**Temperature dependent electrorheological effect and its description with respect to dielectric spectra**

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**Abstract**

Electrorheological (ER) fluids consisting of tremendous kinds of electrically polarizable particles have been presented. However, there is a lack of studies dealing with the temperature dependence of their ER effect which can be an important feature of the ER fluids from the application point of view. The aniline oligomers were synthesized and carbonized in order to obtain materials suitable for the use in ER fluids. Their silicone oil suspensions were prepared as ER fluids and the dependence of their ER performance on temperature was investigated. In the case of the fluid based on particles smaller than 2 μm, high thermal stability and slightly increased ER effect within the 25 – 65 °C was observed. However, the ER effect of the fluid based on particles with size in tens of micrometres (less than 45 μm) considerably increased with the temperature. This can be explained as a consequence of increase in the dielectric relaxation strength. The smaller

particles were probably strongly influenced by Brownian motion at 65 °C which led to the decrease in the dielectric relaxation strength. Therefore, unlikely behaviour at 25 °C, ER efficiency at 65 °C was higher for the fluid based on larger particles at low shear rates.

**Keywords**

Electrorheology, aniline oligomers, carbonization, impedance spectroscopy, Cole-cole model, electrorheological effect, temperature dependence, electric field induced structures

**Introduction**

Electrorheological (ER) fluids are suspensions altering their rheological parameters via an external electric field. These ER fluids are commonly composed of an insulating liquid as a continuous phase and electrically polarizable particles as a dispersed phase. In the absence of electric field, particles are randomly dispersed within the ER fluid; however, upon the application of electric field, the particles start to create organized chain-like structures spanning the electrodes, which leads to a steep increase in their rheological parameters (Mrlik et al., 2013). This change is rapid and completely reversible (Sedlacik et al., 2013a). It is assumed that the conductivity of the particles and dielectric properties of the ER fluid are the relevant factors that determine the degree of the ER effect of the ER fluids (Hao, 2002).

Materials with controlled rheological parameters are highly demanded in certain applications, mainly in robotics (Oh et al., 2013) and hydraulics devices (Kamelreiter et al., 2012). However, the ER fluids have to fulfil a number of demands for their further utilization in the industry, namely the sufficiently high yield stress, thermal and chemical stability, redispersibility, low current density passing through the fluid and last

but not least the wide operating temperature region (Hao, 2002). Many ER fluids composed of various materials have been presented (Sedlacik et al., 2013b; Yin et al., 2014; Zhang and Choi, 2014; Zhang et al., 2014), nevertheless, there is still a lack of studies dealing with a temperature dependence of their rheological behaviour in the absence and in the presence of electric field.

So far presented studies dealing with the dependence of ER effect on the temperature (Belza et al., 2008; Kim et al., 2007; Yin et al., 2011) have shown that the ER effect slightly increases with the increasing temperature. Thus, the temperature can positively influence the ER effect. Nevertheless, the satisfying explanation of such behaviour is still missing. This contribution is focused on the ER fluids composed of particles of various sizes and their temperature dependent rheological performance in the absence and in the presence of external electric field. It describes the temperature dependent ER performance of prepared ER fluids with respect to their dielectric spectra.

**Experimental**

*Preparation of the particles*

The particles were prepared in the same way as mentioned in the literature (Plachy et al., 2014). Briefly, aniline (0.2 M; Sigma Aldrich, USA) was oxidized with ammonium peroxydisulfate (0.2 M; Lach:Ner, Czech Republic) in the aqueous solutions of 0.1 M (product is further labelled as S1) and 2 M (S2) ammonium hydroxide ($NH_4OH$; Lach:Ner, Czech Republic). The products were dried and converted to bases by the overnight immersion in 1 M $NH_4OH$. After drying, the particles were exposed to 650 °C in nitrogen atmosphere in order to obtain carbonaceous nitrogen-enriched structures. When the temperature was reached, the oven was switched off and the products were left to cool down to the room temperature.

*Scanning electron microscopy*

Morphology and dimensions of the particles were investigated using a scanning electron microscope (SEM; VEGA II LMU, Tescan, Czech Republic). The SEM was operated at 10 kV.

