The role of edible oils in Low Molecular Weight organogels rheology and structure

F. R. Lupi[1], M.P. De Santo[2,3], F. Ciuchi[3], N. Baldino[1], D. Gabriele[1]

[1] Department of Information, Modeling, Electronics and System Engineering, (D.I.M.E.S.) University of Calabria, Via P. Bucci, Cubo 39C, I-87036 Rende (CS), Italy

francesca.lupi@unical.it; domenico.gabriele@unical.it;

[2] Department of Physics, University of Calabria, Via P. Bucci, Cubo 31C, I-87036 Rende (CS,) Italy

[3] CNR-NANOTEC c/o Department of Physics, University of Calabria, Via P. Bucci, Cubo 33B, I-87036 Rende (CS) Italy

Corresponding author

Dr. Domenico Gabriele

Department of Information, Modeling, Electronics and System Engineering (D.I.M.E.S.)

Via P. Bucci – Cubo 39C

I-87036 Arcavacata di Rende (CS), Italy

Email: domenico.gabriele@unical.it

Tel. +39 0984 496687; Fax +39 0984 494009

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ABSTRACT

In this paper, the role of solvent characteristics on the rheological and physicochemical properties of organogels was investigated using different techniques. Vegetable oils, such as rice, sunflower and castor oil were used as solvents, for producing organogels with monoglycerides of fatty acids or a mixture of fatty alcohols (policosanol) as gelators. Moreover, two non-edible oils (silicon and paraffin oil) were also used for analysing the properties of solvents completely different in nature with respect to the edible ones, for a better interpretation of the given results. Organogels were investigated from a rheological point of view and through a microscopic analysis, given by polarised light (POM) and atomic force (AFM) microscopy, and X-rays to study the crystallinity of the system. The IR technique was used to analyse the intermolecular interactions, resulting in interesting information about the effect of oil polarity on the driving forces promoting structuration. This investigation showed that when solvents of a similar chemical nature are used, their physical properties, mainly oil polarity, are strictly related to the properties of the organogel, such as the onset of crystallisation temperature, the stiffness of the final material and its crystallinity. Anyway, these physical parameters seem insufficient to describe properly the role of solvents when oils of a different chemical nature are compared.

Keywords: *organogels; polarity; rheology; X-ray; Interfacial Tension (IFT); Atomic Force Microscopy (AFM); Fourier Transform Infrared Spectroscopy (FTIR); Polarised Optical Microscopy (POM)*

1. INTRODUCTION

Low molecular weight (LMW) organogels are soft solids with gel characteristics, where an organic solvent (typically an oil) is structured thanks to the self-assembly action of LMW organogelator molecules, mainly interacting among themselves with weak interaction such as H-bonds or van der Waals forces (Lupi et al, 2016; Lupi et al, 2017; van Esch & Feringa, 2000). Organogels are very interesting for their potential uses in different fields; in particular, in the food industry, they are used for replacing saturated and hydrogenated fats with a healthier lipid phase (Marangoni & Garti, 2011). The main characteristics of organogels have been deeply investigated by research, in particular the rheological properties (Calligaris et al, 2014; Chaves et al, 2017; Co & Marangoni, 2012; Lupi et al, 2012; Lupi et al, 2013; Morales-Rueda et al, 2009; Ojijo et al, 2004), the microstructural arrangements of crystals (Schaink et al, 2007; Toro-Vazquez et al, 2013), and also the weak interactions which give particular properties to these systems (Lupi et al, 2016; Zweep et al, 2009). An interesting topic not yet completely investigated is the effect of the solvent on these properties. In particular, it is remarkable to understand how the chemical characteristics of the solvent can affect the consistency, the structuration, but also the strength of the interactions among crystals and the thermorheological parameters (*Tco*, onset of crystallisation temperature and *Tg*, gelation temperature) of these materials, keeping constant the quantity and the kind of organogelator. On this topic, an interesting work was published by Calligaris et al. (2014) on the effect of oil type (viscosity and polarity) on the firmness and thermal properties of samples prepared with sitosterol and γ-oryzanol. The authors found that highly-viscous and polar solvents gave less structured organogels; according to the authors, this can be attributed to the increased difficulty of β-sitosterol and γ-oryzanol molecules to pack together as the oil viscosity

increased, whereas the increased polarity of the solvent could change the solvent-gelator interaction, lowering gelator-gelator interaction as a consequence. A similar study was carried out by Sawalha et al. (2013) for organogels structured with the same gelators. They measured oil polarity through the evaluation of the dielectric constant; according to the authors, polarity increases if the dielectric constant also increases. With their work, the authors concluded that fibres constituting the network were more stable, decreasing the polarity of the oil. Moreover, the gels prepared with polar oils, i.e. sunflower oils and eugenol, were generally transparent, whereas gels prepared with low polarity oils were opaque after a short time of preparation. Recently, in an interesting work, Hwang et al. (2014) investigated the effects of polar compounds and fatty acids profile on macroscopic properties of organogels and margarines prepared with sunflower wax and different edible oils; the authors did not observe a clear relation between the firmness of obtained systems and amount of polar compounds and fatty acids, concluding that, even if some organogel properties could be dependent on them, other factors probably pay a relevant role (such as the position of fatty acids on the glycerol units or minor components).

According to Zhu and Dordick (2006) and Wu et al. (2013) the structuration of LMW organogels is a result of the nature of gelator-gelator and solvent-gelator interactions, and this process involves specific and nonspecific intermolecular forces (H-bonds and weak interactions). Moreover, the network formation is dominated by the polarity of the solvent and the hydrophobic/hydrophilic characteristic of the gelator. In general, according to the authors, gelation is better achieved by using a solvent that has limited interaction with the organogelator, because restricted solvent-gelator interaction enhances the growth of thin and highly branched fibres, leading to stronger and more stable gels. On the contrary, strong solvent-gelator interactions allow the clustering of gelator aggregates, resulting in

less stable gels. Therefore, gelation process can be properly tuned by adjusting the solvent polarity with the addition of cosolvents to a gelator solution at room temperature. Zweep et al. (2009) investigated the effect of the solvent-gelator interactions, concluding that polar solvents allow the formation of weak H-bonds and hence gelation occurs if a sufficient compensation is provided by the van der Waals interactions contribution. Therefore, the authors concluded that in polar solvents structuration, van der Waals interactions play a dominant role, whereas in apolar solvents H-bonding interactions dominate. Similar results were also described by de Vries et al. (2017), who investigated the effect of protein aggregates in structuring vegetable oils (extra virgin olive oil, sunflower oil and castor oil) with different polarities. The authors found that gel strength is affected by the polarity of the solvent, and weaker gels are built in more polar oils, as a result of larger gelator solvent interactions. Currently, despite the efforts made in finding the exact process occurring during organogelation, a scarce literature is currently available on the role of commercial edible oils as solvents interacting with gelators for oleogel formation. In the present work, a deep understanding of the interactions among different edible oils with commercial organogelators (monoglycerides of fatty acids, MAGs, and policosanol, a mixture of fatty alcohols) is presented, in an attempt to investigate the rheological and microstructural characteristics of gels produced with them. Edible oils investigated in this work are sunflower oil, rice oil and castor oil (to be assumed in a small amount, according to the Food Agricultural Organization (Johnson, 2007)). In addition a mineral oil, i.e. paraffin oil, and silicon oil were also studied as a sort of benchmark having chemical characteristics different with respect to those of triglycerides systems (even if some physical properties are similar).

2. MATERIALS AND METHODS

2.1 Materials

Different oils were used to examine the effect of the solvent on the properties of organogels. In particular, organogels were prepared with sunflower oil 'SO' (Fabiano, Italy), castor oil 'CO' (Sigma-Aldrich, Germany), rice oil 'RO' (Dr. Taffi, Italy), paraffin oil 'PO' (Sigma-Aldrich, Germany) and silicon oil 'SiO' (VWR Chemicals, France).

Two kinds of LMW organogelators were used: a mixture of fatty alcohols (policosanol, ACEF, Italy) (Lupi et al, 2016; Lupi et al, 2017) and distilled monoglycerides of saturated fatty acids (with an equal mass fraction of glyceryl monostearate and glyceryl monopalmitate) prepared from kosher palm feedstock and glycerol (Myverol 18 04 K, Kerry group, Ireland). All reactants were used without further purification. The physical properties of the oils are described in table 1 and the methods used for their analysis are described in detail in section 2.3.

2.2 Samples preparation

All organogels were prepared with the same amount (5% w/w) of Myverol, and only for silicon oil, one organogel sample was produced also with the same amount of policosanol. Samples were prepared following the procedure already described in previous works (Lupi et al, 2016; Lupi et al, 2017). The oil was stirred continuously with an overhead stirrer (RW 20, IKA-Werke, Germany) and it was warmed up to 70°C or 85°C according to the different organogelator used (70°C for MAGs organogels and 85°C for policosanol organogels) with a thermostated water bath (Arex, Velp scientific, Italy). Organogelator was added to the hot oil, stirring for a further 10 minutes to guarantee the complete melting of the gelator before starting the measurements. Organogel samples are labelled,

in the text, with two letters, the first one indicating the initial of the oil ('S' for sunflower oil, 'C' for Castor oil, 'R' for rice oil, 'P' for paraffin oil and 'Si' for Silicon oil), and the other one related to the organogelator used ('M' for Myverol and 'P' for Policosanol).

2.3 Pure oils characterisation: viscosity, interfacial tension, dielectric constants and fatty acids profile

Oils were characterised with different techniques aiming at better understanding the potential effects of an organogelator on different solvents. First of all, the rheological properties of oils were investigated performing Step Rate Temperature Ramp tests (SRTRTs) with the controlled stress rheometer MARS III (Thermo Scientific, Germany) adopting a parallel plates geometry (P50 Ti L, diameter 50 mm, gap=1 ± 0.1 mm) and a Peltier system for temperature control. A constant value of shear rate of 10 s^{-1} was used and the tests were carried out from 70°C (only for silicon oil, used to prepare policosanol organogels, tests started at 80°C) down to 10°C with a cooling rate of 1°C/min. All samples were examined three times and experimental results are shown in terms of average values and standard deviation.

