

Taraneh Javanbakht

Department of Chemistry and Biochemistry, Department of Physics, Concordia University, Richard J. Renaud Science Complex, 7141 Sherbrooke Street West, Montreal, Quebec, Canada H4B 1R6, e-mail: taraneh.javanbakht@concordia.ca, ORCID 0000-0002-2658-330X.

## INVESTIGATION OF RHEOLOGICAL PROPERTIES OF A NANOCOMPOSITE OF SUPERPARAMAGNETIC IRON OXIDE NANOPARTICLES WITH POLYETHYLENE GLYCOL

Received: November 22, 2022 / Revised: January 19, 2023 / Accepted: February 9, 2023

© Javanbakht T., 2023

<https://doi.org/10.23939/ujmems2023.01.035>

**Abstract.** This paper presents the results of a new investigation of the rheological properties of a nanocomposite of superparamagnetic iron oxide nanoparticles (SPIONs) with polyethylene glycol (PEG). The surface of the nanocomposite had no electrical charge and the SPIONs were coated with the polymer. The investigations were performed at different temperatures and the results were compared on different rheological parameters. The steady-state behavior of samples was observed at 20 °C and 40 °C and a small increase of viscosity versus shear strain, shear rate or time was revealed at 60 °C. Moreover, the shear stress increase was observed with the increase of shear rate and shear strain. The slopes of the corresponding changes were higher at 20 °C and decreased with the increase in temperature. The torque values increased with shear strain and time. The same phenomenon concerning the different slopes at different temperatures was observed for the torque-shear strain and torque-time variations. These results showed that the rheological properties of the nanocomposite depended on the temperature and could change with the temperature increase. An advantage of this study was that the comparative investigation of the rheological properties of nanocomposite at different temperatures was carried out. The other advantage was that the effect of the coating of the SPIONs with the polymer was observed in the obtained results. This new investigation of the nanocomposite of SPIONs-PEG coated with PEG can provide comparative data for more investigations of the surface charged SPIONs coated with this polymer. These studies can provide information for a further investigation of the effect of the surface charge of SPIONs in the polymeric matrix on their rheological properties.

**Keywords:** rheology, SPIONs, hydrogel, PEG, mechanical engineering.

### Introduction

Nanomaterials have gained importance in recent years concerning their rheological properties. These materials are investigated at different levels: viscous nature and solid-like behavior corresponding to their low filler loading and high concentration [1–3]. Their rheological properties determine processing performance for the preparation of these materials or their composites. When a few percent of these materials are increased, their rheological properties can be modified due to weight change. Polymer composites are materials made of one or several nanocomposites with polymers. The rheological properties of these materials can be studied by computer modeling and simulation. In such an investigation, the mechanisms at the molecular level are explored to improve the dispersion of nanoparticles in matrices. Moreover, such a study can provide information on the effects of

nanoparticles on the samples' chain conformation and glass transition temperature as well as their viscoelastic properties [4, 5].

The molecular weight of the selected polymer matrix and the presence of branched structures can affect their rheological properties [6–8]. These materials can show different behaviors depending on their values of shear rate. Increasing the nanomaterials loading in the polymeric matrix at low shear rate values can lead to the stiffening of polymer chains and agglomeration as well as the increase in the viscosity of nanocomposites [9–12]. This phenomenon can be due to the confinement of the polymer chains with the embedded nanofiller. However, the differences between nanocomposites and corresponding matrices become less evident at high shear rates. This can correspond to the shear thinning behavior, the wall slip phenomenon, and the unaffected material viscosity after the change in the nanomaterial content. For the nanocomposites with high molar mass and low melt flow index, the viscosity values can decrease in the high shear rate region and the nanocomposites containing low amounts of nanomaterials can show lower viscosity values in comparison with the unfilled matrix. This can be due to the higher viscosity of the polymeric matrix when shear stress is high and the nanocomposite shows low flow resistance. A variety of nanofillers with different properties due to their difference in chemical nature, shape, and morphology has been prepared and investigated in recent years. Among these materials are several kinds of nanoparticles such as metals, ceramics, or carbon-based fillers, embedded in thermoplastic or thermoset matrices, to prepare high-performing nanomaterials [13–18].

Nanosized fillers have large surface areas that make polymer nanocomposites better materials than other composites with microsized fillers. It is worth noting that well-dispersed states are required in order to maximize these enhancements [19]. Intercalation of polymers from solution, *in situ* intercalation, or melt intercalation are the common methods used for improving the quality of filler dispersions in these nanocomposites [20–22]. Also, the use of compatibilizers [23–25], nanofiller surface treatments [26–28] or the application of an electric field to clay nanocomposites [29–31] can improve the quality of filler dispersions.

