UNDERSTANDING RHEOLOGICAL BEHAVIOUR OF GRAPHENE-POLYSTYRENE NANOCOMPOSITES USING A MATHEMATICAL MODEL

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Abstract

This paper presents a theoretical analysis of the rheological behaviour of graphene-filled polystyrene nanocomposites using an existing FENE (finitely extensible non-linear elastic) model based on the stochastic differential equations. A series of these nanocomposites were prepared by in situ polymerization of styrene monomer. During polymerization, graphene was added and a number of composites were prepared by varying the percentage of graphene in the step of 0.25wt % Nanocomposite samples were hot pressed as discs and then characterised for their rheological behaviour. Experimentally, it was observed that rheological properties such as storage modulus (G') loss modulus (G'') and complex viscosity $\eta*$ increased with increasing graphene weight percentage. Using the FENE model it was predicted that graphene as a filler either affected the extension of the springs or spring constant. Consequently, a larger force was required to deform which improved the rheological properties of the polymer nanocomposites.

Keywords: Rheology, Polymer Nanocomposites, modelling, stochastic

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1 Introduction

Polymer nanocomposites are advanced materials which have found numerous applications in various sectors. Consequently, a lot of research work has been done on these materials to characterize and understand their behaviour using mathematical models. Studies on the dynamic behaviour of polymeric solutions and melts have been done based on various molecular theories using mathematical models [1]. A dumbbell model having spherical beads connected with finitely extensible non-linear elastic (FENE) springs is used to simulate polymer molecules and intermolecular chains. The molecular dynamics (MD) simulations are done using numerical integration of the equations of the motion of the beads, which in the presence of Brownian forces become stochastic differential equations (SDE). Rheology of polymers in small amplitude oscillatory flow have been studied using such dumbbell models in the past [2,3]. These dumbbells assumed to be Hookean were then replaced by nearly Hookean dumbbell to calculate the stress tensor [4]. Same models were modified to study flow behaviour of concentrated solution and melts using anisotropic Brownian and hydrodynamic forces [5,6]. Subsequently probability distribution function was introduced in the model to understand the rheological behaviour [7]. It has also been reported that a non-inertial Hookean dumbbell could not estimate the polymer coil [8]. A combination of all these models was used to obtain viscosity at low shear rates [9,10]. Compared to pure polymers, very few studies on theoretical modelling of rheological properties of nanocomposites have been reported. Comprehensive review and studies on rheology of polymer nanocomposites are available in the literature [11-15] and cross references therein. In this study, rheological properties of graphene-polystyrene nanocomposites were mathematically analysed using an existing FENE dumbbell model and matched with the experimental data obtained on the same composites.

2.0 Experimental

2.1 Materials and methods

Details about the samples and their preparation can be found elsewhere [16]. The strain amplitude sweep and frequency sweep measurements on the nanocomposite samples (circular discs of 25 mm in diameter and 1 mm in thickness) were carried out using a parallel plate rheometer (Bohlin C-VOR instrument). Strain and frequency dependent storage modulus (G′), loss modulus (G¨), tan δ and complex viscosity (η) were measured at a strain amplitude sweep at 200ºC at a fixed frequency of 1 Hz. This was done to determine the linear viscoelastic region (LVR). Frequency sweep of nanocomposites was conducted at a fixed strain of 0.01 at 200ºC in the frequency range of 0.01 − 100Hz.

2.2 Theory of stochastic differential equations (SDEs)

The mathematical theory of stochastic variable and stochastic differential equations has found a large number of applications in understanding materials behaviour. These equations use a small time-increment of a stochastic variable which comprises a deterministic increment and a completely uncorrelated stochastic contribution. In the case of polymer, SDEs have been used to solve kinetic equations in rheology [9, 10]. A typical SDE consists of Gaussian Stochastic variable, Wiener Process and Brownian forces [17]. It has been shown that the summation of uncorrelated stochastic variables gives rise to a stochastic variable with Guassian distribution. Likewise, it has also been shown that the Weiner process W(t) is a time dependent Gaussian variable.

$\Delta W_i = W(t_i+\Delta t_i) - W(t_i)$ are uncorrelated i.e.