Transient interfacial tension profiles of oils, at water interface, were measured with the automated pendant drop tensiometer FTA200 (First Ten Angstrom, USA, software of analysis Fta32 v 2.0). The Axisymmetric Drop Shape Analysis (ADSA) was used to calculate drop volume, area and interfacial tension profile (Seta et al, 2014). A water droplet (twice-distilled water obtained from a Milli-Q purification system (Millipore, USA)) of a volume of 30 μL was forced to be formed inside a quartz cuvette containing the oil to be tested; images were taken every 10 s for a total time of 120 min. A quasi-

equilibrium value of interfacial tension (IFT) was assumed when change with time was lower than 0.5 mN/m in 30 min. The analysis procedure is described in detail by Seta et al. (2012).

The relative dielectric constant of oils (ε_r') was also analysed, since it can be considered an indirect measurement of oil polarity (Sawalha et al, 2013; Wang, 2011). The dielectric constant was inferred from Complex Impedance measurements acquired at room temperature by a potentiostat/galvanostat/impedentiometer EG&G model 273A in frequency range 0.1-10^5 Hz. In the experimental set-up, a wire acted as working electrode, whereas the counter electrode was short-circuited with the reference wire. The amplitude of the sinusoidal applied voltage, V_0 = 1000 mVrms, was chosen because measurements at lower voltages give the same results but introduce more noise. Two gold electrodes were evaporated on glass substrates, then glasses were assembled with two 12 μm mylar spacers: the active area of the cells (inner surfaces coated with gold) was A ~ 1 cm^2. The thickness was checked by the interferometric method with an AVANTES (200-1000 nm) spectrophotometer. Finally, the cell was filled with oil by capillarity. From complex impedance measurements the real part of the relative dielectric constant at different frequency is obtained using Eq. 1, modeling the cell as a circuit formed by a Resistance and a Capacity (Barsoukov & MacDonald, 2005):

$$\varepsilon'_r = \frac{Z_{im}}{Z_{real}^2 + Z_{im}^2} \frac{d}{A 2\pi f} \quad (1)$$

Z_{im} and Z_{real} are the imaginary and the real part of the measured impedance, respectively, d is the cell thickness, A the electrode area and f the frequency.

FT-NIR (Fourier Transform Near Infrared) spectroscopy is a technique already used for investigating the acidic profile of vegetable oils, as deeply discussed by Azizian and Kramer (2005), Casale et al. (2012), Galtier et al. (2007) based on the creation of an average absorption file for (several) reference vegetable oil samples, used in the development of a classification or quantification model. These models were then used to classify oils having a similar Fatty Acids (FA) composition at a 99% confidence interval or to quantify for FA composition.

The fatty acids content of vegetable oils was measured with an FT-NIR spectrometer (MPA, Bruker, Germany), previously calibrated through the investigation of a wide number of vegetable oils used as references, aiming at evaluating the properties of solvents as a function of the Fatty Acids content (SFA Saturated Fatty Acids, Mono-Unsaturated Fatty Acids, MUFAs, and Poly-Unsaturated Fatty Acids, PUFAs). The oil to be tested was simply filled at room temperature into an 8 mm glass vial, and measured in the sample compartment of the spectrometer. The OPUS software (Bruker Optics, USA) was used to collect and handle the experimental data with a chemometric analysis.

2.3 Organogel characterisation: rheological investigation, FTIR spectroscopy, X-rays, Polarization Microscopy, Atomic Force Microscopy

The rheology of organogels was investigated with a controlled strain rheometer (ARES RFS, TA Instruments, USA, parallel plates 50 mm, gap 1.0 ± 0.1 mm). Preliminarily, strain sweep tests were carried out at different constant temperatures from the preparation value, i.e. 70 °C or 80° when policosanol was used, down to 10 °C almost every 10 °C to investigate potential changes in the linear viscoelastic region.

Dynamic temperature ramp tests were performed at 1 Hz in the linear viscoelastic regime, cooling the sample from the starting temperature of preparation down to 10 °C with a cooling ramp rate of 1°C/min. Even in this case, all samples were examined three times and experimental results are shown in terms of average values and standard deviation. Observed average error was lower than 10%, larger deviations were seldom observed for data at high temperature, owing to instrument limits, or in the transition crystallization region, owing to the fast structuring phenomena.

The onset of crystallization (*Tco*) was defined as the temperature corresponding to the sudden increase of complex modulus *G** (or the abrupt decrease of the loss tangent curve) in temperature ramp as already discussed in previous papers (Lupi et al, 2013).

The gelation temperature (*Tg*), that is, the temperature at which crystal clusters or fibres of organogelators begin to interconnect, was evaluated as the temperature corresponding to the crossover of dynamic moduli (phase angle equal to 45°) (Lupi et al, 2012).

The weak interactions, thanks to which the organogel is formed, were analysed with a Fourier Transform Infrared Spectroscope (FT-IR Nicolet IS-10, Thermo Scientific, USA), equipped with a sampling accessory smart Itx ATR (attenuated total reflectance, data spacing 0.482 cm^{-1}, 64 scans for each test). The same tests were also carried out for pure oils to have a comparison of gels properties with respect to solvents. Organogels made for these investigations were prepared as previously described, and afterwards cooled down to room temperature. Once the gels were formed, an average sample amount of 20 mg was loaded into the instrument to be analysed.

An Atomic Force Microscope (AFM), Multimode 8 equipped with a Nanoscope V controller (Bruker), was used to have an inspection of the topography of samples on a

length scale varying from few nm to one hundred of μm. Organogels were deposited using a spatula on a sample holder and heated to temperatures higher than their melting point to allow the sample to spread and rearrange over the surface creating an almost flat air/organogel interface. Then, samples were cooled down to 25°C in a thermostatic water bath (F25, Julabo, USA). The samples surface was investigated operating the AFM in Tapping mode and using levers with a resonance frequency of 300 kHz and a tip nominal radius of curvature of 10 nm (RTESPA, Bruker). All the measurements were performed in air and at room temperature.

X-rays analysis was carried out with a D8 Discover reflectometer (Bruker axs), wavelength of 1.5418 Å. This instrument was set for transmission measurements with a capillary holder made expressly for these tests. Capillaries had an inner diameter of 1 mm and an outer diameter of 1.01 mm.

For these tests organogels were warmed up to temperature values higher than their melting points, and then poured into capillaries. Afterwards, the capillary was thermostated and cooled down to 25°C with a controlled cooling rate of 1°C/min in order to guarantee the same thermal history used in rheological tests. For each samples, there were two intervals of measurements: 0.8-10 and 19-25 in 2θ ((Δ(2θ)=0.004 scan, velocity=2 s/step).

A Polarized Optical Microscope (POM, Digital-Modul-R Leica, Germany), was used to point out the presence of small birefringent crystalline structures inside the organogels. Samples were prepared confining a small amount of the material between two glass slides, using the same thermal treatment as described previously, and imaged at room temperature between crossed polarizers.

256

257 ## 3. RESULTS AND DISCUSSION

258 ### 3.1. Characteristics of pure oil

259 Pure oils were characterised to understand their effect on the final properties of
260 organogels. Temperature ramp tests (data not shown) evidenced a gradual monotonous
261 increase, with decreasing temperature, without sharp and sudden changes which would
262 be present in case of crystal formation (as it occurs in organogels), this further confirms
263 that oils are liquid within the investigated temperature range. Vegetable oils (SO, CO and
264 RO) are a mixture of triglycerides of fatty acids, which, in turn, are different among
265 themselves. In fact, the three oils are characterised by a different acidic profile, and their
266 fatty acid contents are different; their value is listed in table 1. It is worth noticing that oil
267 viscosities at 25°C decrease with the increase of PUFAs, as shown in Tab. 1. This was
268 expected, considering that the unsaturation of fatty acids attached to glycerol in
269 triacylglycerols allows a higher mobility of the carbon chain, and a bigger steric hindrance
270 which reduces molecular density and oil viscosity as a consequence (Quinchia et al,
271 2012). Moreover, according to Quinchia et al. (2012), the concentration of PUFAs affects
272 the low-temperature viscosity of oils more than the concentration of the other saturated
273 fatty acids.

274 The relative dielectric constant decreases with the following order CO>RO>SO, whereas
275 IFT increases up to a plateau value (SO>RO>CO) therefore it can be noticed that, for
276 vegetable oils, IFT decreases when ε'_r increases (Table 1). It is well-known from the
277 literature that oils have different compositions in terms of impurities such as
278 unsaponifiable lipids, tocopherols, sterols, oryzanol, humidity and so on (Grompone,

279 2011; Kochhar, 2011). This polar “impurities” are mainly responsible for the interfacial
280 activity of oils. Therefore, even if three points are not sufficient to draw conclusions about
281 the material behaviour, it could be speculated that polar compounds, able to increase the
282 polarity of rough oils are also responsible for lowering their interfacial tension.

283 The other two oils chosen for producing organogels were not vegetable, and in fact, they
284 were chosen to understand the effect of oils completely different in nature. Paraffin oil is
285 a mixture of n-alkanes with a very little content of impurities, whereas silicon oil is a
286 polydimethylsiloxane: both of them are characterised by the same value of the dielectric
287 constant (average values overlap within the experimental error range, see table 1) but with
288 different values of interfacial tension. Therefore, it can be speculated that for synthetic
289 oils the interfacial properties are not a function of the dielectric constant, since both these
290 oils do not contain significant amounts of impurities.

291 **3.1. Characteristics of organogels: rheology**

292 Myverol (5% w/w) was used to prepare organogels with all oils, whereas policosanol (in
293 the same amount) was used only with silicon oil (Table 2) to investigate the effects, on
294 non-edible oils, of one gelator which proved to self-assemble in olive oil with a
295 mechanism different than that observed for Myverol (Lupi et al, 2016). Figure 1 shows
296 the dynamic temperature ramp tests of all samples prepared with Myverol in terms of G^*
297 (Fig. 1a) and phase angle, δ, (Fig. 1b) as a function of temperature. At high temperatures,
298 all samples are molten and behave as purely viscous liquids as shown by the phase angle
299 value close to 90° (Fig. 1b). All organogels, in their molten state, show similar values of
300 complex moduli (Fig. 1a) except for sample CM that has values greater than the others.
301 This, apparently, is in contrast with previous literature results (Lupi et al, 2012) where it

was observed that the viscosity of the solvent did not affect the rheological properties of the derived organogels in the molten state. Anyway, it is worth noticing that castor oil viscosity is one order of magnitude greater than the others, therefore it can be concluded that differences in molten organogels reflect potential differences in oils, and cannot be appreciated only when pure oil viscosities are similar (as in the case of sunflower and rice oil).