In previous work, we reported the viscosity values of a nanocomposite of bare superparamagnetic iron oxide nanoparticles (SPIONs) with polyethylene glycol (PEG) [32]. The current paper is the pursuit of that investigation including more results on the rheological properties of the nanocomposite with SPIONs coated with the polymer.

The investigation on the rheological properties of the nanocomposite of SPIONs-PEG coated with the polymer has not been reported, yet. The results of this paper can be used for the preparation improvement and applications of this nanocomposite in materials science and engineering.

## Experimental approach

### *Materials and methods.*

PEG with a molecular weight of 8000 was purchased from Sigma Aldrich. SPIONs were prepared as explained previously [32]. The nanocomposite of SPIONs-PEG coated with the polymer was prepared as explained in the previous publication [32].

The QtiPlot software was used for the determination of parameters such as mean values, standard deviations, and statistical significance, and the graphs were plotted with this software [33–35].

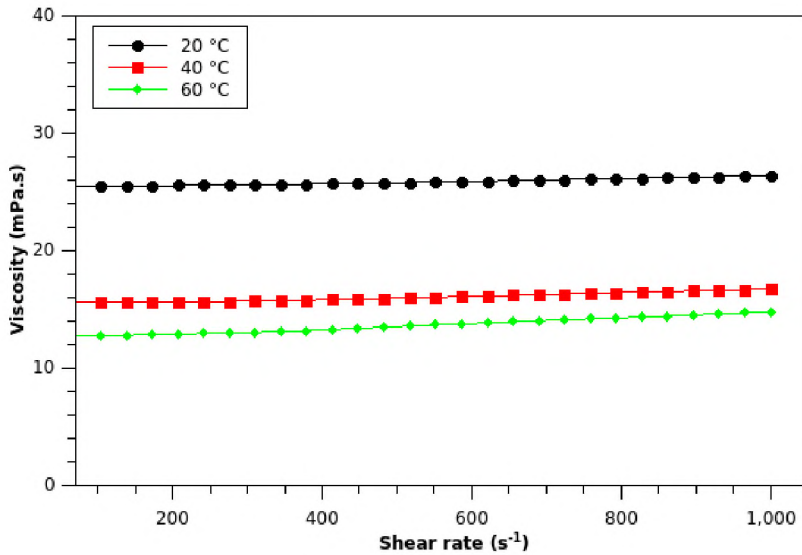
## Results and discussion

Fig. 1 shows the viscosity variations of SPIONs-PEG coated with the polymer versus shear rate at 20 °C, 40 °C, and 60 °C.

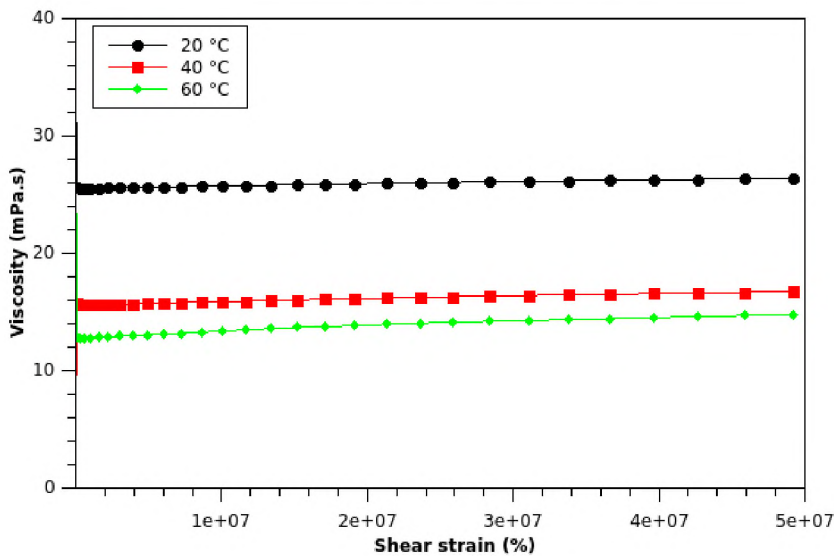
As shown in Fig. 1, the viscosity of the nanocomposite of SPIONs-PEG coated with PEG was constant with shear rate at 20 °C and 40 °C and showed a small increase at 60 °C. As expected, the viscosity values decreased with the increase in temperature.

