

# Prediction of dielectric constant and loss for some polypropylene - additive compounds

Sari J. Laihonon, Joakim P. M. Jämbeck and Mikael Unge

ABB Corporate Research, 72178 Västerås, Sweden

## Abstract

In order to influence properties of polymers, several different type of additives can be used. Often, time consuming experimental work is needed to assess performance and suitable concentrations for the chosen polymer-additive system. Therefore, it is preferable to be able to estimate the properties by means of theoretical work. In the present work, dielectric constant and loss for polypropylene-meso-erythritol compounds were studied. The experimental results were compared to the theoretically assessed properties.

The compounds were prepared in three different concentrations. The obtained samples were pressed to plates which were characterized by dielectric response measurements. The dielectric constants were also assessed using Maxwell-Garnett estimation and molecular dynamics simulations. For the later, both atomistic model and a more coarse multiscale model were used. The Maxwell-Garnett equation gave a good estimation of the dielectric constant level whereas with the molecular dynamics simulations the obtained dielectric constant were in exact accordance to the measured values. With the molecular dynamics simulation, also the loss could be estimated. As expected, the atomistic model gave better correlation to the measured loss levels than the multi-scale model.

## 1. Introduction

The dielectric behavior of a polymer is dependent not only on its chemical composition, how it is processed and used but also on the property modifying additives compounded into it [1-6]. Additives in polymers consist typically of antioxidants, processing aids, possible cross linking agents and many other organic and inorganic performance improving materials [7, 8]. Also impurities and residuals that originate from different processing and handling can be regarded as ingredients in the polymer system. As additives can have a significant influence of the dielectric behavior of the polymer, relationship between their concentration and dielectric performance needs to be assessed. As this laboratory work can be quite time consuming, it is beneficial to be able to estimate the additive influence also theoretically. Numerous physical models to describe the behavior of the multiphase systems has been proposed and used over the years whereas molecular dynamics (MD) and density functional theory (DFT) are increasingly popular

methods in efforts of estimating dielectric properties of polymer-additive systems [1-6, 9-16].

In this paper we discuss the influence of an alcohol, meso-erythritol, Figure 1, on the performance of the polypropylene. The meso-erythritol was compounded into a capacitor grade polypropylene and the dielectric constant and loss were assessed, as reported earlier [17]. The experimental results were then compared to estimations based on MD simulations, both atomistic and multiscale model, and excellent agreement regarding the dielectric constant and good agreement, especially when the complexity of the calculations were taken into account, regarding the loss were reached [17, 18]. As the MD simulations require advanced computer programs and knowledge how to work with them, a more simple approach, using Maxwell-Garnett estimation [9, 10], was also studied. It turned out that also with Maxwell-Garnett estimation, relevant values for the dielectric constant for the studied compounds could be obtained.

## 2. Experimental

### 2.1 Materials and Measurements

Capacitor grade polypropylene (PP) from Borealis was used as a matrix. A polyol with one OH-group per each carbon, a 1,2,3,4-tetrahydroxybutane, also called as meso-erythritol, Figure 1, was purchased from Sigma-Aldrich (CAS 149-32-6).

0.5, 1 and 3 wt-% meso-erythritol was compounded into polypropylene matrix by using a EuroLab twin screw extruder from Thermo Scientific. 1 mm thick plates were prepared using a Servitec Polytech 300 laboratory press. A pressing procedure suitable for the used polypropylene grade was applied. The pellets were kept under the vacuum at 50°C for minimum 24h before pressing, usually longer. The meso-erythritol concentrations refer to the weighted-in concentrations.

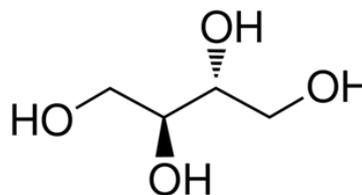


Fig. 1 - Chemical structure of meso-erythritol (C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>).