$\Delta W_i \Delta W_j = \delta_{ij}\Delta t_i$

Hence, the time increment of a Wiener process varies as $\sqrt{\Delta t}$ since $\Delta W^2 = \Delta t$ which implies that it is non differentiable since $(\Delta W/\Delta t)$ diverges for Δt tends to zero.

Thus, a typical stochastic differential equation is written as

$dX = A.dt + B.dW$

where X denotes the position of a Brownian particle and A provides a drift term and second term (stochastic) represents the Brownian motion (B is diffusion tensor). Since the Weiner process is non differentiable, it is expressed as

$$X(t) - X(0) = \int_0^t A(X(t\prime))dt + \int_0^t B(X(t\prime)).dW(t\prime)$$

2.2.1 SDE for a dumb-bell model

For a combination of stochastic-probabilistic method, time evolution of the stochastic variable (p_i, X_i) is given by

$$p_{i+1} = p_i + \dot{p}_i\Delta t$$

$$X_{i+1} = X_i + A(X_i)\Delta t + V_i\Delta t$$

where $V_i = (dX_i/dt) - A(X_i)$

Using this method, stochastic equation for 1D FENE dumb bell is written as

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$$dQ = \dot{\varepsilon}\,Q\,dt - \frac{1}{2}\frac{Q}{1 - Q^2/Q^2_{max}}\,dt + dW$$

where $\dot{\varepsilon} = d\varepsilon/dt$ is the rate of elongation, Q is the length between two beads (or connector vector), and Q_{max} *is* the maximum spring can extend. The first expression on the RHS of equation gives the deformation by virtue of flow, the second expression is by virtue of entropic elastic force and the last expression is due to Brownian motion. The finite extensibility of a polymer is ensured by making the force law of the spring diverge at the maximum length keeping in mind the maximum length is not exceeded. For (L=|Q|) the evolution equation is given by

$$dL^2 = \left(2Q.\dot{\varepsilon}.Q - \frac{L^2}{1 - L^2/L^2_{max}} + 1 \right) dt + 2Q.\,dW$$

Using this equation and solving for quadratic roots a condition is determined for L<L_{max} as shown in Fig. 1 which shows the correlation between the extension of the connector vector (**Q**) and the length of the dumbbell (L).
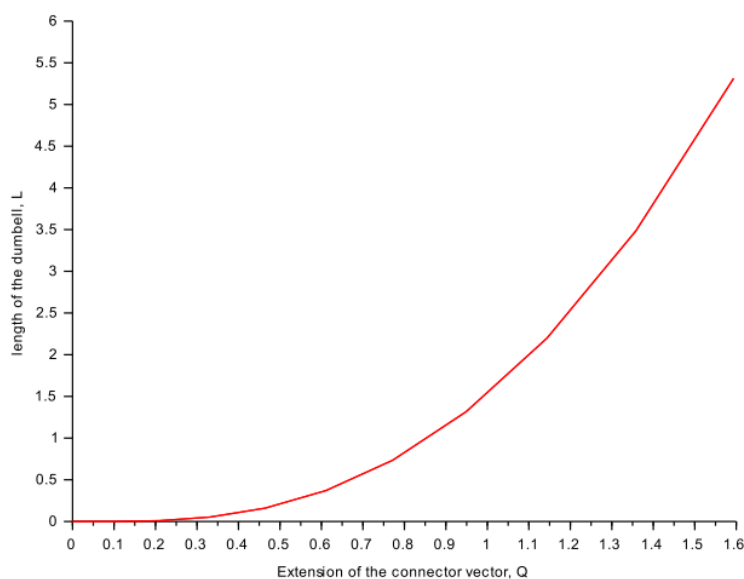

Fig 1: Correlation between extension of connector vector (**Q**) and length of dumbbell (L).

Using the time evolution of **Q,** the polymer stress was calculated using the following formulae

$\tau^p/(nk_BT) = (1/N)\Sigma(\mathbf{QF^c}) - 1$

where the connecting spring force between beads, $\mathbf{F^c} = H\mathbf{Q}$. H is the spring constant, k_B is the Boltzmann constant, T is the absolute temperature, n is the number of dumbbells per unit volume, N is the total number of dumbbells, and **Q** is the connector vector between beads. $\mathbf{F^c}$ can also be written as $\mathbf{F^c} = H\mathbf{Q}/(1 - Q^2/Q^2_0)$, where Q is the distance between the beads, Q_0 denotes the maximum possible spring extension. The finite extensibility parameter, $b = HQ^2_0/(k_BT)$