At the *Tco*, a sudden increase of moduli, and a decrease of phase angle, indicate the beginning of crystallisation. This value depends on the solvent and it decreases with decreasing IFT and with increasing ε'_r (see fig. 2) for all investigated oils that exhibit crystallisation phenomena; in fact it is worth noticing that for silicon oil no crystallisation appears in the investigated range of temperature. Similar results were described by Sawalha et al. (2013) and Calligaris et al. (2014), according to which a decrease in oil polarity lead to a higher structuring temperature, and a self-assembly action of organogelator shaped as tubules. Even the viscosity of the solvent strongly affects the properties of the resulting organogel. Table 2 shows the relationship between the *Tg* of organogels and the solvent viscosity evaluated at *Tg*, evidencing a marked decrease of *Tg* with increasing solvent viscosity. The effect of oil viscosity on organogel properties was already investigated for different organogelators reporting results similar to those observed in the present work; Calligaris et al. (2014) investigated the effect of oil characteristics on β-sitosterol and γ-oryzanol organogels and they found that solvents characterised by different dielectric constants (polarity) and viscosity showed different gelling kinetics, as well. Castor oil (the most polar and viscous oil used by those authors), for example, did not even gel after three months of investigation, whereas the other vegetable oils, all less viscous and polar, required less than 1 h. According to the authors,

who confirmed what was already found by Bot et al. (2006; 2008), the formation of the gel network is the results of two steps: the first one is the self-aggregation of organogelator molecules into tubules and the second one is the junction of tubules forming the network itself. The increase in oil viscosity can decrease the rate of collision between molecules first and tubules later on, delaying the whole process.

Aiming at relating the rheological properties of organogels to physical properties of the solvent, complex modulus and phase angle were plotted as a function of dielectric constant. Anyway, if only the effects of organogelator-oil interactions have to be investigated, data have to be independent of potential differences in liquid oils rheological properties.

When organogel data at temperature higher than *Tco* are considered (see Fig. 1a) it can be noticed that the complex modulus increases slowly with decreasing temperature evidencing an almost linear trend in semi-log scale; in these conditions, where crystals are not yet present, the system behaves as a viscous liquid and complex modulus increases only because of a decrease in molecular mobility (Lupi et al, 2011). As a consequence, a simple exponential model (analogous to the Andrade equation used to fit edible oil viscosity (Noureddini et al, 1992)) can be used to describe complex modulus variation with temperature between *Tco* and 70°C for each system (Eq. 2):

$$G_0^*(T) = A \cdot \exp^{\frac{B}{T}} \tag{2}$$

where *A* and *B* are fitting parameters depending on the specific investigated oil. It can be assumed that, if crystal formation would not occur at *Tco,* eq. 2 could be suitable to describe material behaviour even at lower temperature, therefore it can be used to extrapolate, at temperature lower than *Tco,* the complex modulus of a hypothetical non-

gelled system. Starting from these considerations a dimensionless complex modulus (G_S^*) was defined as the ratio between the complex modulus of the organogel G^*, and the extrapolated complex modulus of a non-gelled oil-organogelator system, G_0^*, at the same temperature obtained with eq. 2:

$$G_s^*(T) = \frac{G^*(T)}{G_0^*(T)} \quad (3)$$

Being G_0^* dependent on the specific oil, the dimensionless modulus G_S^* should be function of organogelator-oil interactions, only. A similar evaluation of a dimensionless phase angle was not necessary because the non-gelled reference (δ_0) is the same for all systems (i.e. approximately 90°). All moduli were evaluated at a constant distance from the onset of crystallisation, i.e. $T_{10}=Tco-10°C$.

Figure 3 depicts the trend of G_S^* with the dielectric constant, evidencing a marked decrease of data with the increase of solvent polarity. A different trend is found if δ is analysed: apparently, a minimum in the curve seems present, which hypothetically should correspond to a maximum of the structuration degree. Nevertheless, the error bar is quite large, with respect to the differences, and this suggests considering constant the phase angle, although further investigations on this topic could be necessary.

An interesting discussion can be carried out if the systems prepared with silicon oil and, in turn, Myverol or policosanol are taken into account. The dynamic temperature ramp tests of samples SiM and SiP are shown in figure 4 in terms of complex modulus and phase angle. As it can be noticed, a huge difference distinguishes the two samples: the former is not crystallised or gelled in the whole range of investigated temperatures (δ is

about 90° in the whole range of temperature), whereas the latter is a gel starting from very high temperatures (74.2 ± 0.2°C), and it shows elastic properties and a strong structuration.

This evidence suggests a potentially different role of the solvent in promoting or disadvantaging gelator-gelator interactions. Consequently, a deeper investigation was carried out with FT-IR tests in an attempt to better understand the nature of these interactions (see section 4.2).

Summarising the results so far discussed, it can be concluded that if organogels based on oils made of triglycerides (i.e. vegetable oils) are considered a clear trend between organogel properties (such as *Tco*, *Tg*, complex modulus) and pure oil physical properties (polarity or interfacial tension) is found. This is probably caused by the similar molecular structure of these oils containing esters derived from glycerol and fatty acids differing among them for the number of carbon atoms and unsaturated bonds, but having the same structure. On the other hand, when other investigated solvents are considered, a more complex behaviour is observed, in fact data obtained for paraffin oil, a mixture of alkanes, are in good agreement with the trend previously discussed. This could be ascribed to the similar molecular structure of the oils where the linear chains are always based on carbon-carbon bonds: differences with respect to vegetable oils arise mainly in the absence of unsaturated bonds and of glyceryl units.

On the contrary, silicon oil based on chain consisting of alternating silicon and oxygen atoms with side chains, exhibit a very different behaviour: it is not gelled by used Myverol fraction within the considered temperature range, although the physical properties of this oil are not so different from those of other solvents. This highlights that physical

parameters, such as polarity, are useful to classify solvents within a "chemical family" (e.g. based on similar polymer chains like triglycerides are) but they seem to lose relevance when materials with different chemical nature are used (for instance comparing solvents based on carbon-carbon chains and silicon-oxygen ones). The solvent viscosity seems to affect strongly the properties of the resulting organogel: in fact, a marked decrease of *Tco* and gelation temperature, *Tg*, with increasing solvent viscosity was found. Anyway it is worth noticing that, for investigated oils (except for silicon oil), a monotonous relation between viscosity, IFT and ε'_r, was observed making difficult the identification of potential single specific effects.

4.2 FTIR tests

IR tests were carried out to provide a microstructural interpretation of the effect of the solvent on the rheological properties of organogels. The ability of an organogelator to produce the network is due to the formation of weak interactions such as H-bonds and/or van der Waals forces (van Esch & Feringa, 2000). The wavenumber region between 2500 and 4000 cm^{-1} corresponds to the OH-stretching vibrational modes, and it is particularly interesting because monoglycerides have two OH groups in the hydrophilic part of the molecule, whereas policosanol (for a sample produced with this gelator) has just one OH group (Chen & Terentjev, 2009; Lupi et al, 2017). According to the literature, in the case of long alkyl chains organogelators, van der Waals forces play also an important role in creating the network (van Esch & Feringa, 2000; Wu et al, 2011). According to Suzuki et al. (2003), van der Waals interactions can be detected in IR spectra as a shift of the absorption bands of symmetric and anti-symmetric CH_2 stretching vibrational modes to lower wavenumber. In particular, for vegetable oils, van der Waals interactions are

highlighted by the shift of the two peaks appearing in the wavenumber region around 2800 and 3000 cm^{-1} (Lupi et al, 2016).

On the basis of the gelator and solvent nature, both forces, or just one of them, can be established. For example, Figure 5 shows the IR spectrum of pure silicon oil compared to those of both organogels based on this oil. In the wavenumber region, where both the cited weak interactions can be found, a broad peak between 3000 and 3800 cm^{-1} appears in the spectrum of sample SiP, whereas it does not appear either in the sample produced with Myverol or in the spectrum of pure silicon oil. As already remarked, the broad peak with a shoulder correspondent to a wavenumber region of about 3500 cm^{-1} can be referred to the vibration of OH groups; the shift of this peak towards lower wavenumber values should indicate the formation of H-bonds between organogelator molecules (Chen & Terentjev, 2009; Lupi et al, 2016; Lupi et al, 2017). On the other hand, the peaks corresponding to the vibration of CH_2 groups, where, potentially, van der Waals interactions could be detected, appear at the same wavenumbers (i.e. 2962 cm^{-1} and 2905 cm^{-1}) for all three samples. Therefore, it can be concluded that the leading force for producing the network with policosanol and silicon oil as the solvent is just the H-bonds formation. This behaviour is quite different with respect to what observed in previous works (Lupi et al, 2016; Lupi et al, 2017) where the spectra of organogels produced with olive oil and policosanol were analysed. In these cases, the predominant interactions between gelators responsible for network formation were van der Waals forces, whereas H-bonds appeared only if a great amount of policosanol (at least 8%w/w) was added to the oil. In different organogels (Zweep et al, 2009) it was observed that, with increasing oil polarity, van der Waals interactions become essential in structure formation, therefore it could be speculated that differences observed between silicon and olive oil are caused

mainly by their distinct chemical nature, more than by simple differences in physical properties.

Similar results were found for the other investigated samples, for which the H-bonding was found to be the leading force. It is worth reminding that, in addition to the shift of peaks, related to the presence of interactions, their intensity can give interesting indications about the "quantity" of links formed during gelation (Brulls et al, 2007; Parolo et al, 2017). In fact, it is known that band intensity indicates the amount of functional groups responsible for IR absorption. From this point of view, figure 8 shows the peak area (i.e. the area under the curves) correspondent to the OH groups' vibration, for all the investigated gels produced with Myverol. It is clear that, for vegetable oils (in Fig. 6 the value for Paraffin oil is properly highlighted), the broadness of the H-bond peak increases with the dielectric constant, i.e. the polarity of the solvent suggesting a direct relationship between polarity and intensity of intermolecular interactions.

