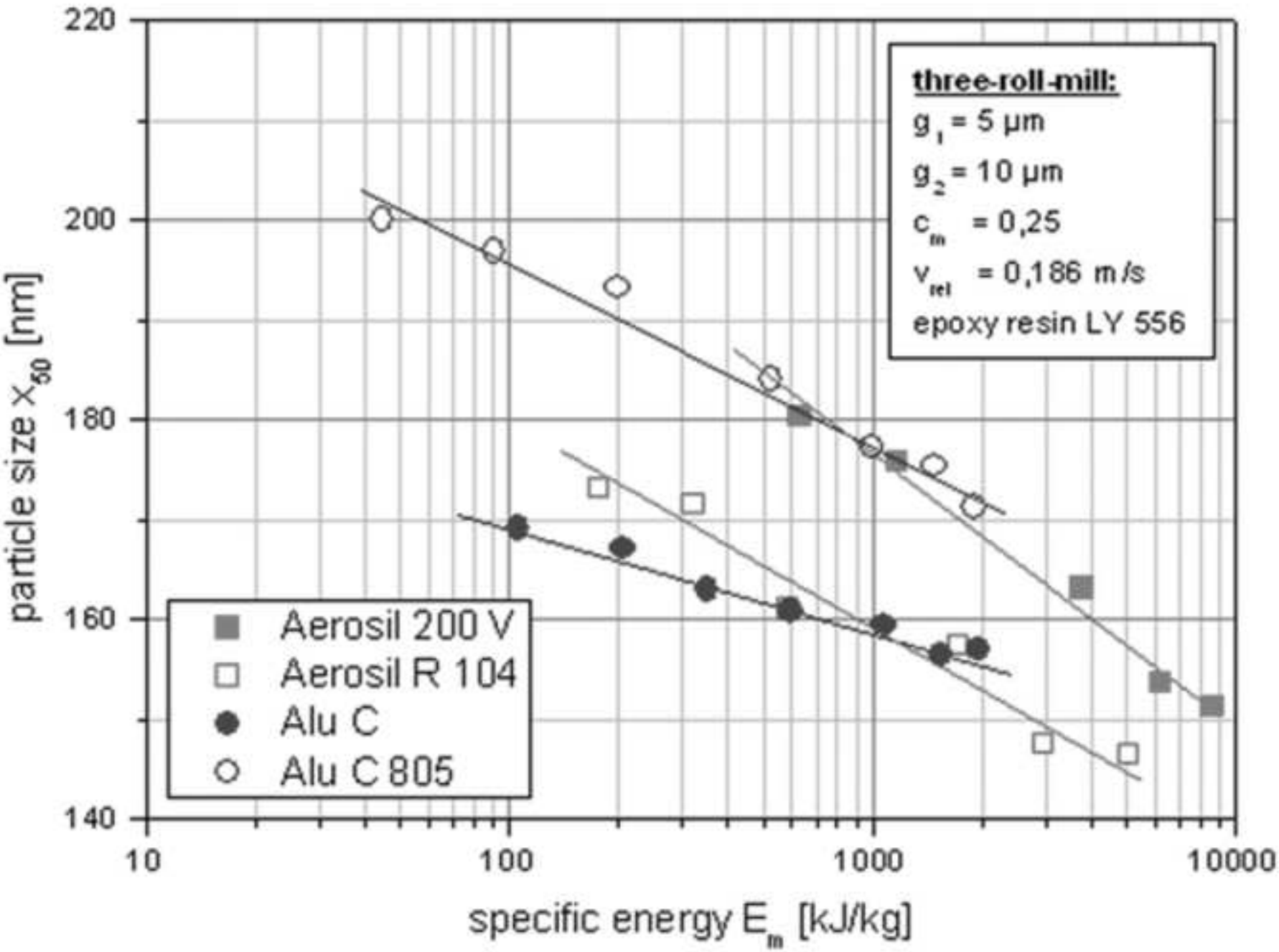
Figure 9



ACCEPTED MANUSCRIPT

Figure 10