*Preparation of ER fluids*

ER fluids of concentration 10 wt% were prepared by mixing of dried particles and dried silicone oil (Lukosiol M200, Chemical Works Kolín, Czech Republic, viscosity $\eta_c = 194$ mPa s, conductivity $\sigma_c \approx 10^{-11}$ S cm$^{-1}$). Before each measurement, the ER fluid was mixed with a glass stick for 5 minutes, approximately, and then sonicated (ultrasound frequency 24 kHz, 50 % amplitude) for 60 s in order to homogenize the ER fluids.

*Rheological measurements*

Rheological parameters of the prepared ER fluids in the absence and in the presence of external electric field were measured using a rotational rheometer Bohlin Gemini (Malvern Instruments, UK) with the coaxial-cylinder geometry (length 27.4 mm, inner cylinder separated by a gap of 0.7 mm) at 25 °C, 45 °C and 65 °C. The external electric fields of electric field strength within $0.5 - 2$ kV mm$^{-1}$ were produced by a DC high-voltage supplier TREK 668B (TREK, USA). The electric field was applied one minute before starting shearing in order to provide time enough for particles to create internal structures. The experiments were performed in steady shear mode in the shear rates range $0.1 - 300$ s$^{-1}$. After each measurement, the fluid was sheared at a shear rate of 40 s$^{-1}$ for one minute in order to destroy residual structures.

*Dielectric measurements*

Dielectric properties of the ER fluids were investigated by Agilent 4294A high precision impedance analyser (Agilent, Japan) in the frequency range from 40 Hz to $10^7$ Hz at 25 °C, 45 °C, and 65 °C.

*Optical microscopy*

Formation of structures created within ER fluids upon an application of electric field strength 1 kV mm$^{-1}$ was observed by means of an optical microscope (N 400M, China) linked to a digital camera. The fluid consisting of 0.5 wt% of particles was placed between two copper electrodes with the gap 1 mm, which were connected to a high-voltage DC source (Keithley 2400, USA).

**Results and discussion**

*Scanning electron microscopy*

From the images obtained from scanning electron microscopy it can be seen that the particles prepared in higher amount of $NH_4OH$ (Figure 1b) are significantly bigger than the particles prepared in lower amount of $NH_4OH$ (Figure 1a). While the particles prepared in 0.1 M $NH_4OH$ solution have a thin PANI layer on their surface preventing them from sintering upon the high temperature, the oligomers prepared in 2 M $NH_4OH$ solution probably sintered together during the carbonization and they broke down to the smaller pieces during the cooling process (Moravkova et al., 2013; Plachy et al., 2014).
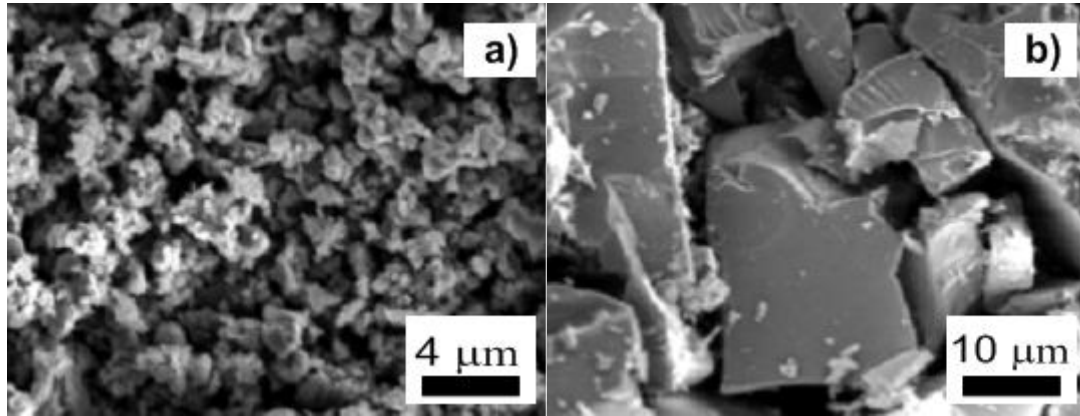
**Figure 1. SEM images of S1 (a) and S2 (b).**