3.0 Results and Discussion

Figure 2 shows an oversimplified hypothetical basic network of a polymer molecule as proposed under the FENE model wherein neighbouring beads are connected by finitely extensible non-linear springs. The finite extension of the springs is supposed to simulate the flow behaviour of polymer nanocomposites when it is subjected to a deformation. In the case of polystyrene graphene nanocomposite, during *in situ* polymerization of styrene monomer, two simultaneous mechanisms might have occurred.
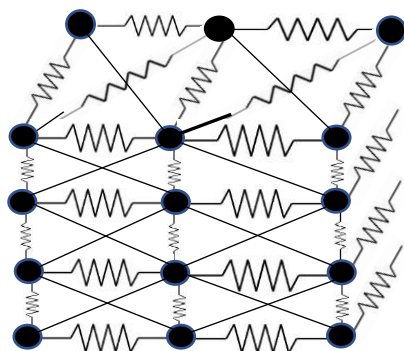
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Fig 2: Schematic of the FENE model. Black spheres denote beads connected with springs

Either graphene as a filler might have got physically entangled with the polymer chains or maybe the intercalation of polymer molecule within the graphene layers might have occurred. With the increase in graphene content, either of these mechanisms might have dominated. Visualising it through the FENE model, it can be assumed that graphene affected the extension of the springs (Q) or it might have changed the spring constant (H) or it might have increased the damping of the springs (b or maximum extension of the spring (Q_0). Consequently, a larger force was required to deform the polymer. This is corroborated by the experimental data (Fig. 3a,b and Fig 4) which show that as the graphene percentage increases, storage modulus and loss modulus of nanocomposites compared with pure Polystyrene shows a monotonic increase[16].
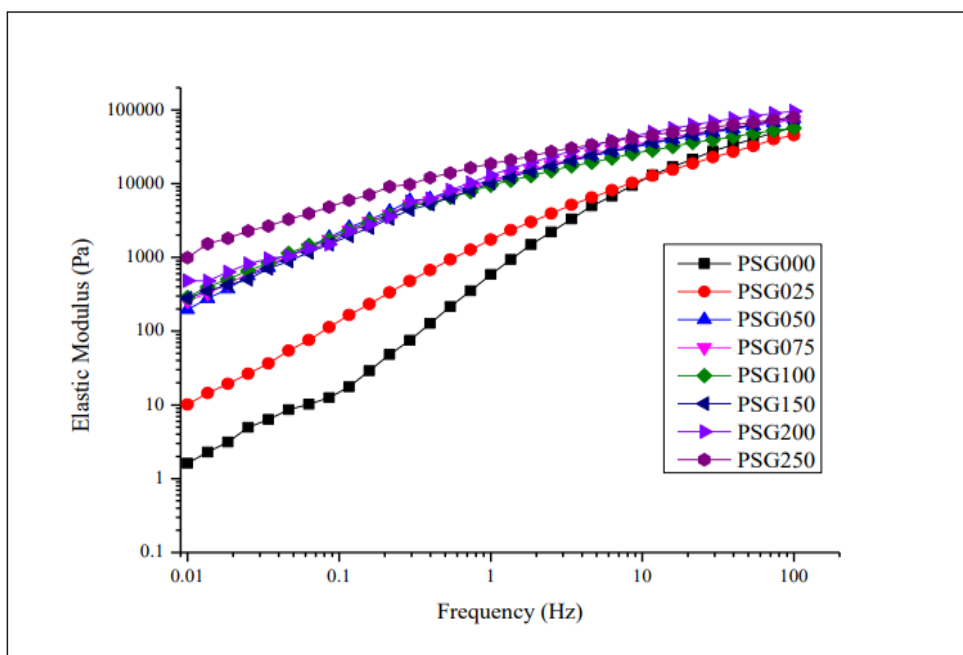