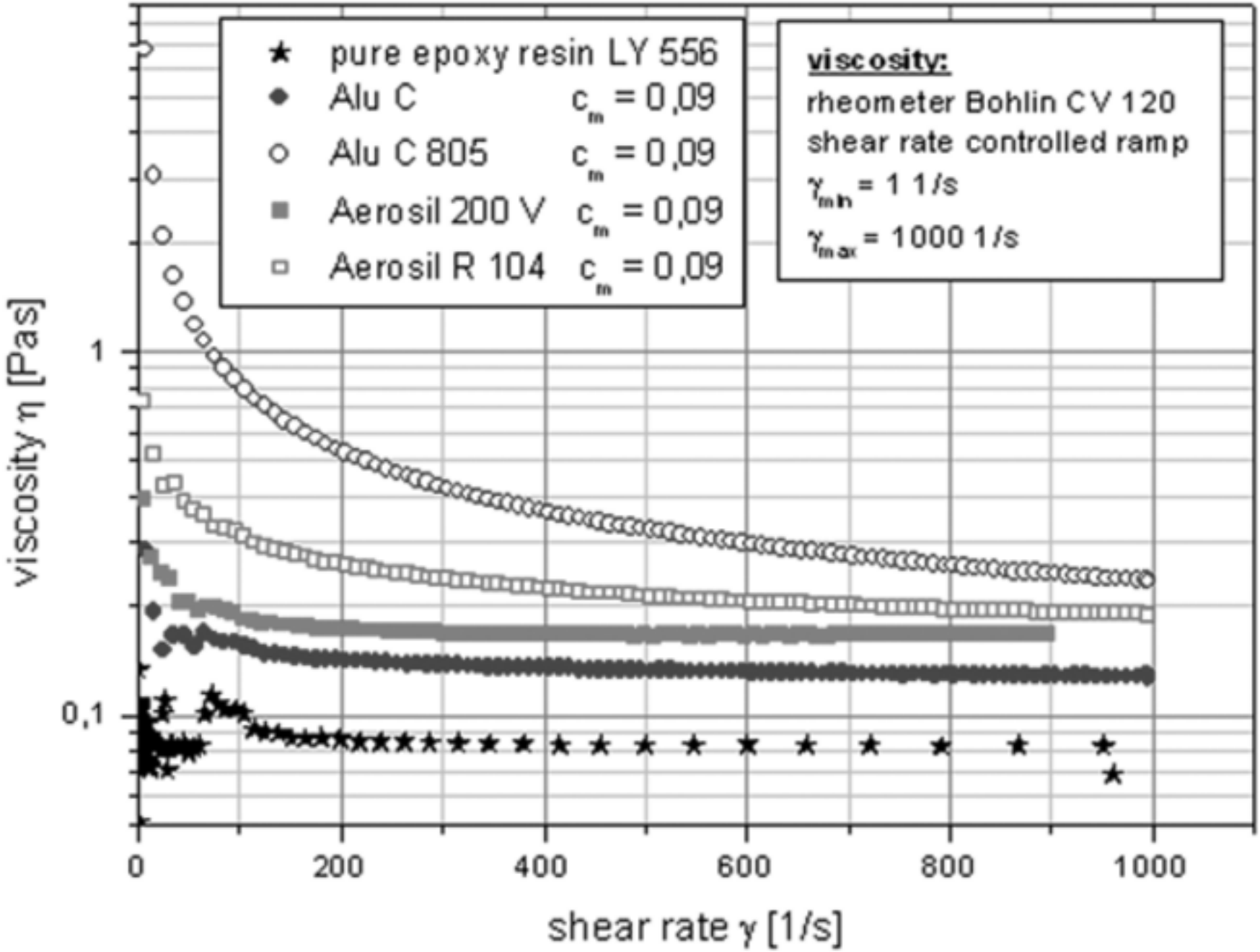


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Figure 