Fig. 2 shows the viscosity variations of the nanocomposite of SPIONs-PEG coated with the polymer versus shear strain at 20 °C, 40 °C, and 60 °C.

As shown in Fig. 2, the same behavior of the nanocomposite of SPIONs-PEG coated with the polymer as presented in Fig. 1 was observed for their viscosity values versus shear strain. In other words, the nanocomposite showed a steady-state behavior at 20 °C and 40 °C and a small increase of viscosity versus shear strain at 60 °C.



**Fig. 1.** Viscosity of SPIONs-PEG coated with PEG versus shear rate



**Fig. 2.** Viscosity of SPIONs-PEG coated with PEG versus shear strain

Fig. 3 shows the viscosity variations of the nanocomposite of SPIONs-PEG coated with PEG versus time at 20 °C, 40 °C, and 60 °C.

The small change of viscosity versus time at 60 °C and the steady-state behavior of the nanocomposite shown in Fig. 3 were following the results presented in the previous figures.

Fig. 4 shows the changes of torque versus shear strain for the nanocomposite at 20 °C, 40 °C and 60 °C. The torque values increased with the increase of the shear strain of the samples.

As shown in Fig. 4, the slope of the torque increase was not the same at different shear strain values. It was high at low shear strain and decreased with the increase of this second. As expected, fewer values of the torque change were needed to be applied to the nanocomposite with the increase of its deformation.

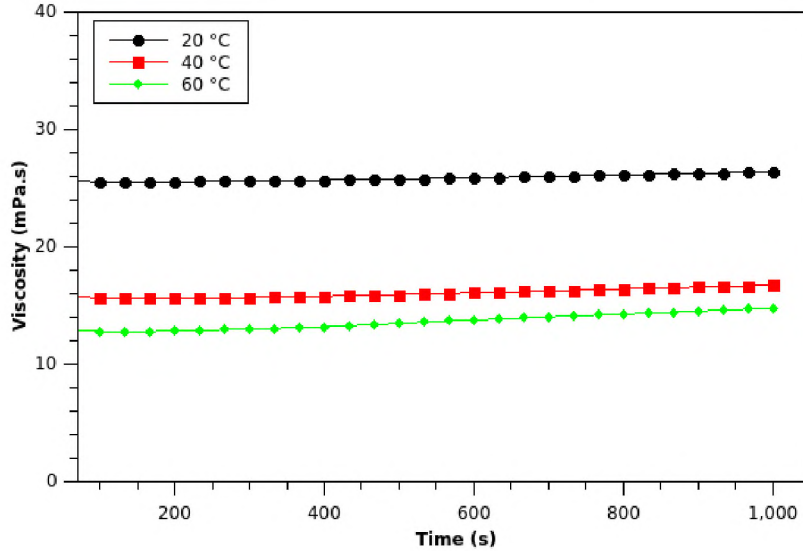


Fig. 3. Viscosity of SPIONs-PEG coated with PEG versus time

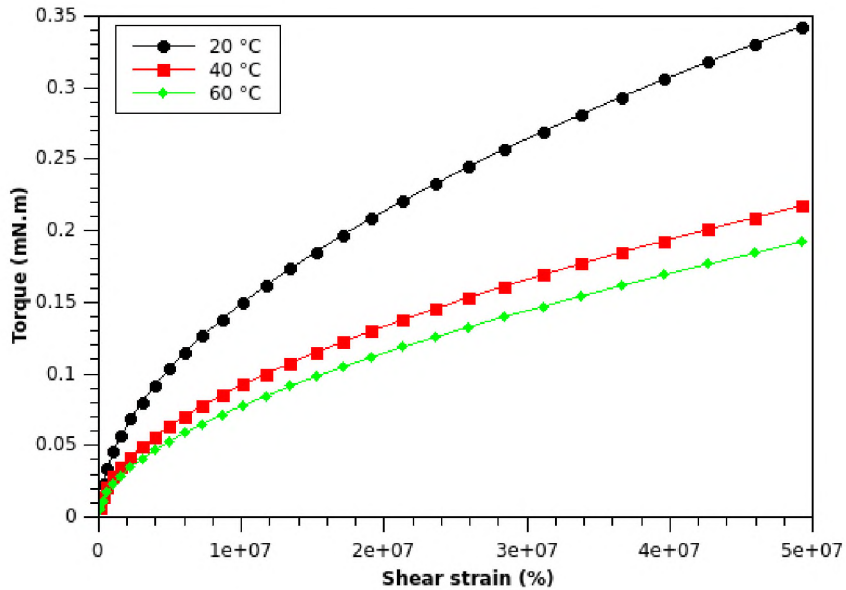


Fig. 4. Torque versus shear strain for SPIONs-PEG coated with PEG

Fig. 5 shows the changes of torque versus time at 20 °C, 40 °C and 60 °C for the nanocomposite.