The dielectric response of the pressed plates was characterized by using Novocontrol Technologies Alpha-A analyser with 150 V test interface. The electrodes and guard were of stainless steel. The diameter of the measurement electrode 85 mm. The heavy weight of the electrodes gave a good contact between the sample and the electrodes. The measurement cell was put into a grounded metal box in order to reduce disturbances from the surroundings during the measurements. 10 frequency sweeps per sample between 0.1-10 kHz were performed at room temperature and average of these was calculated. Prior to measurements, the measured loss error (including cables and connections) as well as level of true instrument zero and possible off-set of it was assessed. As a reference capacitor, a vacuum capacitor (100 pF Capacitor Standard from Beckman Instruments) and a parallel connected, small adjustable air capacitor were used. The capacitance of the reference capacitor was set equal or close to the sample capacitance. The measured sample losses were corrected for the small off-set in instrument zero and other loss errors.

## 2.2 Dielectric permittivity and losses based on molecular dynamics simulations

From the molecular dynamics (MD) simulations the dielectric constant can be obtained from the total dipole moment of the system,  $\mathbf{M}$  according to

$$\varepsilon_0 = \varepsilon(0) = \varepsilon_\infty + \frac{4\pi \langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2}{3 V k_B T} \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature and  $V$  is the volume of the simulation box. As no electrons are present in these simulations  $\varepsilon_\infty$  is assigned a value of 2.24 (measured dielectric constant of the pure PP) in order to account for the electronic contribution to the dielectric constant [19].

To compute  $\text{Tan}\delta$  from the simulations the autocorrelation function (ACF) of  $\mathbf{M}$  must first be calculated [15, 16]

$$\phi(t) = \frac{\langle \mathbf{M}(0)\mathbf{M}(t) \rangle}{\langle \mathbf{M}^2(0) \rangle} \quad (2)$$

where  $\phi(t)$  is the ACF.  $\phi(t)$  is then fitted to the following function form

$$\phi_{fit}(t) = A e^{-\left(\frac{t}{\tau_a}\right)^\alpha} + (1 - A) e^{-\left(\frac{t}{\tau_b}\right)^\beta} \quad (3)$$

From this both the real ( $\varepsilon'$ ) and imaginary ( $\varepsilon''$ ) dielectric constants are computed according to

$$\frac{\varepsilon'(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = - \int \left( \frac{d\phi_{fit}(t)}{dt} \right) \cos(\omega t) dt \quad (4)$$

and

$$\frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_\infty} = - \int \left( \frac{d\phi_{fit}(t)}{dt} \right) \sin(\omega t) dt. \quad (5)$$

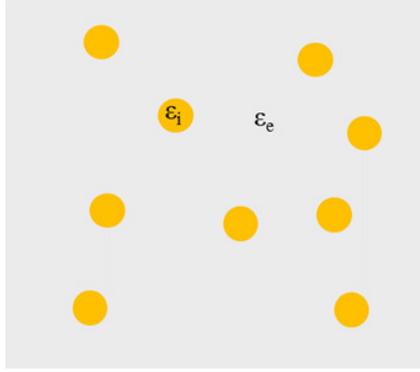
During the MD simulations two different resolutions were used – atomistic (AA) and multi-scale (MS). For the former all the constituting atoms of the material are represented, making these type of simulations the most detailed and therefore also the most time consuming. One way of decreasing the computational efforts is to simplify the systems by decreasing the degrees of freedom, namely the number of particles. This is usually referred to as coarse-graining, where a number of atoms are approximated by larger pseudo atoms or beads. For example a four methylene groups can be simplified to a bead [20]. For a polymeric system this is straightforward but for smaller, polar molecules like meso-erythritol this is considerably more difficult due to the intramolecular hydrogen bonds. One way of solving this is to apply a multi-scale scheme where the polymeric matrix is represented by coarser grains and the meso-erythritol is modelled in a fully atomistic manner. The interactions between the polymers and the additives can then be modelled by so-called virtual sites, as described by Rzepiela et al. [21]. For more details on how this was applied in the current work and more simulation details, see references [17, 18].