11

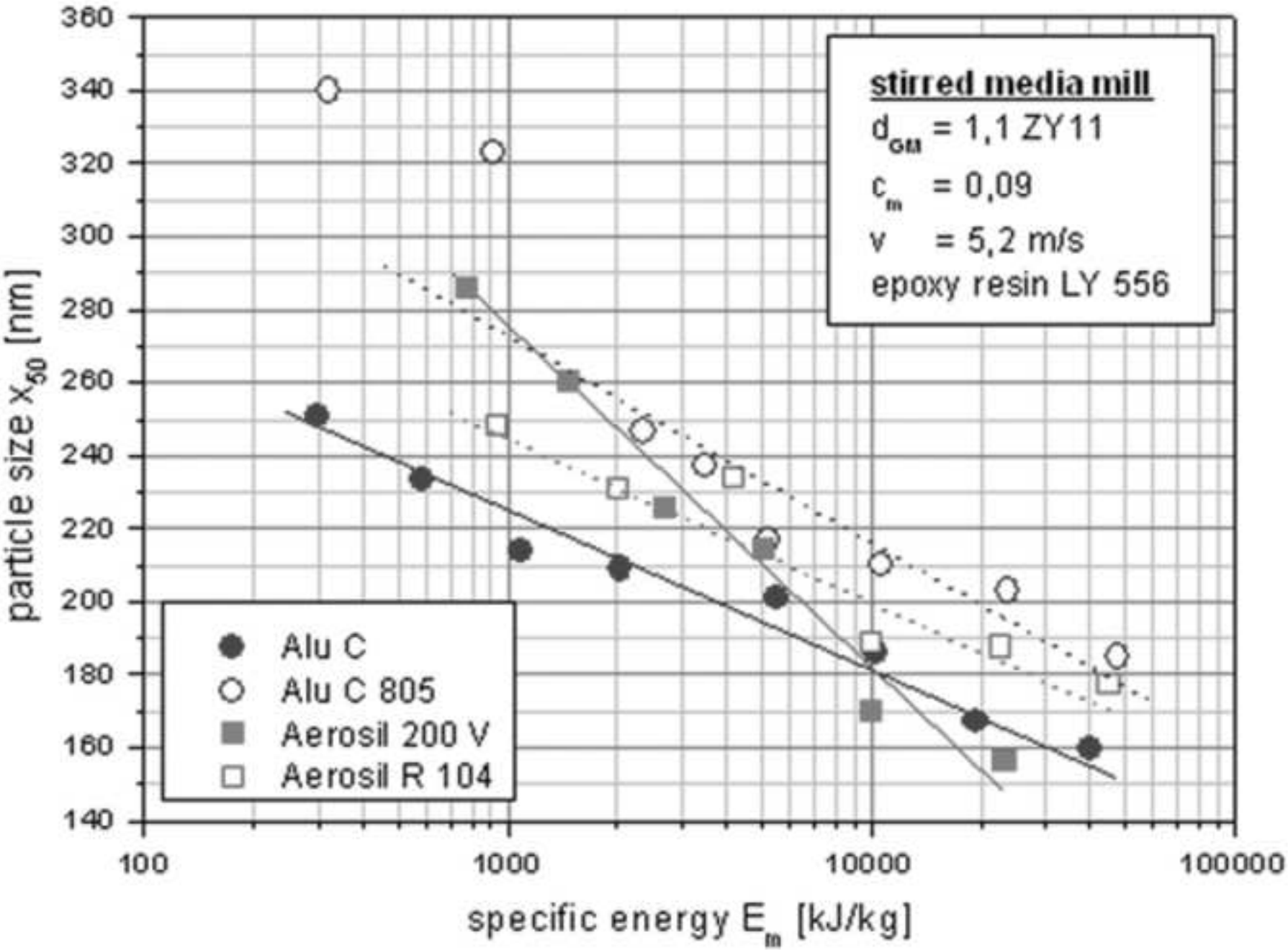

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