As shown in Fig. 5, the slope of the torque increase was constant with time for the nanocomposite, and a linear change of torque versus time was observed. This was expected as no change in the torque increase was applied to the nanocomposite over time.

The results shown in figures 4 and 5 were consistent because a constant increase of torque was observed with time for the nanocomposite. More increase in the torque values was observed when the deformation of nanocomposite was low.

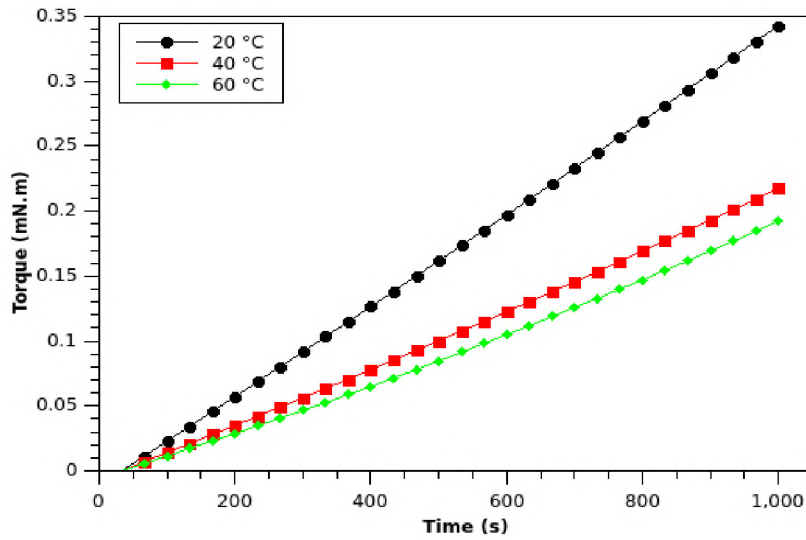


Fig. 5. Torque versus time for SPIONs-PEG coated with PEG

Fig. 6 shows the shear stress applied on the nanocomposite versus the shear rate at 20 °C, 40 °C, and 60 °C. The changes in the shear stress applied on the samples versus the shear rate were linear.

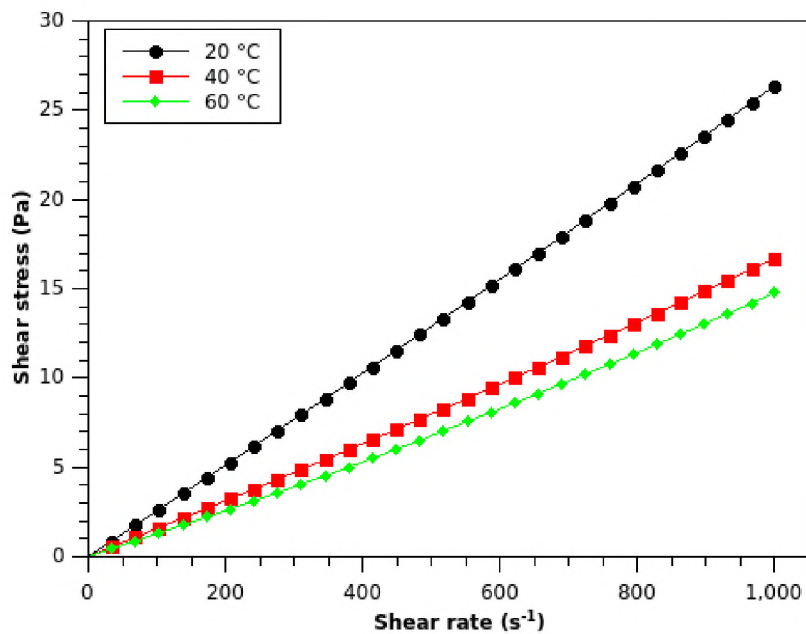


Fig. 6. Shear stress versus shear rate for SPIONs-PEG coated with PEG

As shown in Fig. 6, almost the same slope was observed for the increase of shear stress with the shear rate for the nanocomposite at 40 °C and 60 °C. This indicated that the samples had nearly the same constant rate of shear stress at these temperatures when they changed with the shear rate. However, the slope observed in this figure was higher at 20 °C. This showed that the change of the shear stress applied on the nanocomposite versus the shear rate was higher at a lower temperature.