## 2.3 Maxwell-Garnett estimation of dielectric constant

In order to get an estimate on how large increase of the dielectric constant ( $\varepsilon'$ ) can be expected by compounding the additives into the matrix material, mixing formulas can be applied. The Maxwell-Garnett formula for mixing of spherical inclusions is applied [9, 10]:

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_e}{\varepsilon_{\text{eff}} + 2\varepsilon_e} = f \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} \quad (6)$$

where  $\varepsilon_{\text{eff}}$  is the effective dielectric constant,  $\varepsilon_e$  is the dielectric constant of the matrix,  $\varepsilon_i$  is the dielectric constant of the inclusion and  $f$  is the volume fraction of inclusions, see Figure 2. Maxwell-Garnett equation is based on effective medium theory in which it is assumed for example that the added particles are ellipsoidal, that the distance between them is larger than the characteristic size of the particles, and that they are randomly distributed in the surrounding matrix [9, 10]. The Maxwell-Garnett model has been used in numerous studies, some recent studies are with molecular and polymers inclusions [13, 14].



**Fig. 2** – Schematic illustration of matrix material with spherical inclusions,  $\epsilon_e$  is the dielectric constant of the matrix,  $\epsilon_i$  is the dielectric constant of the inclusion.

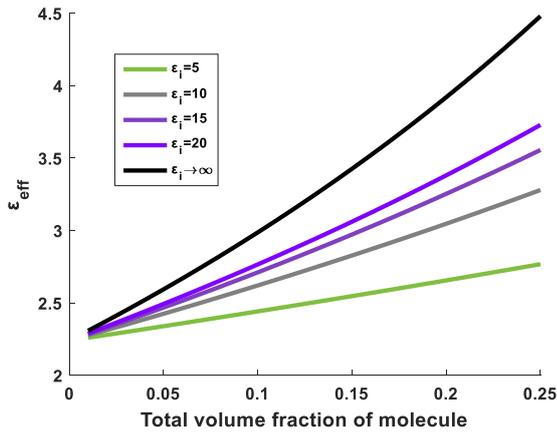
Equation (6) can be rewritten as

$$\epsilon_{\text{eff}} = \epsilon_e \left( 1 + 3f \frac{1 - \epsilon_e/\epsilon_i}{1 - f + \epsilon_e/\epsilon_i (2 + f)} \right) \quad (7)$$

In the limit of inclusions with infinitely high dielectric constant the effective dielectric is

$$\lim_{\epsilon_i \rightarrow \infty} \epsilon_{\text{eff}} = \epsilon_e \left( 1 + \frac{3f}{1-f} \right). \quad (8)$$

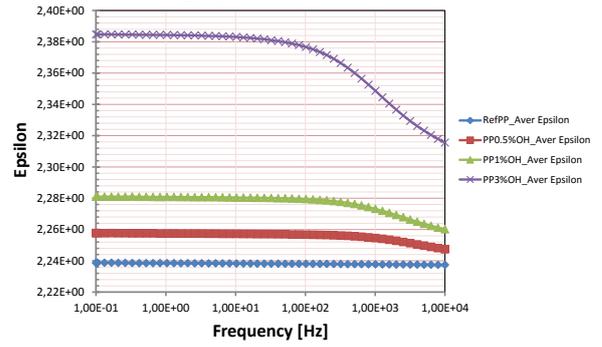
Hence, equation (8) yields an upper limit, within the Maxwell-Garnett model, of effective dielectric constant for the matrix with the additive. In Figure 3, the black line shows the corresponding curve as function of volume fraction of the fillers. This means that – according to Maxwell-Garnett – low additions of polar molecule will not drastically increase the dielectric constant of the compound, even with infinite values of dielectric constant of the inclusion.



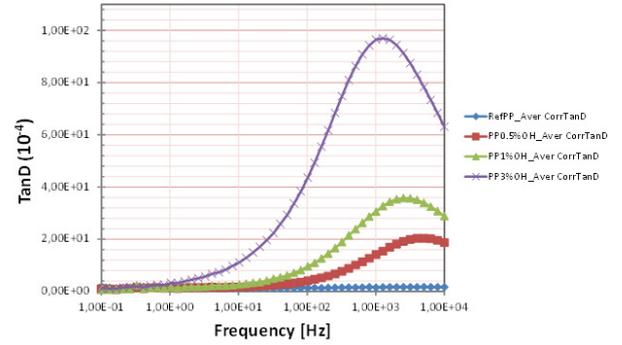
**Fig. 3** – Effective dielectric constant of a medium with a matrix with dielectric constant of 2.24 and inclusion with various dielectric constants. The black line shows the case with an inclusion with infinite dielectric constant.