4.2 Microscopic characterization of organogels

Organogels prepared with Myverol were also tested with X ray diffraction, AFM and POM. X rays spectra of samples are shown in Fig. 7. Sample SM is characterised by a well-defined peak at low angle and one at high angle that can be attributed to Myverol (Calligaris et al, 2010; Marangoni et al, 2007); moreover two broad bands, typical of oil (Calligaris et al, 2010), were observed in both low angle (approximately around 4°) and high angle region (between 19° and 20°). From the angle peak's width, it is possible to estimate sample crystallinity in order to compare the different samples. The RM sample shows a low angle spectrum similar to that of SM, whereas at a high angle the peaks are

less visible, indicating an increased disorder in Myverol chains. The long-range order crystallite dimension is similar to the previous one. Broad bands similar to those observed in SM are present also in this case and can be attributed to the oil contribution. The X-ray diffraction low angle peak in PM is well defined, broad bands are not visible in this case due to the different nature of paraffin oil, while the high angle shows three peaks, i.e. an increased order of Myverol chains. The long-range order crystallite dimension is similar to the previous one. Sample CM shows quite different behaviour: the low angle peak is enlarged and reduced in the intensity and the broad band at low angle seems shifted to higher values; in addition, the high angle peaks are not visible. The castor oil-Myverol interaction seems to induce a change in both the long range and short range Myverol order. The crystallite dimension is hence reduced.

It is worth noticing that differences in the high angle region highlight the dissimilarities in MAGs crystalline phase (Calligaris et al, 2010; Marangoni et al, 2007) among gels prepared with different oils.

For what it may concern the silicon oil organogel, its spectrum is noisy since silicon oil strongly absorbs CuKa X rays due to Si content. Nevertheless, in the high angle region a peak is clearly visible and it can be attributed to policosanol, according to literature data (Kim et al, 2015).

It is worth noticing that the width of low angle peaks increases in the order SiP-CM-RM-SM-PM, as well as the trend of increase of complex modulus G^* of gels at 25°C (see Fig. 1a for confirmation). As foreseeable, an increase in crystallinity coincides with the increase of complex modulus of gels.

Every POM image (Fig. 8) shows birefringent structures that appear strongly interconnected, especially for SM, PM and RM. In CM samples, the birefringent areas are less interconnected suggesting a looser structure. This is in agreement with rheological data evidencing that CM samples are characterized by higher values of phase angle at room temperature (approximately 20°) with respect to other organogels (close to 9° for RM, SM and PM) and therefore exhibit a lower solid-like behaviour.

AFM (Fig. 9) confirms X-ray and POM data, in fact samples SM and PM scans show some geometrical features like cuts or planes that suggests the presence of crystalline structures even on the sample surfaces. In sample RM, this feature is much less evident and it is completely lost in CM confirming that this sample possesses the loosest structure.

4.3 Final discussion

If organogels based on vegetable oils are considered, the onset of crystallisation temperature, Tco, decreases with decreasing IFT of the solvent and with increasing ε'_r. Moreover, at a fixed temperature value lower than *Tco*, complex modulus decreases when polarity increases, as confirmed also by crystallinity degree found by microscopic techniques. Organogels based on non-edible oils exhibit a different behaviour and silicon oil is not gelled by Myverol in the adopted conditions, although its properties (polarity, IFT) are close to those of other solvents.

Microstructural investigation, performed with X-ray, POM and AFM, confirmed rheological data evidencing that more structured systems are characterised by larger crystalline order and more interconnected elements, in addition, the X-ray highlighted the

507 formation of different structures, in tested organogels, evidenced by differences in the
508 high angle region and related to differences in MAG crystalline phases.

509 FT-IR spectra showed that in all the investigated systems, gelation, when occurring, is
510 promoted by H-bonding. This result is in agreement with previous data for Myverol,
511 whereas is quite unexpected for policosanol, because the literature data evidenced that
512 gelation in virgin olive oil occurred mainly owing to van der Waals interactions (the
513 presence of H-bonds was detected only for high amount of policosanol added to the oil).

514

515 **5. CONCLUSIONS**

516 This paper aimed at analysing, with different techniques, the influence of the solvent
517 nature on the rheological and physicochemical characteristics of edible organogels
518 prepared with MAGs or fatty alcohols as gelators. In particular, polarity, interfacial
519 tension and viscosity of three commercial vegetable oils (sunflower oil, rice oil and castor
520 oil) made of triglycerides chains were used as physical parameters to be investigated as
521 potential influencers of the deriving organogels. Moreover, two additional non-edible oils
522 (paraffin, made of alkane chains, and silicon oil based on chains containing alternating
523 silicon and oxygen atoms) significantly different from edible ones, were also studied to
524 assess the behaviour of used edible gelators in solvents with important differences in
525 chemical nature with respect to vegetable ones.

526 It was observed that when oils with similar chemical nature are considered, a relation
527 seems present among different oil and organogel properties. For instance in vegetable oils
528 made of triglycerides chains, interfacial tension, IFT, increases monotonously with
529 decreasing dielectric constant ε'_r, which gives, in turn, a measure of oil polarity; moreover

onset of crystallization and complex modulus of organogels are related to ε'_r (and therefore to other oil properties). On the contrary relevant changes in chemical nature (as those occurring when passing from triglycerides to siloxanes) yield to a different dependence of organogel characteristics on oil properties.Therefore few physical parameters, such as polarity, are useful to compare the behaviour of a solvent during gelation only when materials with similar chemical nature are used.

Finally, it is worth noticing the important ability of policosanol to act as an organogelator also in oils of a chemical nature quite different from triglycerides, in fact, unlike Myverol, it was able to gel silicon oil.

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TABLES CAPTIONS

Table 1 Physical properties of oils; SFAs, saturated fatty acids, MUFAs, Monounsaturated fatty acids and PUFAs, Polyunsaturated fatty acids percentages for vegetable oils are also listed.

Table 2. ID and qualitative composition of organogels (organogelator amount is 5 % w/w for all samples). *Tco*, *Tg* and the viscosity of the pure solvent evaluated at *Tg* ($\mu_{Tg\ solvent}$) are given.

FIGURES CAPTIONS

Figure 1 Dynamic temperature ramp tests at 1 Hz of organogels, in terms of complex modulus, G^*, (a) and phase angle, δ (b). In the legend SM is the organogel produced with SO as the solvent, CM is Castor oil organogel, RM is Rice oil organogel, PM is Paraffin Oil organogel and SiM is Silicon oil organogel. All curves shown in this graphs are related to organogels produced with monoglycerides as gelators.

Figure 2 Trend of interfacial tension IFT (full circles) and relative dielectric constant ε'_r (open circles) of solvents expressed as a function of onset of crystallisation Temperature, Tco, calculated for the corresponding organogel. IFT and ε'_r are evaluated at room temperature.

Figure 3 Dimensionless complex modulus G_s^* at $T_{10,}$ i.e. 10°C below *Tco*, (eq. 2, full circles) and δ (empty circles) *versus* relative dielectric constant ε_r' of the corresponding oil solvent evaluated at room temperature.

Figure 4 Dynamic temperature ramp tests of silicon oil organogels produced with policosanol (SiP, purple circle) and monoglycerides (SiM, red triangle). Complex modulus (full symbols) and phase angle (open symbols) are shown.

Figure 5 FTIR spectra of pure silicon oil (SiO) and organogels produced with policosanol (SiP) and monoglycerides (SiM). Spectra were obtained at room temperature.

Figure 6 Peak Area corresponding to the OH vibrational modes founded in FT-IR spectra at approximately 3500 cm^{-1}. Grey region highlights the area of the peak found in PO spectrum, for differentiating this mineral oil from the others deriving from plant sources. All data were obtained at room temperature.

Figure 7 X Ray diffraction: spectra are vertically shifted with respect to each other for clarity. Spectra were obtained at room temperature

Figure 8 Polarised Light Microscopy (POM) images of a) Sunflower Oil organogel (SM), b) Rice Oil organogel (RM), c) Paraffin Oil organogel (PM), d) Castor Oil organogel (CM). All organogels were structured with monoglycerides and micrographs were taken at room temperature.

583 Figure 9 Atomic Force Microscopy (AFM) images of a) Sunflower Oil organogel
584 (SM), b) Rice Oil organogel (RM), c) Paraffin Oil organogel (PM), d) Castor Oil
585 organogel (CM). All organogels were structured with monoglycerides and images were
586 taken at room temperature.