*Rheological properties*

It can be seen that in the absence of external electric field the ER fluid based on S1 behaves as pseudoplastic liquid rather than Newtonian one (Figure 2a) at low shear rates, while the ER fluid based on the S2 acts as Newtonian fluid over the whole shear rate region (Figure 2b). However, after the application of electric field of strength $2\,kV\,mm^{-1}$ both of them start to act as Bingham fluids. The fluid based on S1 exhibits higher yield stress than the fluid based on S2 at the room temperature. With increasing temperature, the yield stresses for both fluids increase, whereas the increase is more significant for the fluid based on S2, i.e., the fluid based on bigger particles. In the absence of electric field, the higher shear stress at the low shear rates is observed for the fluid based on S1, corresponding to the smaller particles size of the S1. The particles then possess higher specific surface area leading to higher interactions between particles and silicone oil in the case of the fluid based on S1. The shear stress of this fluid in the absence of electric field also does not change significantly with increasing temperature. On the other hand, the shear stress of the fluid based on S2 shows considerable decrease between the 25 °C and 65 °C in the absence of electric field. Thus, the fluid based on

bigger particles seems to be more sensitive to the temperature than the fluid based on smaller particles.
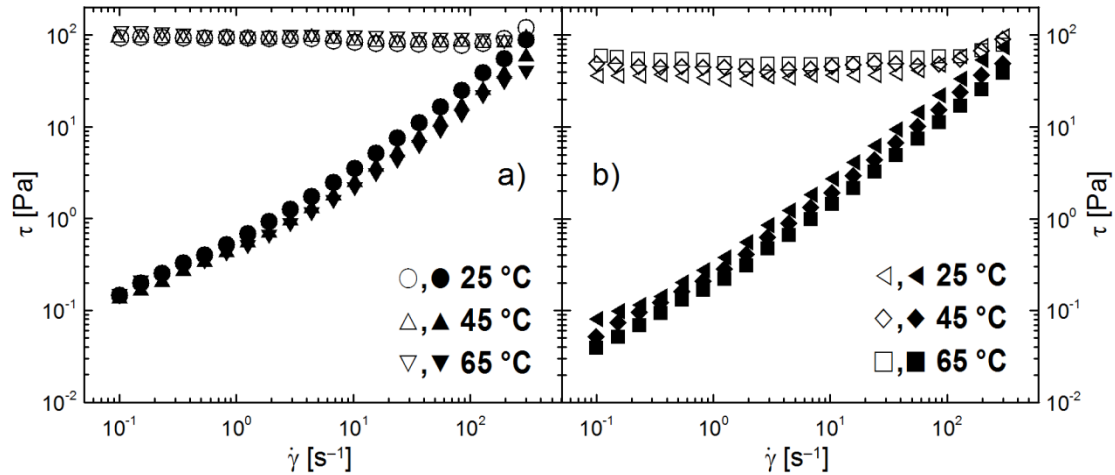


**Figure 2. The log-log dependence of shear stress, $\tau$, on the shear rate, $\dot{\gamma}$, for ER fluids based on S1 particles (a) and S2 particles (b) in the absence (solid symbols) and in the presence of electric field of strength $2\,\text{kV}\,\text{mm}^{-1}$ (open symbols) at various temperatures.**

The influence of temperature on the rheological behaviour of the prepared ER fluids can be more clearly seen from the Figure 3, which depicts the values of shear stresses at shear rate $0.1\,\text{s}^{-1}$ at various temperatures. In the presence of electric field, the slope is evidently higher for the fluid based on S2. The slopes of the linear regressions corresponding to the increase in shear stress values is 0.28 for the suspensions based on S1 and 0.60 for the suspension based on S2, which is twice higher than for the former one. Also the decrease in shear stress in the absence of external electric field with increasing temperature is higher for the fluid based on the S2. This confirms the higher sensitivity of ER behaviour of the fluid based on the S2 than of the fluid based on the S1 to the temperature.
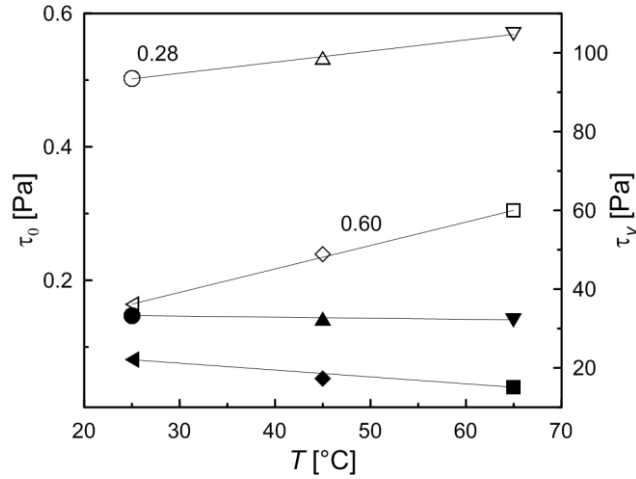
**Figure 3.** **Values of the shear stress for prepared ER fluids in the absence (solid symbols; $\tau_0$) and in the presence of electric field of strength $2\,kV\,mm^{-1}$ (open symbols; $\tau_y$) at shear rate $0.1\,s^{-1}$ at various temperatures. The meaning of the symbol is the same as in the Figure 2.**