### 3. Results and Discussion

The obtained values for the dielectric constant  $\epsilon'$  and the dielectric loss  $\epsilon''$  [17], here expressed as  $\text{Tan}\delta (= \epsilon''/\epsilon')$ ,



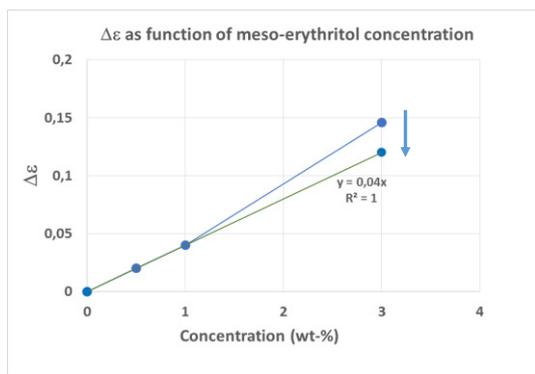
(a)



(b)

**Fig. 4** – (a) Relative dielectric constant  $\epsilon'$  and (b)  $\text{Tan}\delta$  for the three meso-erythritol compounds. Violet line on the top refers to the PP-sample containing 3 wt-%, green line to 1.0 wt-% and red line to 0.5 wt-% meso-erythritol. The blue line refers to the pure PP sample. Note the scale for the y-axis.

for the polypropylene-meso-erythritol compounds are shown in Figures 4(a) and 4(b). The dielectric constant at frequencies below 10 Hz increased almost linearly with increasing meso-erythritol concentration, Figures 4(a) and 5. As the dielectric constant for the PP-sample without meso-erythritol was practically constant over the studied frequency range, the change in dielectric constant was attributed to the orientation of dipoles (OH-groups) in the meso-erythritol molecule. It should be also mentioned that when the dielectric response measurement for the sample with 3 wt-% meso-erythritol was repeated, there was 10% decrease in the maximum epsilon value. This could be either an effect of plate quality giving  $\pm 0.01$  variation in dielectric constant or due to reduced humidity in the sample (the dielectric response measurement was now performed directly after preparation of the plate).



**Fig. 5** – Increase in dielectric constant as a function of meso-erythritol concentration at 1 Hz. The arrow indicates the influence of a reduced time between the plate preparation and measurement.

With increasing frequency the polarizability of the OH-groups declined and the dielectric loss in term of  $\text{Tan}\delta$  increased drastically for the PP-meso-erythritol compounds compared to that of polypropylene, Figure 4. When compared to the loss data for some polyols with similar structures, the appearance of the loss peak originating from meso-erythritol was similar to the other polyols [22-25]. The peak frequency for the dominant  $\alpha$ -relaxation at  $\sim 298$  K for pure threitol (stereoisomer of erythritol) was  $\sim 10$  MHz [23, 24], and for the one and two OH-groups and carbons longer polyol-molecules xylitol ( $\text{C}_5\text{H}_{12}\text{O}_5$ ) and sorbitol ( $\text{C}_6\text{H}_{14}\text{O}_6$ ) at around  $\sim 1$  MHz and  $\sim 10$  kHz, respectively [22-25]. For the studied PP-meso-erythritol compounds, the loss maximums were in the range of 1-10 kHz. This suggests that the presence of polypropylene matrix reduced the movability of the OH-dipoles drastically.

The values for the real part of the dielectric constant,  $\epsilon'$ , obtained from the MD simulations agreed very well with the experimental values, see Table 1. This type of modeling was accurate in reproducing the  $\epsilon'$ -values and that the model can be used to predict values for new materials. The multi-scale model reproduced the values of the atomistic simulations perfectly at a fraction of the time which is compelling e.g. for larger screening studies

**Table 1** – Values for the dielectric constant ( $\epsilon'$ ) from experiments and simulations at 10 kHz. The values in the AA column and MS correspond to the atomistic modeling and the multi-scale modeling, respectively.