587

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Table 1

713

714

Oil type	**Name**	**μ (Pa s)** **(25°C, $\dot{\gamma} = 10\ s^{-1}$)**	**IFT** **(mN/m)**	**ε'$_r$ (-)** **(0.1 kHz)**	**SFAs** **(%)**	**MUFAs** **(%)**	**PUFAs** **(%)**
Sunflower	SO	0.052±0.003	24±1	3.2±0.2	9.4	28.3	62.3
Castor	CO	0.72±0.02	12.9±0.3	4.7±0.2	5.4	83.35	11.25
Rice	RO	0.062±0.001	21.8±0.2	3.8±0.2	22.5	44	33.5
Paraffin	PO	0.082±0.007	32±2	2.9±0.1	-	-	-
Silicon	SiO	0.015±0.001	37.9±0.4	2.9±0.1	-	-	-

715

Table 2

Organogel	**Oil**	**Organogelator**	**Tco (°C)**	**Tg (°C)**	**$\mu_{Tg\ solvent}$ (Pa s)**
SM	SO	Myverol	50±1	48±1	0.022±0.003
CM	CO	Myverol	29.8±0.3	28.5±0.2	0.57±0.02
RM	RO	Myverol	46.6±0.6	43±2	0.033±0.001
PM	PO	Myverol	59.7±0.3	57±1	0.016±0.001
SiM	SiO	Myverol	-	-	-
SiP	SiO	Policosanol	79.2±0.3	74.2±0.2	0.009±0.001

716

Figure 1a

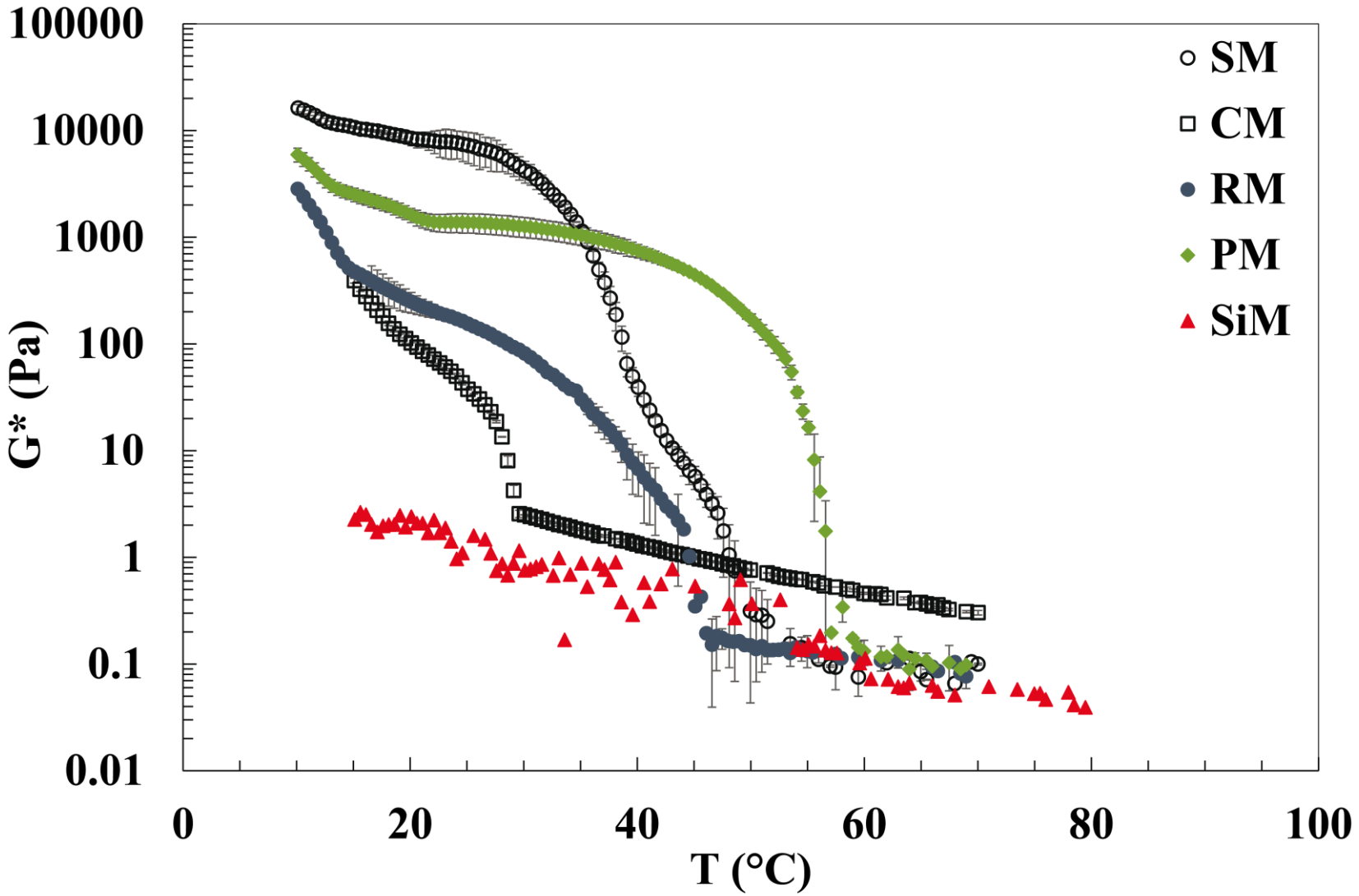

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Figure 1b

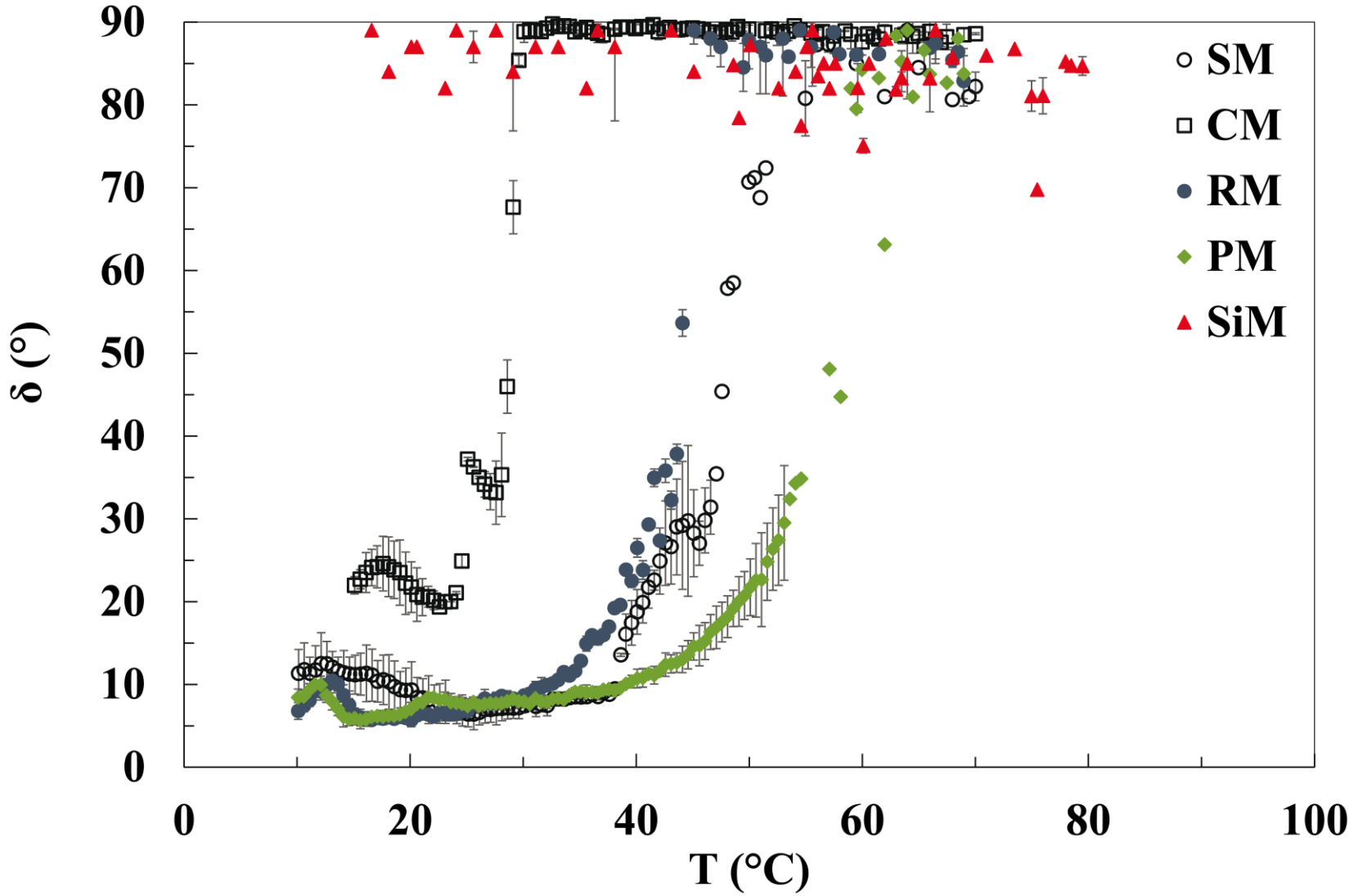

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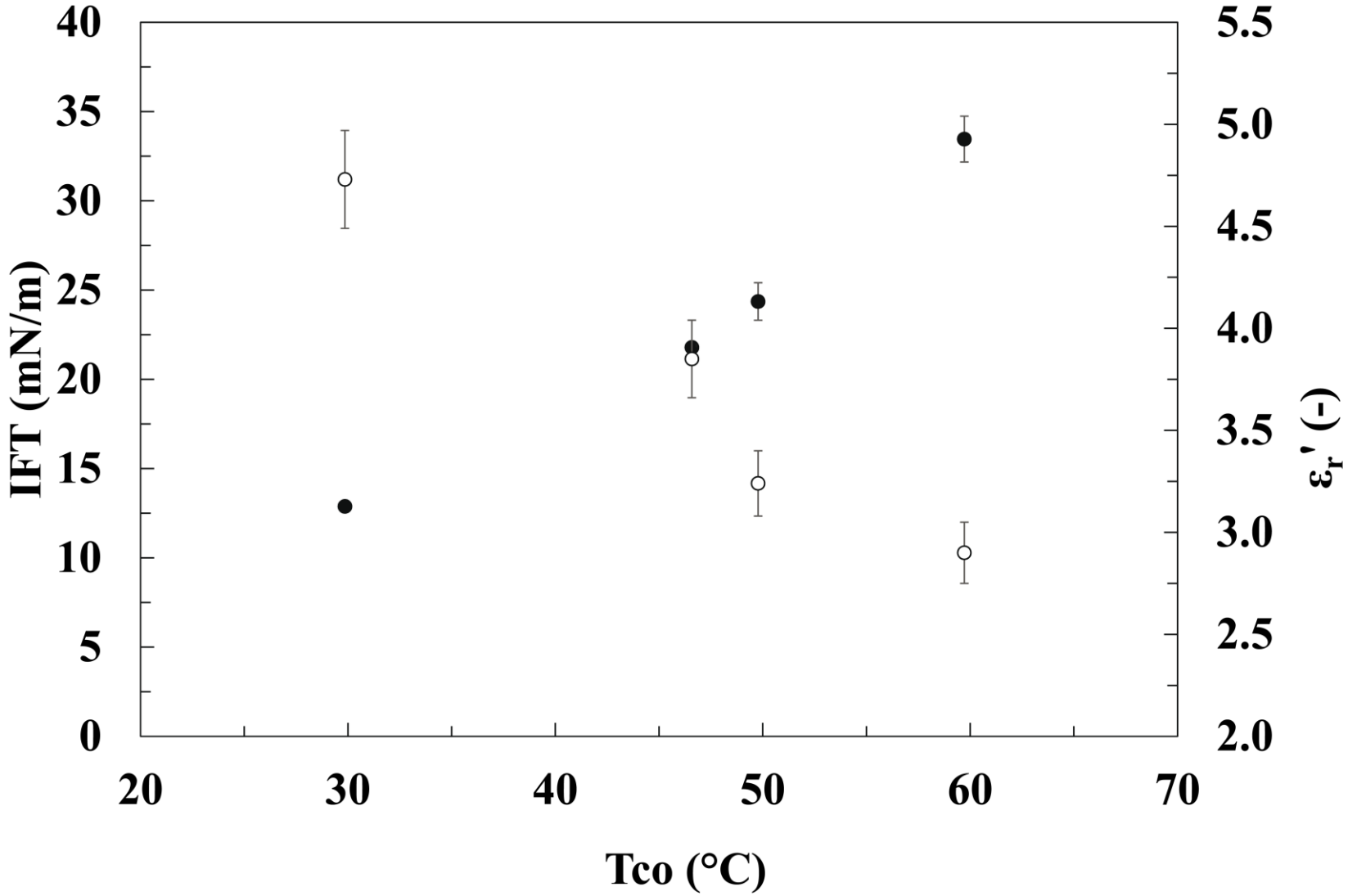
Figure 2