Fig 3a: Elastic modulus vs. frequency of polystyrene-graphene nanocomposites [16]
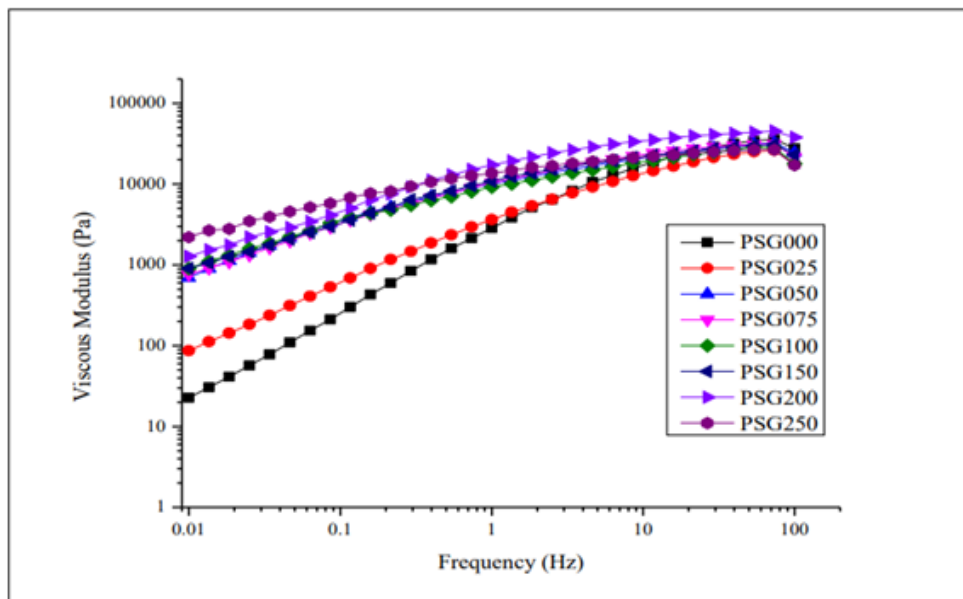
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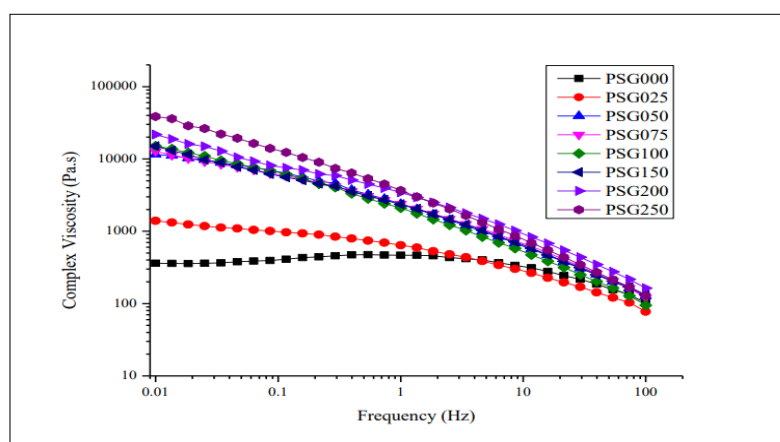**Fig 3b**: Viscous modulus vs. frequency polystyrene-graphene nanocomposites [16]

Fig 4: Complex viscosity vs. frequency of polystyrene–graphene nanocomposites [16]

Using SCILAB software [18], time evolution of connector vector (**Q**) was calculated using Euler forward difference method for three different elongation rates (dε/dt) and is shown in Fig. 5. In the FENE model, finite extensibility parameter (b) and hence the spring constant was changed gradually and stress was calculated using time evolution of Q.
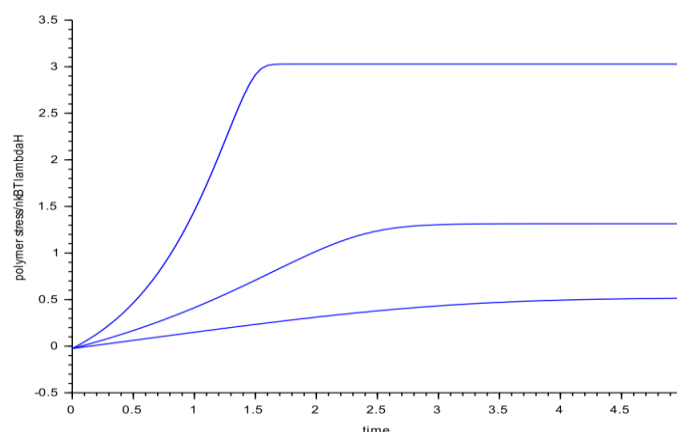