Amount of polyol (wt-%)	Experiment	Modeling	
		AA	MS
0.5	2.25	2.25	2.25
1.0	2.26	2.28	2.27
3.0	2.32	2.31	2.31

In Table 2 the experimental  $\text{Tan}\delta$  values are compared to the ones obtained from the different MD simulations. The more detailed atomistic simulations were able to

reproduce the experimental values well, albeit a slight underestimation. Due to the long time scales and the limitations of the MD simulations (e.g. no explicit polarization due to the lack of electrons) it would be difficult to obtain a perfect agreement.

For the multi-scale simulations the agreement was not as good as for the atomistic although still being satisfactory. As a large number of the constituting atoms of the materials were removed and replaced by large pseudo-atoms in order to speed the calculations the larger disagreement is expected. During the removal of the explicit atoms the potential energy landscape becomes smoother and the friction between the polymer chains and the meso-erythritol compounds becomes smaller and therefore the dielectric losses are decreased with respect to the values from the atomistic simulations.

**Table 2** – Dielectric loss, here express as  $\text{Tan}\delta$  values from experiments compared to simulations at 10 kHz. The values in the AA column and MS correspond to the atomistic modeling and the multi-scale modeling, respectively.

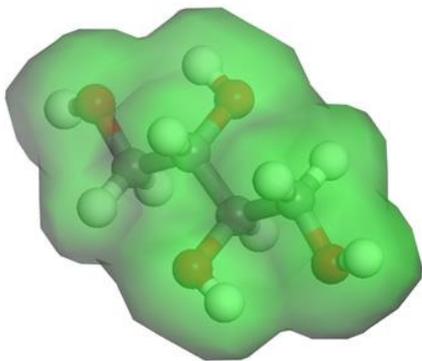
Amount of polyol (wt-%)	Experiment	Modeling	
		AA	MS
0.5	0.0018	0.0013	0.0004
1.0	0.0031	0.0026	0.0018
3.0	0.0065	0.0048	0.0043

The reason for the systematic underestimation of the dielectric losses in both the atomistic and multi-scale modelling could be due to the simplifications of the models – the lack of explicit electrons. With the lack of explicit electrons the polymer's contribution to the dielectric constant is not present. It is plausible that if this contribution was included the agreement could be improved. However, it should be mentioned that this inclusion would increase the computational time significantly.

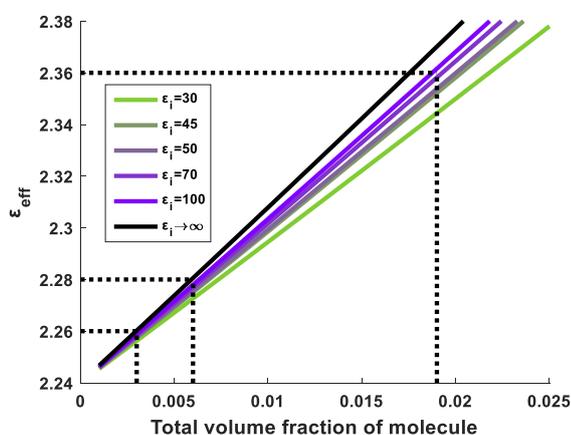
A more easy approach to estimate the influence of polar additive on the dielectric constant of polypropylene was the Maxwell-Garnett estimation. The van der Waals surface of a molecule, determined from the atomic van der Waals radii, give the volume that the individual molecule occupy. In Figure 6 the van der Waals surface of the meso-erythritol molecule is shown and is approximately spherical. Hence, with the low studied concentrations and the shape of the molecule, the basic conditions for using Maxwell-Garnett estimate were fulfilled [9, 10].

To calculate the dielectric constant of PP with an additive it was also needed to include that the PP is semicrystalline and that the additive molecule will mix in the amorphous phase only. Hence, first equations (7) and (8) should be used for the inclusion in the amorphous phase of PP. Then equation (7) should be used once more

for the mixture of amorphous and crystalline phases. This was done for a set of values of  $\epsilon_i$  including the limit of infinite dielectric constant, see Figure 7.