Fig. 7 shows the shear stress applied on the nanocomposite versus shear strain at 20 °C, 40 °C, and 60 °C. Non-linear changes were observed for the shear stress applied to the samples and the shear stress increased with the increase of the shear strain values.

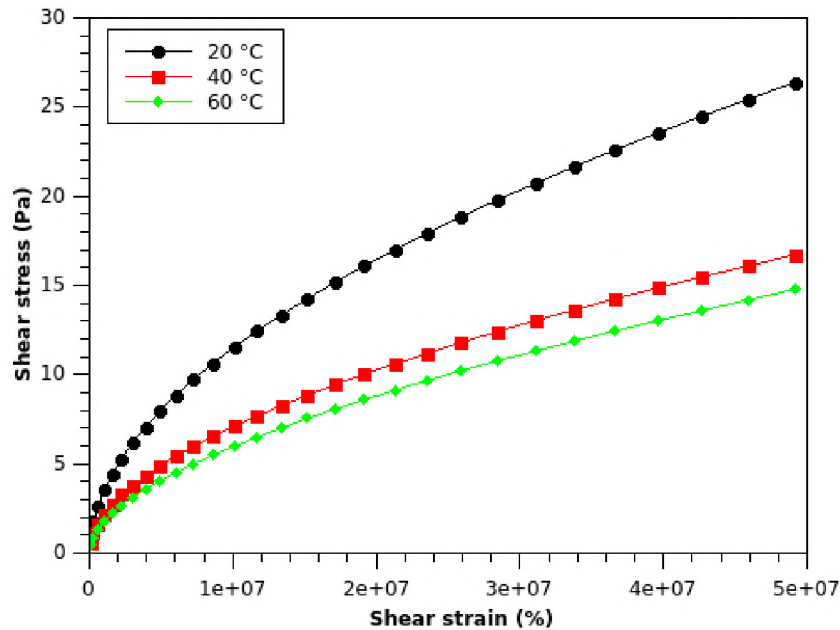


Fig. 7. Shear stress versus shear strain for SPIONs-PEG-coated with PEG

As shown in Fig. 7, the samples showed almost the same slopes for the increase of shear stress with shear strain at 40 °C and 60 °C. This indicated that the samples had nearly the same increase rate of the shear stress versus shear strain. However, the slope observed in this figure was higher at 20 °C. This showed that the change of the shear stress of the nanocomposite versus the shear strain was higher at a lower temperature.

The observations of the variations of the shear stress with shear rate and shear strain were applied to explain how these parameters changed for the nanocomposite of SPIONs-PEG coated with the polymer. The comparisons of the obtained results in this paper showed that although shear stress increased with the shear rate for the nanocomposite, its viscosity values versus shear rate, shear strain or time were almost constant at different temperatures.

This investigation was carried out to provide the required information to improve the properties of this nanocomposite. Previously, some materials with diverse applications were studied [36–48]. Some materials have shown non-Newtonian behavior that could be maintained when they were prepared in polymeric matrices [49–51]. Investigating these materials and their nanocomposites prepared with polymers can provide important information for improving their mechanical properties.

More investigations are needed to correlate the structural properties of nanocomposites to their rheological properties. The results of this research work can be applied in materials science and engineering.

### Conclusions

This paper investigated the rheological properties of a nanocomposite of SPIONs-PEG coated in the polymer. The results obtained in this research showed that the nanocomposite's rheological properties depended on the temperature and could change with the temperature increase. The investigated samples showed steady-state behavior at 20 °C and 40 °C and a small increase of viscosity versus shear strain, shear rate, or time at 60 °C. In all the experiments, the shear stress increased with shear rate and shear strain. The slopes of these changes were higher at 20 °C and decreased with the increase in temperature. The results obtained in this work can be used for the preparation improvement of this nanocomposite and the correlation of its physical properties to its rheological properties. More investigations will be performed for the comparison of the rheological properties of the surface-charged nanoparticles in the polymeric matrices with those of the nanocomposite presented in this paper.

### Acknowledgments

The author gratefully thanks Professor Ingo Salzmann, Professor Sophie Laurent, and Dr. Dimitri Stanicki for the provision of PEG and SPIONs.