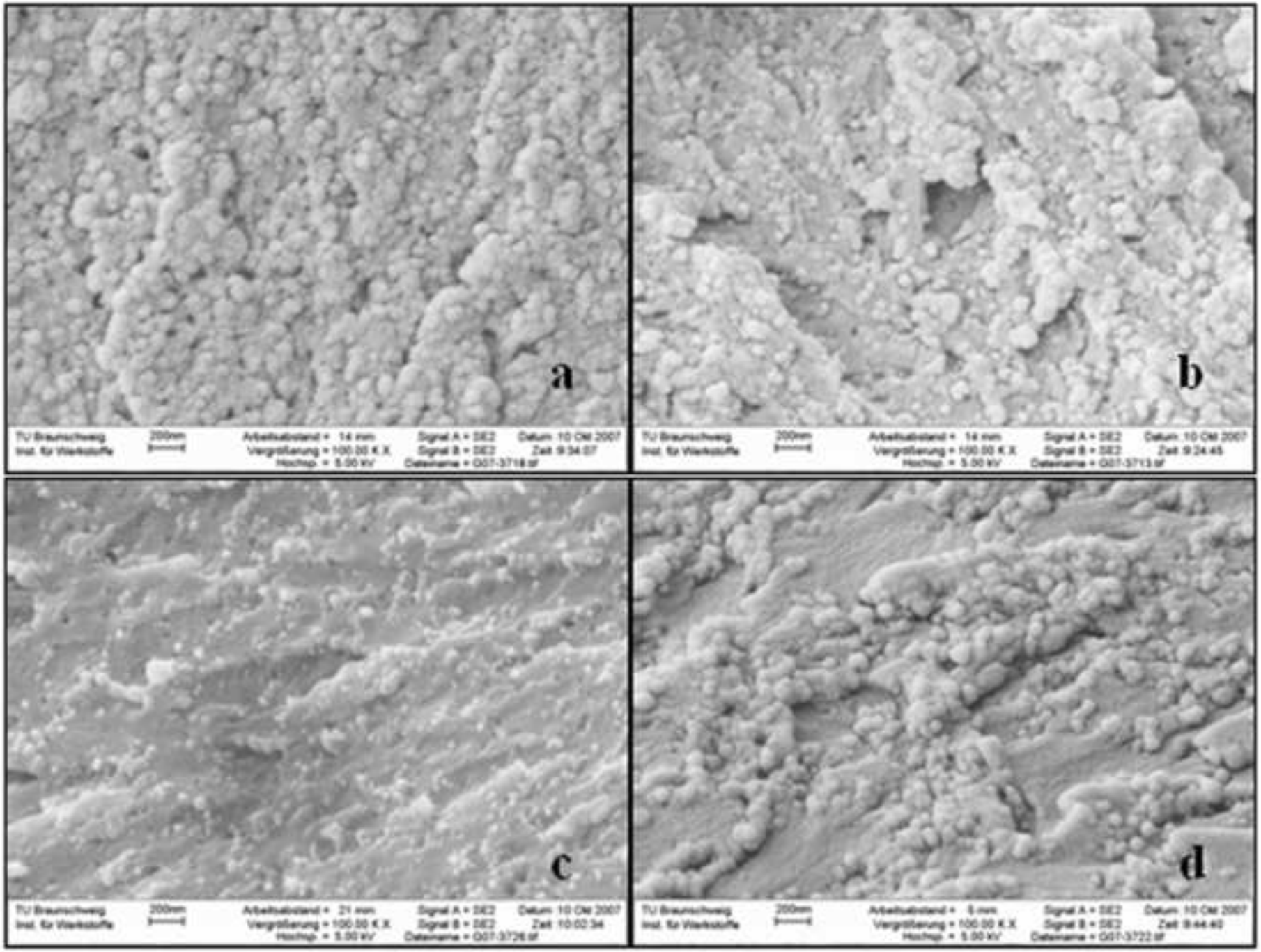
Figure 12