IFT (mN/m)
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15
20
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40
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60
70
Tco (°C)
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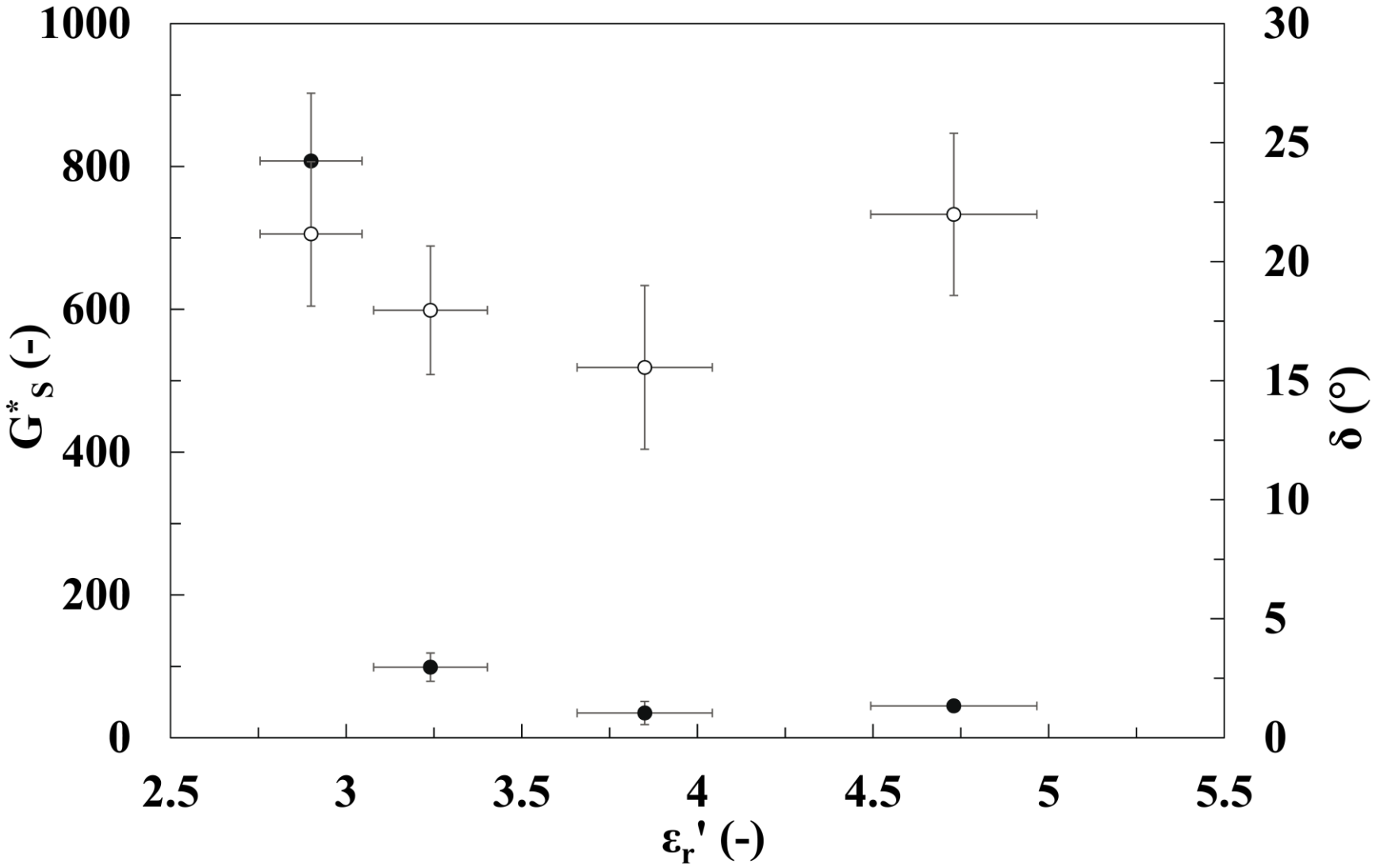
3.0
3.5
4.0
4.5
5.0
5.5
ε_r' (-)

719

Figure 3


1000
800
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400
200
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G^*_S (-)
30
25
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15
10
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δ (°)
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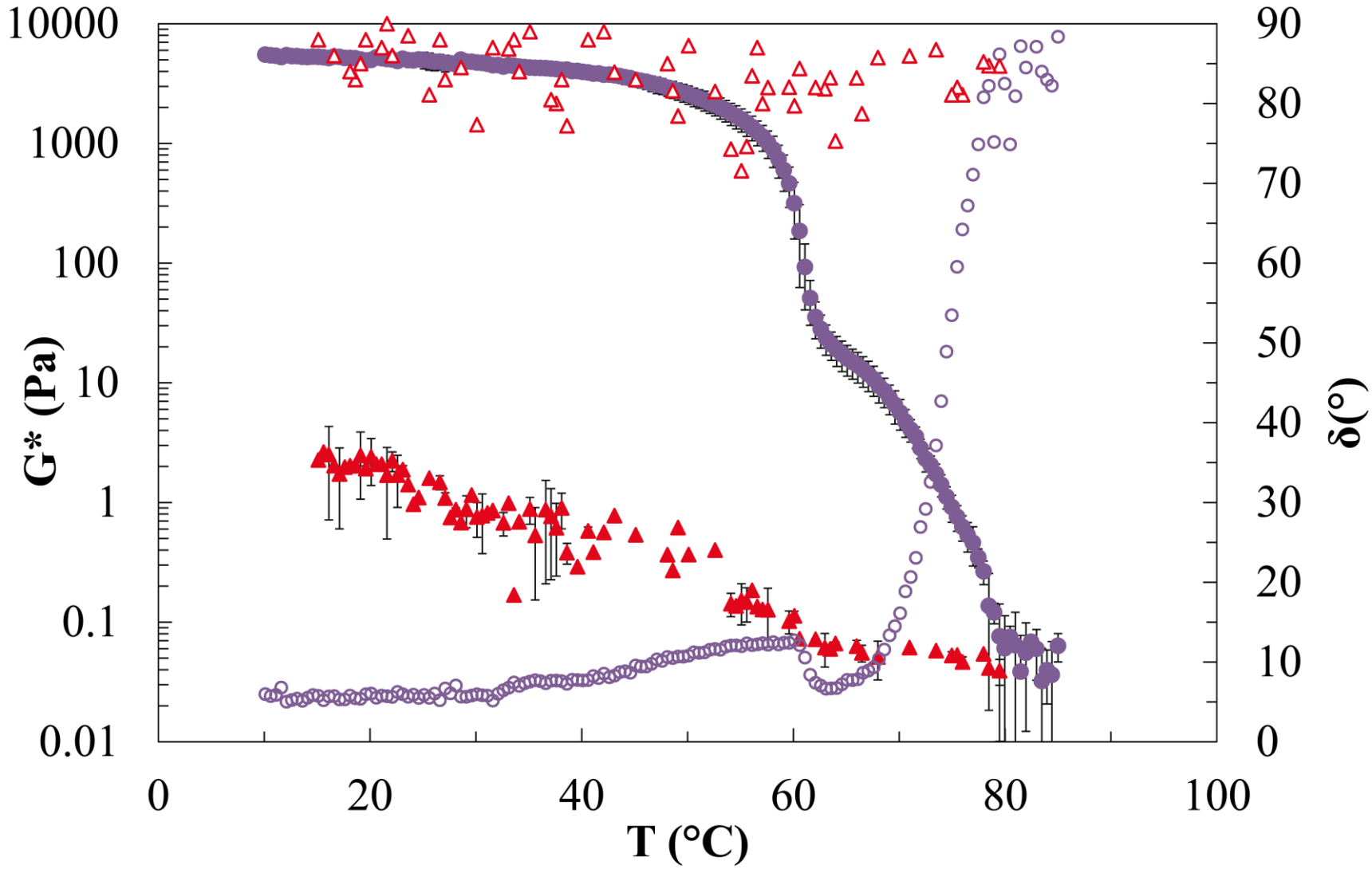
3
3.5
4
4.5
5
5.5
ε_r' (-)