### References

- [1] Pelto J. et al. "Tribological performance of high density polyethylene (HDPE) composites with low nanofiller loading", *Wear*, vol. 460–461, 203451, 2020. <https://doi.org/10.1016/j.wear.2020.203451>.
- [2] Choudhury A. et al. "Effect of various nanofillers on thermal stability and degradation kinetics of polymer nanocomposites", *Journal of Nanoscience and Nanotechnology*, vol. 10(8), pp. 5056–5071, 2010. <https://doi.org/10.1166/jnn.2010.3030>.
- [3] Wu W. et al. "Multidimensional (0D-3D) nanofillers: Fascinating materials in the field of bio-based food active packaging", *Food Research International*, vol. 157, 111446, 2022. <https://doi.org/10.1016/j.foodres.2022.111446>.
- [4] Chevigny C. et al. "Polymer-grafted-nanoparticles nanocomposites: Dispersion, grafted chain conformation, and rheological behavior", *Macromolecules*, vol. 44, 1, pp. 122–133, 2011. <https://doi.org/10.1021/ma101332s>.
- [5] Peng W. et al. "Viscoelastic and dynamic properties of polymer grafted nanocomposites with high glass transition temperature graft chains", *Journal of Applied Physics*, vol. 126(19):195102, 2019. <https://doi.org/10.1063/1.5119694>.
- [6] Arrigo R. and Malucelli G. "Rheological behavior of polymer/carbon nanotube composites: An overview", *Materials*, vol. 13(12), 2771, 2020. <https://doi.org/10.3390/ma13122771>.
- [7] Dobkowski Z. "Application of rheological techniques for investigations of polymer branched structures", *Fluid Phase Equilibria*, vol. 152, 2, pp. 327–336, 1998. [https://doi.org/10.1016/S0378-3812\(98\)00187-3](https://doi.org/10.1016/S0378-3812(98)00187-3).
- [8] Wang L. et al. "Rheology and crystallization of long-chain branched poly(l-lactide)s with controlled branch length", *Ind. Eng. Chem. Res.*, vol. 51, 33, pp. 10731–10741, 2012. <https://doi.org/10.1021/ie300524j>.
- [9] Nuryawan A. et al. "Enhancement of oil palm waste nanoparticles on the properties and characterization of hybrid plywood biocomposites", *Polymers*, vol. 12(5), 1007, 2020. <https://doi.org/10.3390/polym12051007>.
- [10] Zahedi M. et al. "A comparative study on some properties of wood plastic composites using canola stalk, Paulownia, and nanoclay", *Journal of Applied Polymer Science*, vol. 129(3), 2013. <https://doi.org/10.1002/app.38849>.
- [11] Karak N. "Fundamentals of nanomaterials and polymer nanocomposites", chapter 1, *Nanomaterials and Polymer Nanocomposites*, pp. 1–45, 2019. <https://doi.org/10.1016/B978-0-12-814615-6.00001-1>.
- [12] Yu W. et al. "Structure and linear viscoelasticity of polymer nanocomposites with agglomerated particles", *Polymer*, vol. 98, 2016. <https://doi.org/10.1016/j.polymer.2016.06.028>.
- [13] Akca E. and Gursel, A. "A review on the matrix toughness of thermoplastic Materials", *Periodicals of Engineering and Natural Sciences*, 3, pp. 1–8, 2015. <https://doi.org/10.21533/pen.v3i2.52>.
- [14] Lanfant N. P. and Alglave H. L. "Manufacturing process of a thermoplastic material part incorporating metal fillers", Patent FR3111585A1, 2020.
- [15] Mhike W. et al. "Rotomolded antistatic and flame-retarded graphite nanocomposites", *Journal of Thermoplastic Composite Materials*, vol. 31(4), 089270571771263, 2017. <https://doi.org/10.1177/0892705717712634>.
- [16] Kim K.-W. et al. "Comparison of the characteristics of recycled carbon fibers/polymer composites by different recycling techniques", *Molecules*, vol. 27, 5663, 2022. <https://doi.org/10.3390/molecules27175663>.
- [17] Yang B. "Swelling of carbon nano-filler modified polydimethylsiloxane", PhD thesis, University of Alberta, 2018.
- [18] Antunes R. A. et al. "Carbon materials in composite bipolar plates for polymer electrolyte membrane fuel cells: A review of the main challenges to improve electrical performance", *Journal of Power Sources*, vol. 196(6), pp. 2945–2961, 2011. <https://doi.org/10.1016/j.jpowsour.2010.12.041>.
- [19] Akpan E. I. et al. Design and synthesis of polymer nanocomposites, in "Polymer Composites with Functionalized Nanoparticles, Synthesis", *Properties and Applications Micro and Nano Technologies*, pp. 47–83, 2019. <https://doi.org/10.1016/B978-0-12-814064-2.00002-0>.
- [20] Shen Z. et al. "Comparison of solution intercalation and melt intercalation of polymer–clay nanocomposites", *Polymer*, vol. 43, pp. 4251–4260, 2002. [https://doi.org/10.1016/S0032-3861\(02\)00230-6](https://doi.org/10.1016/S0032-3861(02)00230-6).
- [21] Chen Y. et al. "In-situ intercalation of montmorillonite/urushiol titanium polymer nanocomposite for anti-corrosion and anti-aging of epoxy coatings", *Progress in Organic Coatings*, vol. 165, 106738, 2022. <https://doi.org/10.1016/j.porgcoat.2022.106738>.