From the application point of view, ER fluids have to exhibit high difference between the viscosity in the presence and in the absence of electric field. This difference is well embodied in the formula of ER efficiency, $e$, $e = (\eta_E - \eta_0)/\eta_0$, which captures both the viscosity in the presence of electric field, $\eta_E$, and the viscosity in the absence of electric field, $\eta_0$. For both prepared ER fluids, the ER efficiency increases with increasing temperature (Figure 4). At 25 °C, the ER efficiency is higher for the fluid based on S1. The smaller difference at the low shear rates is caused by high field-off viscosity of the fluid based on S1 due to the presence of the small particles. However, at the temperature 65 °C in low shear rates region, the ER efficiency is higher for the fluid based on S2 as a result of its significantly enhanced ER effect and lowered field-off viscosity. Nevertheless, at the shear rates higher than $1°s^{-1}$ the ER efficiency is again higher for the fluid based on the S1. This is a consequence of the high pseudoplastic behaviour of

the fluid based on S1 at lower shear rates leading to significantly higher viscosity than in the case of the fluid based on the S2 (bigger particles).
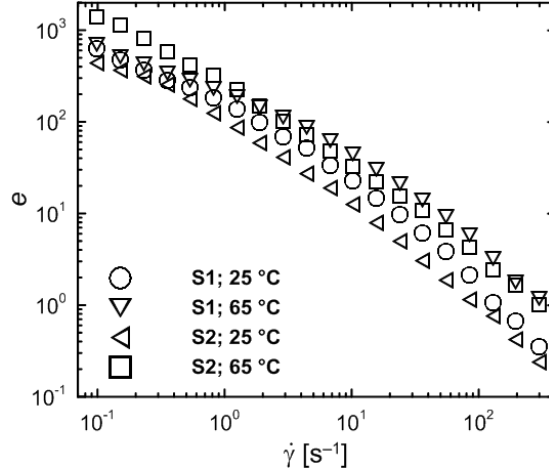


**Figure 4. The dependence of ER efficiency, *e*, on the shear rate, $\dot{\gamma}$, for ER fluids based on S1 and S2 in the presence of electric field of strength 2 kV mm$^{-1}$ at 25 °C and 65 °C.**

*Dielectric properties*

The observed dielectric relaxation process (Figure 5) cannot be explained by the Debye model, as the center of the semicircle is not in the abscissa axis. Due to the spectrum symmetry the Cole–Cole formalism was employed for data analysis (Cole and Cole, 1941):

$$\varepsilon^* = \varepsilon_\infty + \frac{\left(\varepsilon_S - \varepsilon_\infty\right)}{1 + \left(i\omega \cdot \tau_{rel}\right)^{1-\alpha}} \tag{1}$$

where $\varepsilon^*$ stands for complex permittivity, $\varepsilon_S$ and $\varepsilon_\infty$ are the "static" and "infinite frequency" relative permittivities, $\omega$ represents the angular frequency and $\tau_{rel}$ the relaxation time. $\Delta\varepsilon$, which is the algebraic difference between $\varepsilon_S$ and $\varepsilon_\infty$ is the dielectric relaxation strength. The $\alpha$ parameter, which is called the Cole-Cole exponent, describes the broadness of the relaxation time distribution (Cole and Cole, 1941).
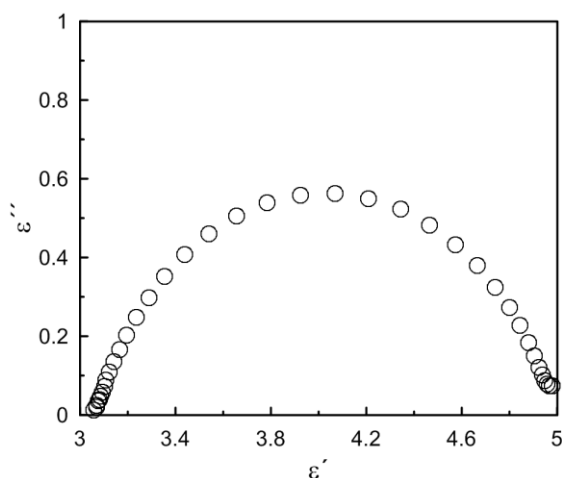