720

Figure 4


10000
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G* (Pa)
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80
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δ(°)
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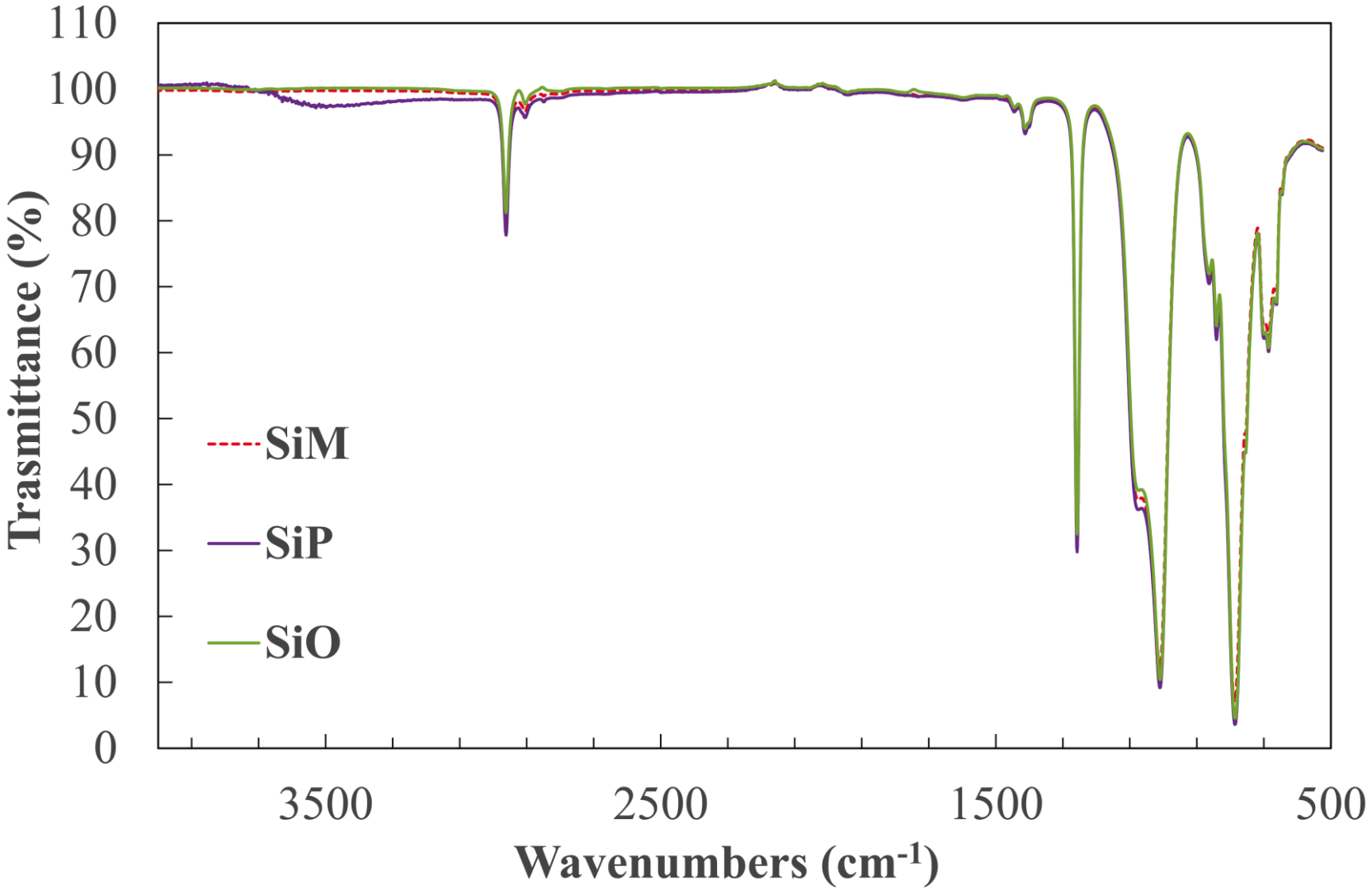
80
100
T (°C)

721

Figure 5


110
100
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80
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60
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40
30
20
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Trasmittance (%)
SiM
SiP
SiO
3500
2500
1500
500
Wavenumbers (cm-1)