**Fig. 6** – Meso-erythritol molecule enclosed by its Van der Waals surface.



**Fig. 7** – The predicted and measured dielectric (dashed lines) constants of a PP (50% crystallinity) compound with 0.3, 0.6 and 1.9 vol% of meso-erythritol, respectively.

Experimental results on the influence of the different concentrations of meso-erythritol in PP are marked in Figure 7. The weight-% of 0.5, 1.0 and 3.0 were calculated to volume fractions; 0.003, 0.006 and 0.019 respectively. The dielectric constant value of 28 for meso-erythritol at 129°C was noted from the data-sheet [26]. By comparing the dielectric constant data from similar type of molecules, room temperature value for the dielectric constant of meso-erythritol was estimated to be around 45 [24, 27].

For low concentrations, the influence of  $\epsilon_i$ -values on the final dielectric constant of the compound was small, Figure 7. Above 1 vol% (0.01 volume fraction) the difference becomes larger. Overall, the calculated effective dielectric constants were in good agreement with the experimental results and within the accuracy of the experimental methods (which was estimated to be  $\pm 0.01$ , mainly due to accuracy of the sample thickness). This result means that at least for small concentrations of rather round molecules, the Maxwell-Garnett equation

can be used in predicting of maximum possible dielectric constant of a compound, at least for moderate frequencies.

## 4. Conclusions

The few weight-% addition of meso-erythritol into polypropylene had relative small effect to the dielectric constant whereas the dielectric loss increased drastically. Both the atomistic and the much faster multi-grain DFT simulations could predict the increase in real part of dielectric permittivity correctly. The loss prediction was more challenging, but with the atomistic model the simulated  $\text{Tan}\delta$ -values were 15-30 % lower than the measured one, which can be regarded very satisfactory. The more coarse multi-scale model could not predict the  $\text{Tan}\delta$ -values for the lowest concentration but with the highest concentration the difference between the two methods was small. As the meso-erythritol molecule was approximately round and the concentration of it in PP low, the Maxwell-Garnett equation predicted the dielectric constant values well, when good polarization of the dipoles could be expected (in this work < 10 Hz). The limes-analysis suggests that there is a maximum value for the effective dielectric permittivity of the composite.

## Acknowledgements

Dr. Linnea Petersson and MSc. Wangshu Li are acknowledged for preparing the compounds. Wangshu Li is acknowledged for performing the dielectric response measurements and Mr. Kenneth Johansson for the assessment of the loss error.

## References

- [1] C.C. Ku and R. Liepins, Electrical properties of Polymers; Chemical Principles, Hanser Publishers, Munich, 1987
- [2] T. Blythe and D. Bloor, Electrical properties of Polymers; 2<sup>nd</sup> ed., Cambridge University Press, Cambridge, 2008
- [3] A. K. Jonscher, Dielectric Relaxation in Solids, Chelsea Dielectric Press, London, 1983
- [4] L.A. Dissado and J. C. Fothergill, Electrical Degradation and Breakdown in Polymers, Peter Peregrinus Ltd., London, 1992
- [5] A. K. Jonscher, Universal Relaxation Law, Chelsea Dielectric Press, London, 1996
- [6] T. Tanaka and A. S. Vaughan, ed., Tailoring of Nanocomposite Dielectrics, From Fundamentals to Devices and Applications, Pan Stanford Publishing Pte. Ltd, 2017, Singapore
- [7] G. Pritchard, ed., Plastics Additives, An A-Z reference, Chapman&Hall, London, 1998