**Figure 5. Cole-Cole plot for the S1 sample at 25 °C.**

Mrlik et al. has comprehensively described temperature dependence of dielectric spectra of particles based on aniline oligomers showing strong dependence on the temperature (Mrlik et al., 2014). The dependence of the dielectric spectra on the temperature for prepared ER fluids is depicted in Figures 6 and 7. The behaviour of dielectric relaxation strength for both fluids considerably differs with the change in temperature (Figures 6a and 7a). While for the fluid based on S2 the dielectric relaxation strength increases with increasing temperature, in the case of the fluid based on S1 it decreases instead (Table 1). The decrease in the dielectric relaxation strength can be caused by the disturbing of the smaller particles through the Brownian motion. The significant increase in dielectric relaxation strength of ER fluid based on S2 is also confirmed by its

higher relaxation peaks at 45 °C and 65 °C than at 25 °C (Figure 7b). Increasing the temperature, the relaxation times are significantly shifted to higher frequencies for both ER fluids (Figures 6b and 7b). It has been found that for the high ER effect the relaxation time of the fluids should lay within frequencies $10^2$–$10^5$ Hz and preferably closer to the higher border ($10^5$ Hz). In this region also the interfacial polarization, which is responsible for the ER effect, occurs. The shift to higher frequencies can thus be one of the phenomena responsible for the increase in ER effect of the fluids (Plachy et al., 2013). On the other hand, the lower ER effect of the fluid based on S2 can be explain as the consequence of its slower relaxation process. The relaxation at lower frequencies does not contribute that much to the ER effect as the interfacial polarization does; therefore, the ER effect of this ER fluid is not as high as in the case of the ER fluid based on S1, where the relaxation process occurs only in the desired region of interfacial polarization. Nevertheless, the increased dielectric relaxation strength of the ER fluid based on the S2 also considerably contributes to the steeper increase of its ER effect.
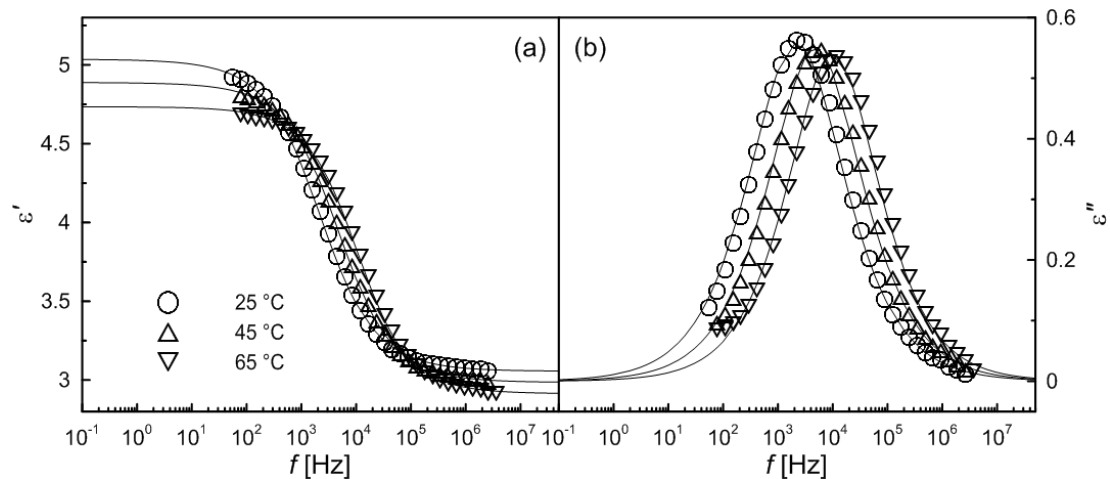


