Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Applied Science Research, 2023, 15 (1) 01-07
(http://scholarsresearchlibrary.com/archive.html)

Rheological Studies of Hybrid Composites of Polypropylene

Himani J[1*], Purnima J[2]

[1]*Department of Applied Sciences, Guru Tegh Bahadur Institute of Technology, GGSIPU, New Delhi, India*

[2]*School of Applied Sciences, NSUT, New Delhi, India*

***Corresponding Author:** Himani J, Department of Applied Sciences, Guru Tegh Bahadur Institute of Technology, GGSIPU, New Delhi, India*

E-mail: joshihimani.chem@gmail.com

Received: 01 Apr, 2023, Manuscript no. AASR-23-87201; **Editor assigned:** 03 Apr, 2023, Pre QC no. AASR-23-87201 (PQ); **Reviewed:** 17 Apr, 2023, QC no. AASR-23-87201; **Revised:** 02 Jun, 2023, Manuscript no. AASR-23-87201 (R); **Published:** 09 Jun, 2023

ABSTRACT

Melt rheological properties of Polypropylene and its composites with various GF and WF loadings have been systematically studied in this work. In all the compositions of "A", "B" and "C", loss modulus (G'') is more than the storage modulus (G') indicates that the viscous behaviour dominates over the elastic behaviour. All the composites show long term stabilities as observed in the graphical presentations of loss modulus, storage modulus, loss factor and complex viscosity values. Loss modulus is highest for the composition having both grafted PP and impact modifier at high frequency. Hybrid composites have greater values of storage modulus than neat PP indicating the increased stiffness of the composites than the polymer. The values of complex viscosity show significant difference at the low frequency region.

Keywords: Thermoplastics, Polymer composites, Rheological characterization, Loss modulus, Storage modulus, Damping factor, complex viscosity.

INTRODUCTION

Rheological techniques reveal valuable information on the process behaviour of polymer melts. Moreover, structural information like molar mass distribution, degree of crosslinking or branching as well as crystallization effects are related to the rheological behaviour of polymeric systems. Mostly oscillatory testing with rotational rheometers and parallel plate geometries is used for these investigations. Rheological measurements on polymeric samples require an accurate temperature control over an extended temperature range. Typically, Peltier controlled and electrically heated systems are used for measurements with parallel plate geometries while convection ovens can also be used for parallel plate [1].

To reduce the time for rheological characterization, user needs for preparing and running a test to employ a sophisticated control of the rheometer and an intuitive user interface for the software. With such an approach the test itself can be preconfigured running afterwards fully automatically including the analysis of data. However, before the sample loading, cleaning of the fixtures is needed which often takes the longest time. In addition, loading and cleaning requires frequent interaction of user when multiple samples are to be run. Although, high throughput screening technologies have been employed in a wide range of testing applications. But in the case of rheological measurements, there are only a few devices available. For example, microrheological techniques have been employed by breaded and pine for measuring aqueous block co polypeptide solutions. Recently, polymeric composites have increased interest in the development of damping materials due to their relatively high strength and excellent damping characteristics [2].

A combinatorial squeeze flow setup was described for the rheological characterization of asphalt. A prototype device consisting of an array of couette cells with embedded permanent magnets moved by an oscillating magnetic field has been reported as well. Although these techniques are valuable for certain applications, they all lack the ability to test the samples with the flexibility like it is done using standard rotational rheometers [3].

In this study, the rheological properties of the PP/GF/WF, PP/GF/WF/gPP and PP/GF/WF/gPP/IM composites are reported by the measurements of the dynamic rheology. Dynamic measurements were carried out using advanced Anton paar physical rheometer [4].

The frequency sweeps from 0.1 to 100 rad/s were performed at 230°C under dry nitrogen condition. For all the measurements, the polypropylene hybrid composite samples were tested within the linear viscoelastic strain range.

This article explains the rheological behaviour of various compositions in terms of loss modulus, storage modulus and complex viscosity. This paper explains and compares the rheological properties of the various compositions. The effect of percentage of fillers wollastonite fibers and chopped glass fibers on the rheological properties of hybrid composites is described. Furthermore, comparison studies have been carried out when additional components *i.e.,* grafted Polypropylene (B) or both grafted PP and impact modifier are added to the various compositions of the hybrid composites (C). The master curves are plotted with the help of the results in data form. The master curve is calculated from several frequency sweep curves at different temperatures and from this calculation the curve displays values below and above the measuring range of a Rheometer. (10^{-6} to 10^{6} Hz). Master curves are an important tool to analyse the polymer melts [5].

MATERIALS AND METHODS

Various compositions prepared in single and twin screw extruder are tabulated (Tables 1 and 2). Preparations of test specimens by injection molding are briefly explained. Measurements and analysis procedures for mechanical properties, morphological studies, crystallization studies and rheological studies are explained [6]. The materials employed in this investigation were Polypropylene (Repol grade 11MA) supplied by reliance petrochemicals with a melt flow index of 11 g/10 min. The glass fibers used were chopped E-glass fiber strand T-480 supplied by Nippon Electric Glass Co. Ltd. (Malaysia). The grade of wollastonite used for preparing different compositions was Fillex-11AB3 (surface treated) *i.e*., supplied by Wolkem India Limited. Grafted PP used is OPTIM, grade is 425. It was supplied by pluss polymers, Gurgaon. The impact modifier used was engage 8200 supplied by polmann India Ltd., Bahadurgarh, Haryana [7].