Fig 5: Time evolution of polymer stress at three different elongation rates (top curve 2, middle curve 1 and bottom curve 0.5)

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The change in the spring constant corresponded to the change in the graphene percentage. These results are shown in Figure 6a-c which indicate that graphene plays a significant role in modifying the rheological behaviour of polystyrene (PS).
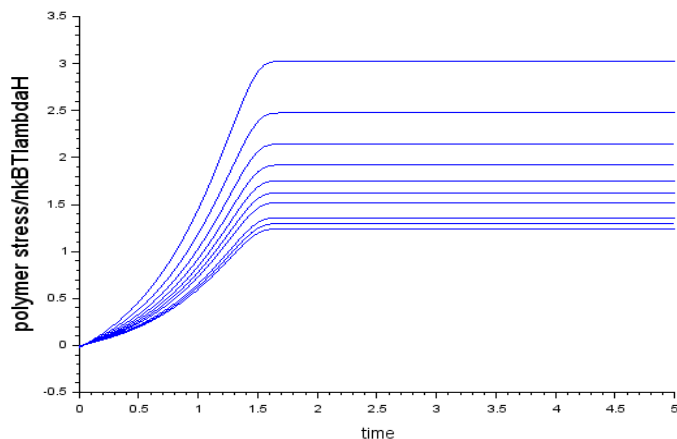

Fig. 6a: Time evolution of polymer stress at different finite extensibility parameter, b (top curve b=25, and bottom curve b=300) (b corresponds to the spring constant and hence to the graphene percentage)
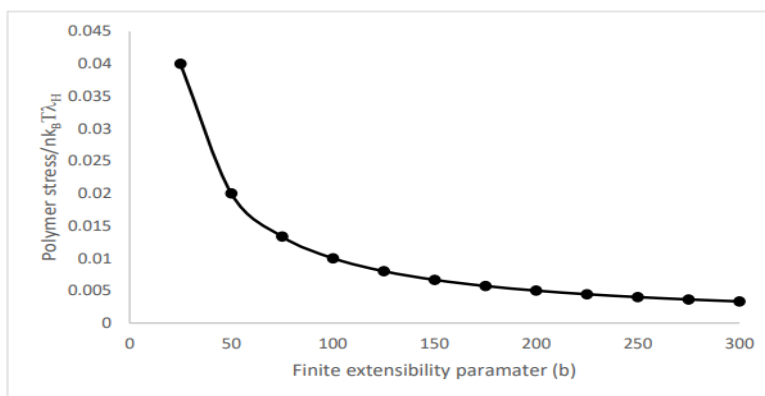

Fig 6b: Variation of Polymer stress with increasing finite extensibility parameter b (which corresponds to the spring constant and hence to the graphene percentage)
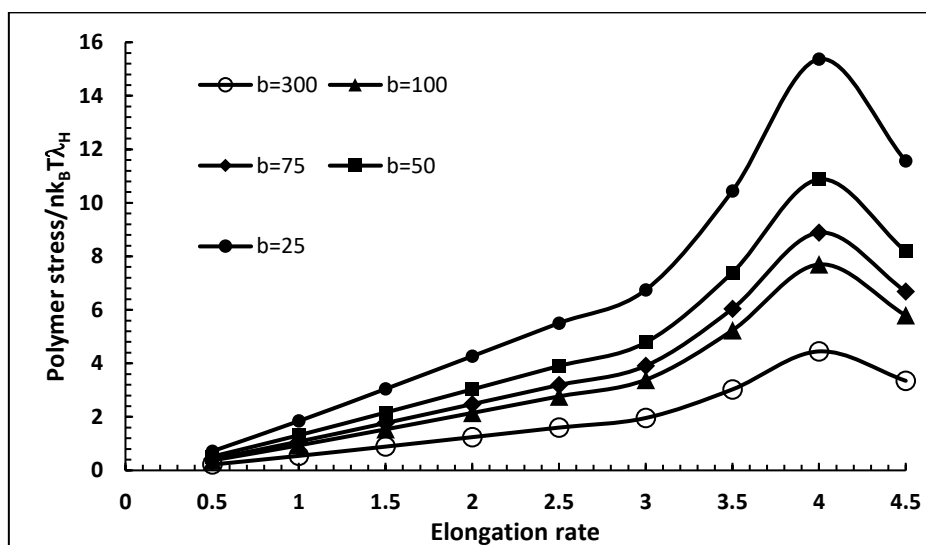