**Figure 6. Dielectric spectra of relative permittivity (a) and dielectric loss factor (b) for the prepared ER fluid based on S1 at various temperatures.**
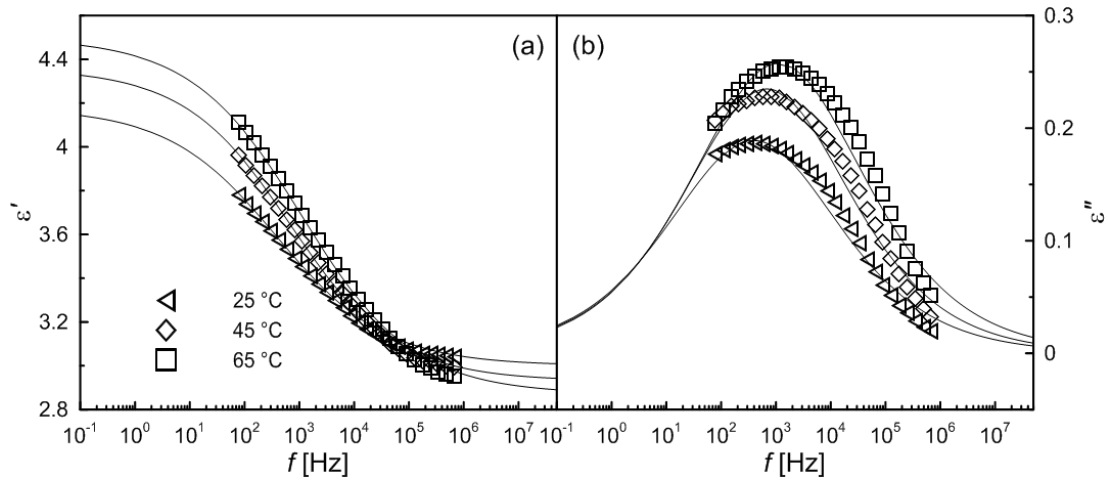
**Figure 7. Dielectric spectra of relative permittivity (a) and dielectric loss factor (b) for the prepared ER fluid based on S2 at various temperatures.**

**Table 1 – Dielectric parameters of prepared ER fluids obtained from Cole-Cole model at various temperatures.**

| Parameter | Fluid based on S1 | | | Fluid based on S2 | | |
|---|---|---|---|---|---|---|
| | 25 °C | 45 °C | 65 °C | 25 °C | 45 °C | 65 °C |
| $\varepsilon_S$ | 5.04 | 4.89 | 4.73 | 4.18 | 4.36 | 4.50 |
| $\varepsilon_\infty$ | 3.06 | 2.99 | 2.92 | 3.00 | 2.93 | 2.89 |
| $\Delta e$ | 1.98 | 1.90 | 1.81 | 1.18 | 1.43 | 1.61 |
| $\tau_{rel}$ [s] | $7.28\times10^{-5}$ | $3.29\times10^{-5}$ | $1.56\times10^{-5}$ | $4.11\times10^{-4}$ | $2.33\times10^{-4}$ | $1.44\times10^{-4}$ |
| $\alpha$ | 0.65 | 0.66 | 0.68 | 0.39 | 0.40 | 0.39 |

The values of the Cole-Cole exponent, which are far from 1.0, show that the relaxation process is not represented by a unique relaxation, i.e., the Debye model is not useful to

characterize these materials. A distribution of relaxation times is then observed (Chihaoui et al., 2013; Macdonald, 1987).