- [22] Di Y. et al. "Nanocomposites by melt intercalation based on polycaprolactone and organoclay", *Journal of Polymer Science Part B: Polymer Physics*, vol. 41, pp. 670–678, 2003. <https://doi.org/10.1002/polb.10420>.
- [23] Mittal V. and Chaudhry A. U. "Effect of amphiphilic compatibilizers on the filler dispersion and properties of polyethylene–thermally reduced graphene nanocomposites", *Journal of Applied Polymer*, vol. 132, 42484, 2015. <https://doi.org/10.1002/app.42484>.
- [24] Martínez-Gómez A. et al. "Searching for effective compatibilizing agents for the preparation of poly(ether ether ketone)/graphene nanocomposites with enhanced properties", *Composites Part A: Applied Science and Manufacturing*, vol. 113, pp. 180–188, 2018. <https://doi.org/10.1016/j.compositesa.2018.07.027>.
- [25] Patti A. et al. Influence of filler dispersion and interfacial resistance on thermal conductivity of polypropylene/carbon nanotubes systems, *Proceedings*, vol. 1914, 030014, 2017. <https://doi.org/10.1063/1.5016701>.
- [26] Wood W. "Processing, wear, and mechanical properties of polyethylene composites prepared with pristine and organosilane-treated carbon nanofibers", PhD thesis, Washington State University, 2012.
- [27] Musanje L. and Ferracane J. L. "Effects of resin formulation and nanofiller surface treatment on the properties of experimental hybrid resin composite", *Biomaterials*, vol. 25, 4065–4071, 2004. <https://doi.org/10.1016/j.biomaterials.2003.11.003>.
- [28] Amini M. et al. "Engineering the shape memory parameters of graphene/polymer nanocomposites through atomistic simulations: On the effect of nanofiller surface treatment", *Smart Materials and Structures*, vol. 31, 025010, 2021. <https://doi.org/10.1088/1361-665X/ac4194>.
- [29] Ock H. G. et al. "Effect of electric field on polymer/clay nanocomposites depending on the affinities between the polymer and clay", *Journal of Applied Polymer Science*, vol. 133, 43582, 2016. <https://doi.org/10.1002/app.43582>.
- [30] Rozynek Z. et al. "Organoclay polypropylene nanocomposites under different electric field strengths", *Applied Clay Science*, pp. 67–72, 2014. <https://doi.org/10.1016/j.clay.2014.03.011>.
- [31] Piao S. H. et al. "Stimuli-responsive polymer-clay nanocomposites under electric fields", *Materials*, 9, 52, 2016. <https://doi.org/10.3390/ma9010052>.
- [32] Javanbakht T., Laurent S., Stanicki D. and David E. "Related physicochemical, rheological, and dielectric properties of nanocomposites of superparamagnetic iron oxide nanoparticles with polyethyleneglycol", *Journal of Applied Polymer Science*, vol. 137, pp. 48280–48289, 2019. <https://doi.org/10.1002/app.48280>.
- [33] Tamhane D. and Anantharaman M. R. "Design and fabrication of a simple and inexpensive measurement probe for the evaluation of thermal conductivity of nanofluids", *Nanofluids*, vol. 6, pp. 390–396, 2017. <https://doi.org/10.1166/jon.2017.1309>.
- [34] Belosi F. et al. "Comparison between two different nanoparticle size spectrometers", *Journal of the Air and Waste Management Association*, vol. 63, pp. 918–925, 2013. <https://doi.org/10.1080/10962247.2013.800169>.
- [35] Cetrangolo G. P. et al. "Determination of picomolar concentrations of paraoxon in human urine by fluorescence-based enzymatic assay", *Sensors*, vol. 19, 4852, 2019. <https://doi.org/10.3390/s19224852>.
- [36] Legare S. et al. "Improved SARS-CoV-2 main protease high-throughput screening assay using a 5-carboxyfluorescein substrate", *Journal of Biological Chemistry*, vol. 298, 101739, 2022. <https://doi.org/10.1016/j.jbc.2022.101739>.
- [37] Garg K. et al. "Preparation of graphene nanocomposites from aqueous silver nitrate using graphene oxide's peroxidase-like and carbocatalytic properties", *Scientific Reports*, vol. 10, 5126, 2020. <https://doi.org/10.1038/s41598-020-61929-9>.
- [38] Javanbakht T. et al. "Comparative study of physicochemical properties and antibiofilm activity of graphene oxide nanoribbons", *Journal of Engineering Sciences*, vol. 7, pp. C1–C8, 2020. [https://doi.org/10.21272/jes.2020.7\(1\).c1](https://doi.org/10.21272/jes.2020.7(1).c1).
- [39] Javanbakht T. and Sokolowski W. "Thiol-ene/acrylate systems for biomedical shape-memory polymers", in *Shape memory polymers for biomedical applications*, Sawston, Cambridge: Woodhead Publishing, 2015, chapter 8, pp. 157–166. <https://doi.org/10.1016/B978-0-85709-698-2.00008-8>.
- [40] Djavanbakht T. et al. "Effets d'un chauffage thermique sur les performances de miroirs multicouches Mo/Si, Mo/C et Ni/C pour le rayonnement X mou", *Journal de Physique IV France*, vol. 10, pp. 281–287, 2000.
- [41] Javanbakht T. and David E. "Rheological and physical properties of a nanocomposite of graphene oxide nanoribbons with polyvinyl alcohol", *Journal of Thermoplastic Composite Materials*, 0892705720912767, 2020. <https://doi.org/10.1177/0892705720912767>.