722

Figure 6

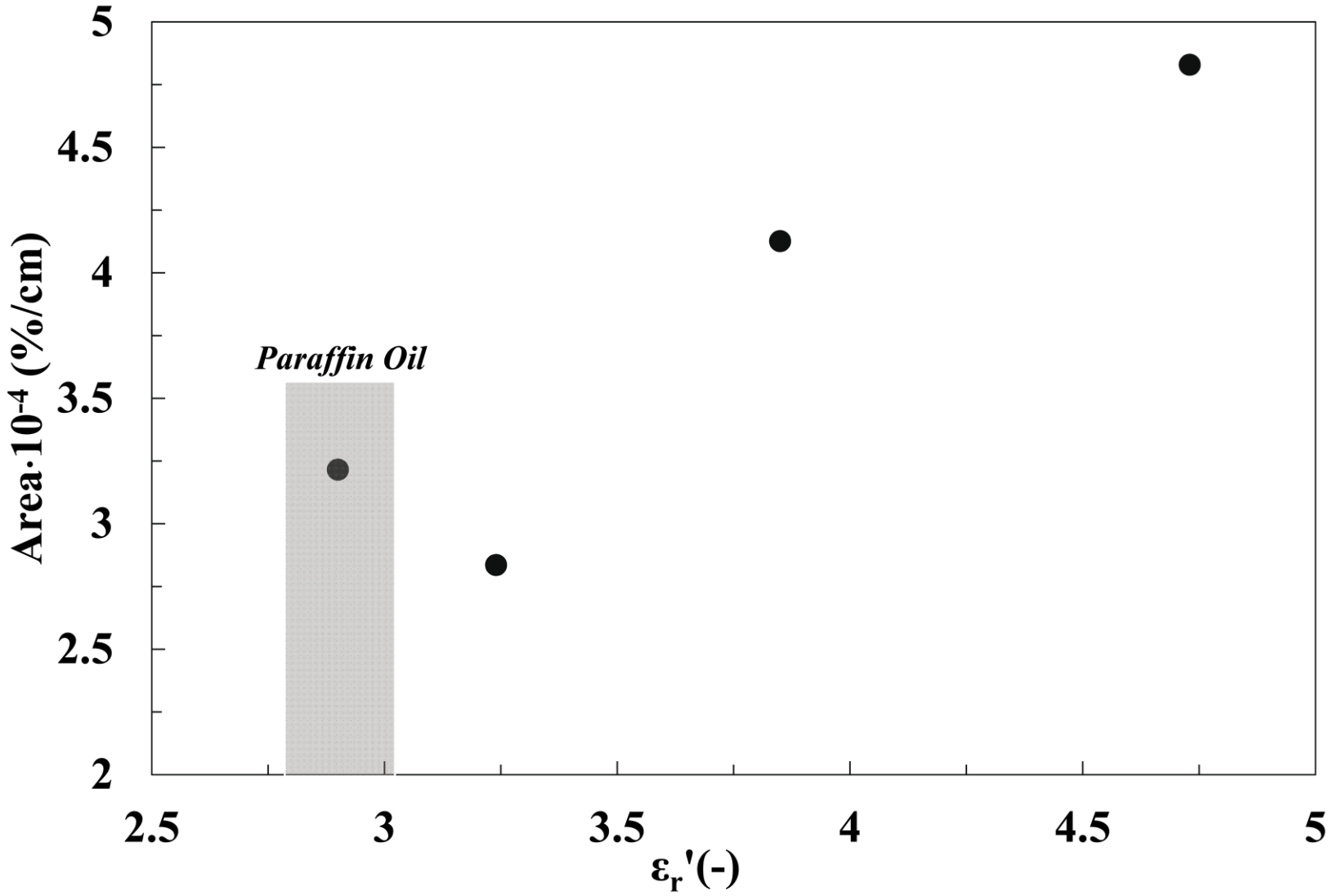

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Figure 7

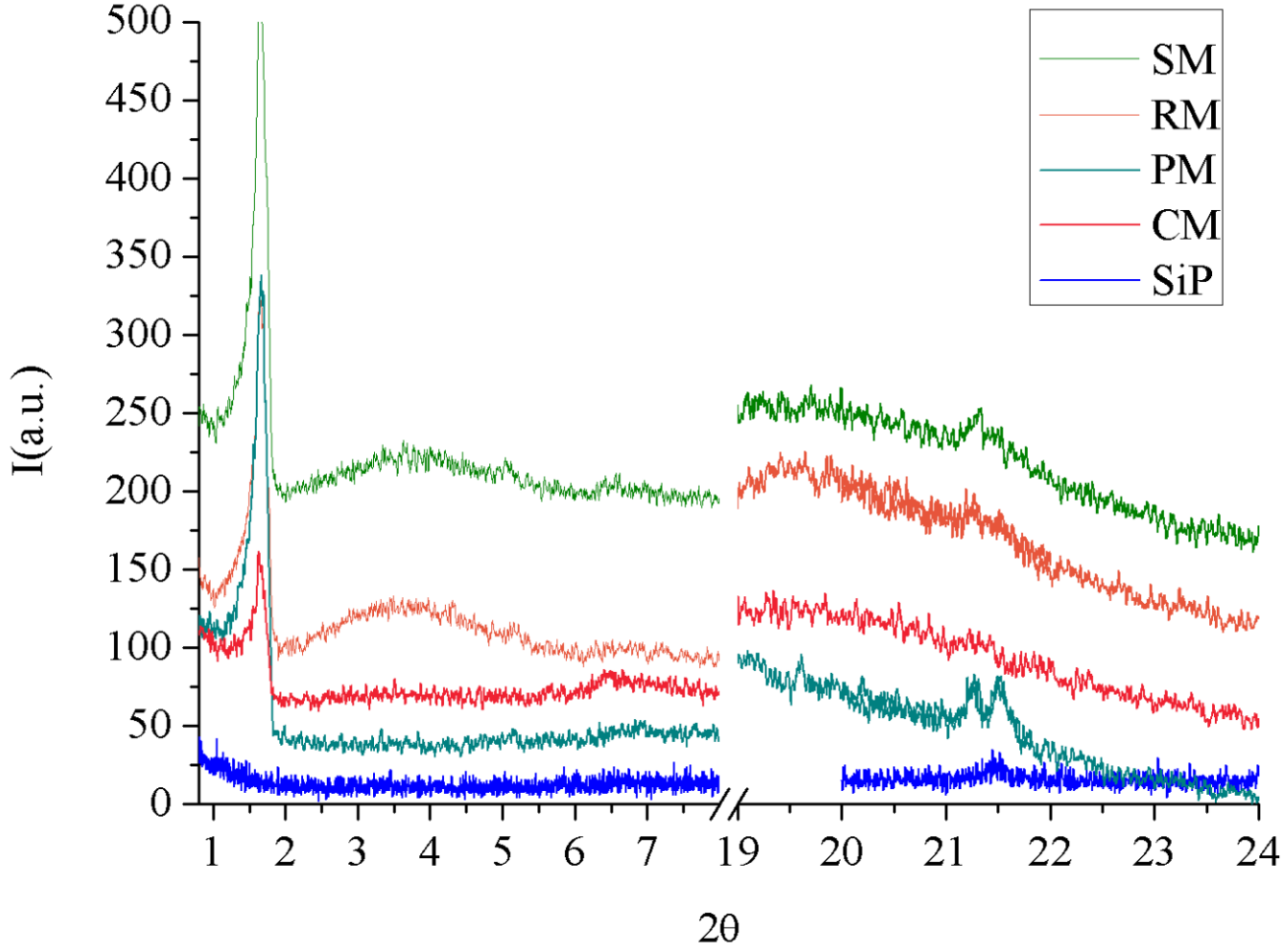
SM
RM
PM
CM
SiP
I(a.u.)
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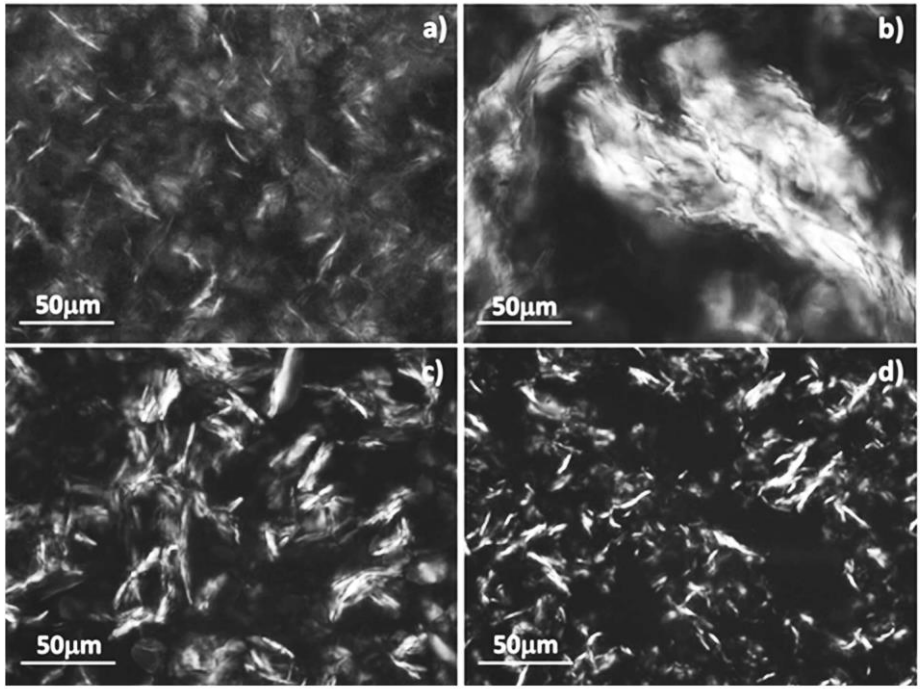
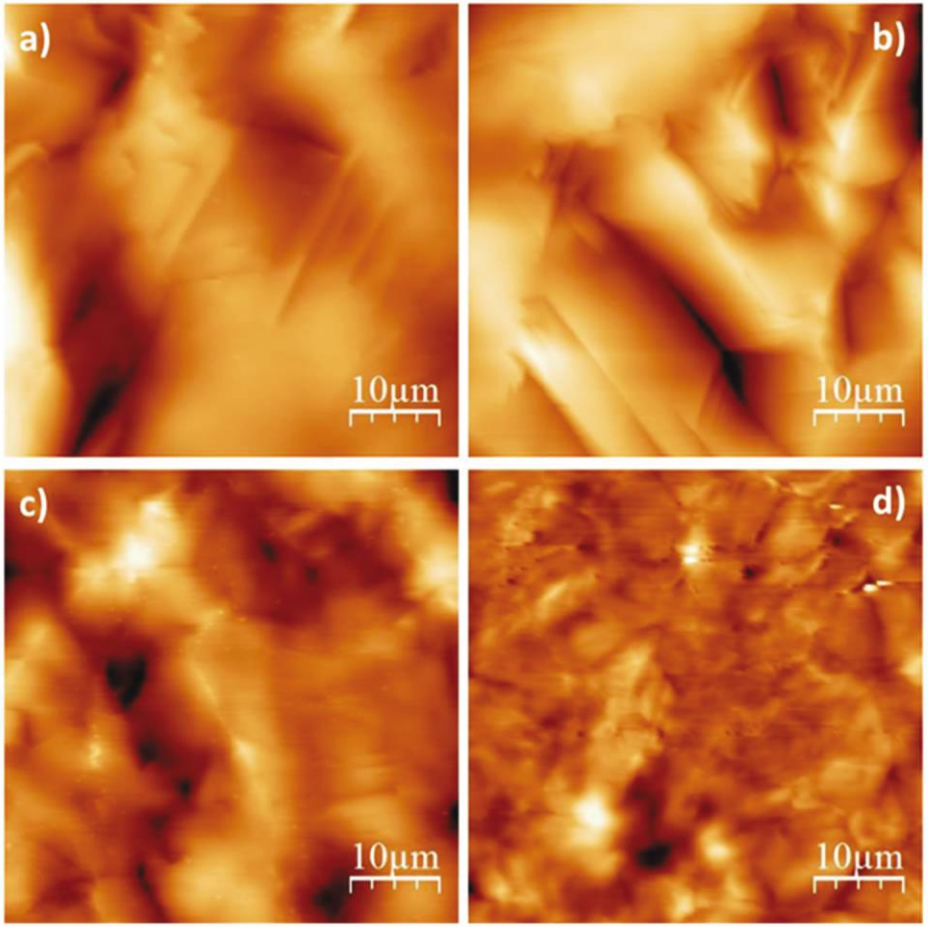
Figure 8

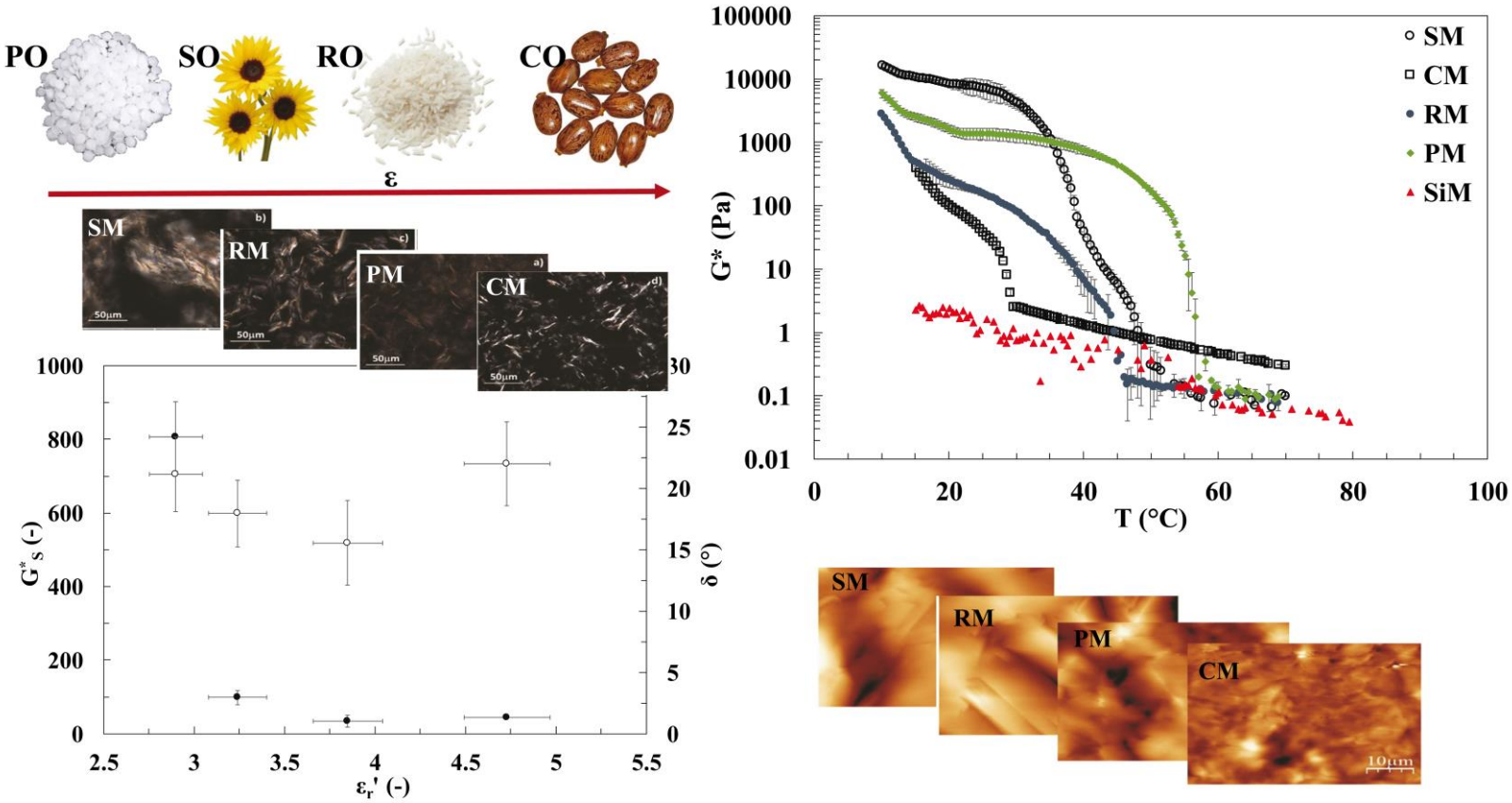


725

Figure 9



726



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