- [8] C. Maier and T. Calafut, *Polypropylene, The Definitive User's Guide and Handbook*, Plastics Design Library, USA, 1998
- [9] A. Sihvola, *Electromagnetic mixing formulas and applications*, IEE, London, 1999
- [10] Maxwell, J. C. "Colours in metal glasses and metal films", *Transactions of the Royal Society, CCII*, 385-420, 1904
- [11] M. Wang and N. Pan, "Predictions of effective physical properties of complex multiphase materials", *Mat. Sci. Eng, R 63* (2008) pp. 1-30
- [12] E. Mårtensson, *Modelling electrical properties of composite materials*, PhD Thesis, Royal Institute of Technology, Stockholm, 2003
- [13] G. Pilania, C. C. Wang, K. Wu, N. Sukumar, C. Breneman, G. Sotzing and R. Ramprasad, "New Group IV Chemical Motifs for Improved Dielectric Permittivity of Polyethylene," *Journal of Chemical Information and Modeling*, vol. 53, pp. 879-886, 2013
- [14] M. L. T. Asaki, A. Redondo, T. A. Zawodzinski and A. J. Taylor, "Dielectric relaxation and underlying dynamics of acetonitrile and 1-ethyl-3-methylimidazolium triflate mixtures using THz transmission spectroscopy," *J. Chem. Phys.*, vol. 116, pp. 10377-10385, 2002.
- [15] M. Neumann, "Dipole moment fluctuations in computer simulations of polar systems," *Mol. Phys.*, vol. 50, pp. 841-858, 1983
- [16] M. Neumann, O. Steihauser, and G. S. Pawley, "Consistent calculation of the static and frequency-dependent dielectric constant in computer simulations," *Mol. Phys.*, vol. 52, pp. 97-113, 1984
- [17] J. P. M. Jämbeck, M. Unge, S. J. Lahonen, "Development of simulation methods for dielectrics," 2016 IEEE International Conference on Dielectrics (ICD), Montpellier, 2016, pp. 995-998.
- [18] J. P. M. Jämbeck, M. Unge, and S. Lahonen, "Determining the dielectric losses in polymers by using molecular dynamics simulations," *Electrical Insulation and Dielectric Phenomena (CEIDP)*, 2015 IEEE Conference on, Ann Arbor, MI, 2015, pp. 146-149
- [19] M. Misra, M. Agarwal, D. W. Sinkovits, S. K. Kumar, C. Wang, G. Pilania, R. Ramprasad, R. A. Weiss, X. Yuan, and T. C. M. Chung, "Enhanced polymeric dielectrics through incorporation of hydroxyl groups," *Macromolecules*, 47, 2014. pp. 1122-1129.
- [20] S. J. Marrink, H. J. Risselada, S. Yefimov, D. P. Tieleman, and A. H. de Vries, "The martini force field: Coarse grained model for biomolecular simulations," *J. Phys. Chem. B*, vol. 111, pp. 7812-7824, 2007
- [21] A. J. Rzepiela, M. Louhivuori, C. Peter, and S. J. Marrink, "Hybrid simulations: combining atomistic and coarse-grained force fields using virtual sites," *Phys. Chem. Chem. Phys.*, vol. 13, pp. 10 437-10 448, 2011
- [22] A. Minoguchi, K. Kitai and R. Nozaki, "Difference and similarity of dielectric relaxation processes among polyols" *Physical Review E* 68, 2003, pp. 031501-1 - 031501-7
- [23] A. Minoguchi, T. Kaneko, H. Sotokawa and R. Nozaki, "Dielectric relaxation processes in supercooled polyhydric alcohols and their mixtures", *J Non-Cryst. Solids*, 352, 2006, pp. 4742-4745
- [24] M. Nakanishi and R. Nozaki, "Systematic study of the glass transition in polyhydric alcohols", *Physical Review E* 85, 2011, pp. 051503-1 - 051503-5
- [25] S. Kastner, M. Köhler, Y. Goncharov, P. Lukenheimer and A. Loidl, "High-frequency dynamics of type-B glass formers investigated by broadband dielectric spectroscopy", *J Non-Cryst. Solids*, 357 (2), 2011 pp. 510-514
- [26] [www.instrumatics.co.nz](http://www.instrumatics.co.nz)
- [27] M. Nakanishi and R. Nozaki, "Dynamics and structure of hydrogen-bonding glass formers: Comparison between hexanetriol and sugar alcohols based on dielectric relaxation", *Physical Review E* 81, 2010, pp. 041501-1 - 041501-6