- [42] Javanbakht T., Laurent S., Stanicki D. and Salzman I. “Rheological properties of superparamagnetic iron oxide nanoparticles”, *Journal of Engineering Sciences*, vol. 8, pp. C29–C37, 2021. [https://doi.org/10.21272/jes.2021.8\(1\).c4](https://doi.org/10.21272/jes.2021.8(1).c4).
- [43] Ryu C. et al. “Highly optimized iron oxide embedded poly(lactic acid) nanocomposites for effective magnetic hyperthermia and biosecurity”, *International Journal of Nanomedicine*, vol. 17, pp. 31–44, 2022. <https://doi.org/10.2147/IJN.S344257>.
- [44] Abdul-Raheim A. M. et al. “Modified starch iron oxide nanocomposites as low cost absorbents for selective removal of some heavy metals from aqueous solutions”, *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, vol. 6, pp. 1198–1212, 2015.
- [45] Ghane-Motlagh B., Javanbakht T. et al. “Physicochemical properties of peptide-coated microelectrode arrays and their *in vitro* effects on neuroblast cells”, *Materials Science and Engineering C*, vol. 68, pp. 642–650, 2016. <https://doi.org/10.1016/j.msec.2016.06.045>.
- [46] Javanbakht T. et al. “Comparative study of antibiofilm activity and physicochemical properties of microelectrode arrays”, *Microelectronic Engineering*, vol. 229, pp. 111305, 2020. <https://doi.org/10.1016/j.mee.2020.111305>.
- [47] Javanbakht T. “Investigation of rheological properties of graphene oxide and its nanocomposite with polyvinyl alcohol”, *Ukrainian Journal of Mechanical Engineering and Materials Science*, vol. 7, pp. 23–32, 2021. <https://doi.org/10.23939/ujmems2021.01-02.023>.
- [48] Javanbakht T., Laurent S., Stanicki D. and Frenette M. “Correlation between physicochemical properties of superparamagnetic iron oxide nanoparticles and their reactivity with hydrogen peroxide”, *Canadian Journal of Chemistry*, vol. 98, pp. 601–608, 2020. <https://doi.org/10.1139/cjc-2020-0087>.
- [49] Hojjat M. et al. “Rheological characteristics of non-Newtonian nanofluids: Experimental investigation”, *Int. Commun. Heat Transf*, vol. 38, pp. 144–148, 2011. <https://doi.org/10.1016/j.icheatmasstransfer.2010.11.019>.
- [50] Chhabra R. P. et al. “*Non-Newtonian Flow and Applied Rheology: Engineering Applications*”, Butterworth-Heinemann: Oxford, UK, 2011.
- [51] Jamshed W. et al. “Partial velocity slip effect on working magneto non-Newtonian nanofluids flow in solar collectors subject to change viscosity and thermal conductivity with temperature”, *PLoS ONE*, 16, e0259881, 2021. <https://doi.org/10.1371/journal.pone.0259881>.