*Optical microscopy*

The viscosity of the medium, in which the particles are dispersed, also plays important role in the formation of organized structures upon the application of the electric field. Figures 8 and 9 show the images of the prepared ER fluids of the concentration 0.5 wt% in the absence and in the presence of electric field of strength 1 kV mm$^{-1}$, respectively. In the case of the ER fluid based on S1, the transition in distribution of the particles from random (Figure 8a) to highly organized structures after the application of the electric field is clearly seen (Figure 8b). On the other hand, the particles of the fluid based on the S2 were not able to properly join themselves within the fluid after the application of electric field (Figure 9). It can be assumed that the mobility of the particles is not high enough in order to join themselves. However at 65 °C, the viscosity of the liquid medium (silicone oil) significantly decreases. One of the possible consequences of such decrease could be also a decrease in energy barrier hindering the particles in movement. Therefore, this could lead to enhanced ability of particles to join themselves together under applied electric field.
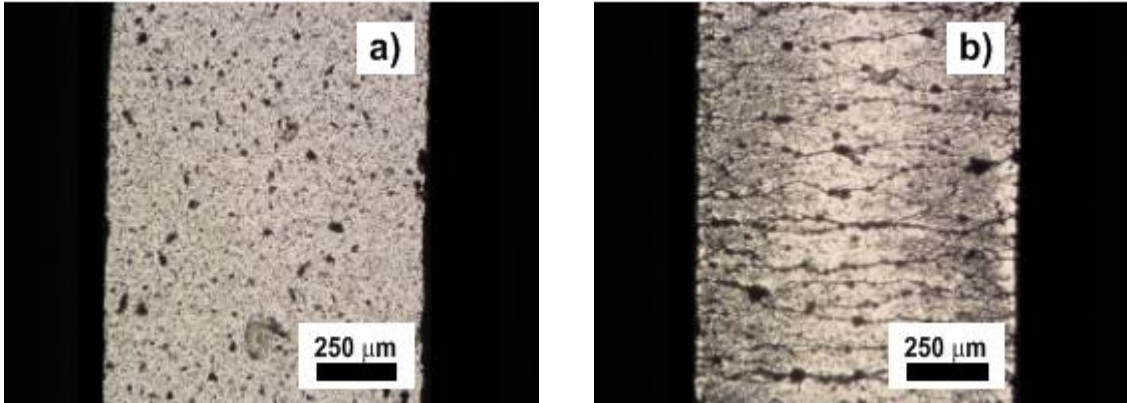
**Figure 8. Optical microscopy of ER fluid based on the S1 particles (0.5 wt%) under various electric field strengths, $E$,: 0 kV mm$^{-1}$ (a), 1 kV mm$^{-1}$ (b).**
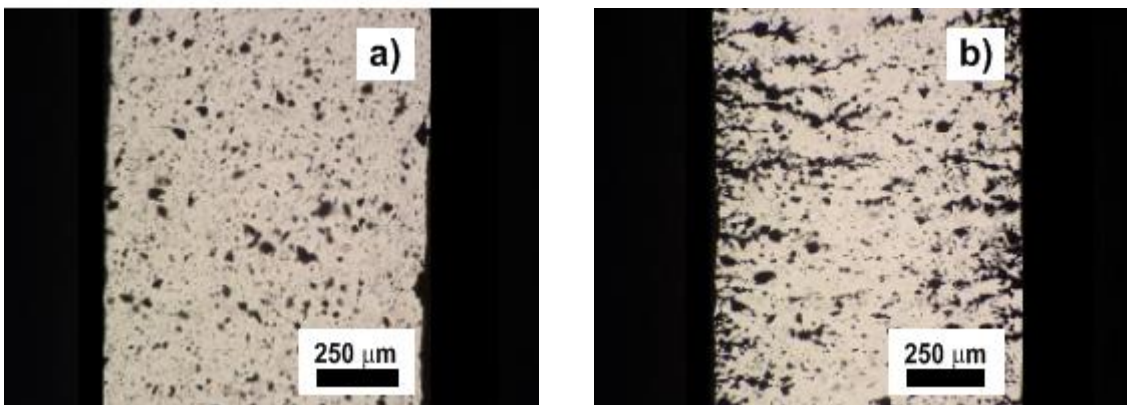


**Figure 9. Optical microscopy of ER fluid based on the S2 particles (0.5 wt%) under various electric field strengths, $E$,: 0 kV mm$^{-1}$ (a), 1 kV mm$^{-1}$ (b).**

## Conclusion

The study describes the temperature dependent rheological behaviour of prepared ER fluids based on carbonized aniline oligomers in the absence and in the presence of external electric field. The ER effect increased with increasing temperature, while the increase was more significant in the case of the ER fluid based on the bigger particles.

Impedance spectroscopy was used in order to elucidate the temperature dependent ER behaviour. The dielectric relaxation strength decreases in the case of the fluid based on the smaller particles, however, increases for the fluid based on the bigger particles. Thus, even though the dielectric relaxation strength decreased for the ER fluid based on the carbonized particles prepared in 0.1 M $NH_4OH$ solution, the ER effect in both cases increased probably due to the shorter relaxation times. At 65 °C, the dielectric relaxation strengths were nearly the same for both ER fluids. Nevertheless, the relaxation process of the ER fluid based on the carbonized particles prepared in 2 M $NH_4OH$ solution occurs outside the region of frequency range for interfacial polarization which leads to the lower ER effect of the ER fluid based on such particles. Also the decrease of the viscosity of the liquid medium can play an important role in the forming of chain-like structures from particles upon the application of external electric field.

**Acknowledgments**

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