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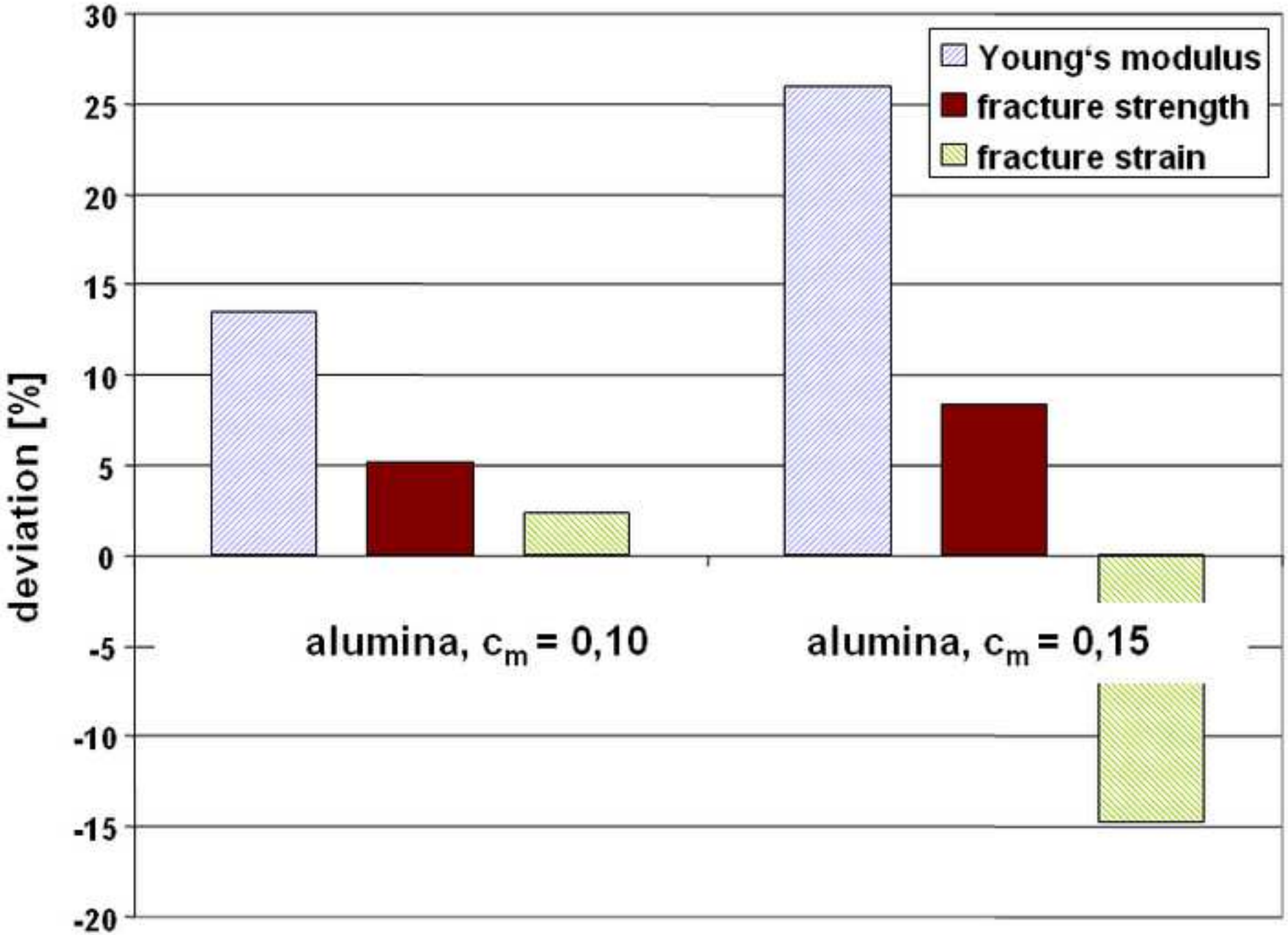
Figure 13