Fig. 6c: Variation of Polymer stress with increasing elongation rate at different finite extensibility parameter b (which corresponds to the spring constant and graphene percentage)

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4.0 Conclusion

Rheological properties of the graphene filled polystyrene nanocomposites were analysed using a theoretical model based on FENE bead-spring network. Material functions related to rheological properties were computed numerically and compared with experimentally measured values pertaining to storage modulus, loss modulus and complex viscosity of nanocomposites. The improvement in rheological properties of polystyrene on addition of graphene as a filler has been linked to the entanglement of graphene with polymer chains or intercalation of polymer chains within graphene layers. Theoretically it was visualised that spring constant or extension of springs that simulated flow was affected by the addition of graphene.

Conflict of interest

There is no conflict of interest

Acknowledgement

References

1. Larson R.G., (1988), *Constructive Equations for polymer Melts and Solutions*, Butterworth, AT T, Boston.
2. Warner Jr., H.R., (1972). *Kinetic Theory and Rheology of Dilute Suspension of finitely extensible Dumbbells*, Ind. Eng. Chem. Fundam , 11 : 379.
3. Christiansen, R.L. and R.B. Bird, (1977/1978),. *Dilute Solution Rheology: Experimental Results and Finitely Extensible Non-linear Elastic Dumbbell Theory*, J. Non-Newtonian Fluid Mech, 3 : 161.
4. Armstrong, R.C. and S. Ishikawa, (1980), *A Rheological Equation of State for Dilute Solutions of Nearly-Hookean Dumbbells*,, J.Rheol. , 24 : 143
5. Bird, R.B. and J.R.Deaguiar, (1983), *An Encapsulated Dumbbell model for Concentrated Polymer Solution and Melts. I. The Theoretical Development and Constitutive Equation*, J. Non-Newtonian Fluid Mech. , 13 : 149
6. Bird,R.B, J.M. Wiest, (1985),*Anisotropic Effects in Dumbbell Kinetic Theory*,J. Rheol., 29:519.
7. Fan, X.J. (1985), Viscosity, *First Normal-Stress Coefficient, and Molecular Stretching in Dilute Polymer Solution*,, J. Newtonian Fluid Mech., 17 : 125
8. Schieber, J.D., (1993), *Internal Viscosity Dumbbell Model with Gaussian Approximation*, J. Rheol. , 37 : 1003
9. Ottinger, H.C., B.H.A.A. van den Brule and M.A. Hulsen, (1997), *Brownian Configuration Fields and Variance Reduced CONFFESSIT*, , J. NonNewtonian Fluid Mech. , 70 : 255
10. Vaccaro, A. and G. Marrucci, (2000) *A model for the Nonlinear Rheology of Associating Polymers*, J. Non-Newtonian Fluid Mech. , 92 : 261
11. Y.S Song and Jae Ryoun Youn, (2004) *Modeling of rheological behavior of nanocomposites by Brownian dynamics simulation*, Korea-Australia Rheology Journal, 16-(4), 201-212
12. P.K. Valavala and G.M. Odegard, (2005) *Modeling techniques for determination of mechanical properties of polymer nanocomposites*, Rev.Adv.Mater.Sci., 9, 34-44
13. Abraham J, Sharika T, George SC, Thomas S (2017) *Rheological Percolation in Thermoplastic Polymer Nanocomposites*, Rheol: open access, 1: 102.
14. M. Giovino, Julia Pribyl, Brian Benicewicz, S Kumar, Linda Schadler, (2017), *Linear rheology of polymer nanocomposites with polymer-grafted nanoparticles*, Polymer, 131-(22): 104
15. Sabu Thomas, Rene Muller, Jiji Abraham, (2016), *Rheology and Processing of Polymer Nanocomposites,* Ed(s), Online ISBN:9781118969809 DOI:10.1002/9781118969809
16. S.Basu et.al. 2013, *Dielectric, Electrical and Rheological Characterization of graphene Filled polystyrene nano composites*, Polymer Composites , 34-(12) : 2082
17. E.A.J.F. Peters, (2000), *Polymers in flow: Modelling and simulation*, Ph.D Thesis, published by Ponsen and Looijen, The Netherlands ISBN 90-3700183-1
18. SCILAB; open access software

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