Table 1: Composite codes for PP/GF/WF, PP/GF/WF/gPP/IM and PP/GF/WF/gPP/IM composites prepared in Single Screw Extruder (SSE)

Composite name	Composite code PP/GF/WF/gPP/IM	PP (% by weight)	GF (% by weight)	WF (% by weight)	gPP (% by weight)	IM (% by weight)
A2	A 70/30/0	70	30	0	-	-
A3	A 70/20/10	70	20	10	-	-
A4	A 70/15/15	70	15	15	-	-
A5	A 70/10/20	70	10	20	-	-
A6	A 70/0/30	70	0	30	-	-
B2	65/30/0/5	65	30	0	5	-
B3	65/20/10/5	65	20	10	5	-
B4	65/15/15/5	65	15	15	5	-
B5	65/10/20/5	65	10	20	5	-
B6	65/0/30/5	65	0	30	5	-
C2	60/30/0/5/5	60	30	0	5	5
C3	60/20/10/5/5	60	20	10	5	5
C4	60/15/15/5/5	60	15	15	5	5
C5	60/10/20/5/5	60	10	20	5	5
C6	60/0/30/5/5	60	0	30	5	5

Table 2: Composite codes for PP/GF/WF composites prepared in Twin Screw Extruder (TSE)

Composite name	Composite code PP/GF/WF	PP (% by weight)	GF (% by weight)	WF (% by weight)
Neat PP	PP	100	0	0
S2	70/30/0	70	30	0

S3	70/20/10	70	20	10
S4	70/15/15	70	15	15
S5	70/10/20	70	10	20
S6	70/0/30	70	0	30

Hybrid composites of PP reinforced with chopped glass fibers and wollastonite were prepared by using melt mixing technique in a single screw extruder as well as in a twin screw extruder. The composites were prepared by one step process technique of melt compounding [8].

RESULTS AND DISCUSSION

Determination of linear viscoelastic region

When small deformation is applied to the polymeric material or when the deformation rate is very low, the polymer structure remain unaltered. This is because of the fact that the molecules have enough time to relax. This deformation when the entangled state of molecules of polymers is not disturbed is said to be in the linear viscoelastic range.

An amplitude sweep (Figure 1a) was performed prior to the frequency sweep (Figure 1b). To determine the Linear Visco Elastic Region (LVER) of the material a strain sweep was carried on sample A4 (70/15/15). With respect to the LVER a strain of 0.05% was chosen for all the measurements of frequency sweep. Melting was tried at 180°C onwards and found the melt was proper and uniform at 230°C. This temperature was used for all the tests [9].

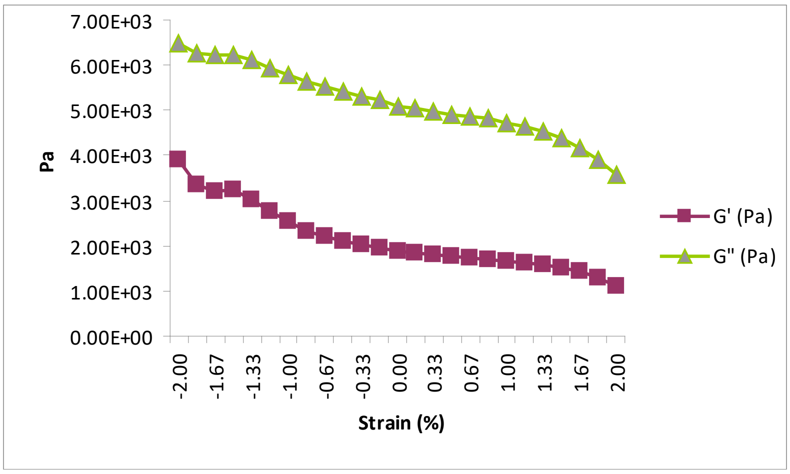

Figure 1(a). Amplitude sweep

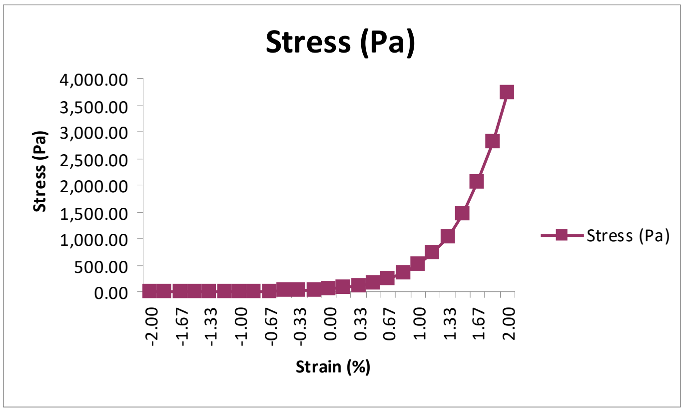

Figure 1(b). Plot of strain stress curve for A4 (PP/GF/WF)

From the amplitude sweep tests, the limiting value of LVER was determined. The strain for all the following frequency sweeps was fixed at 0.05% for all the measurements.

Loss modulus of PP/GF/WF, PP/GF/WF/gPP, PP/GF/WF/gPP/IM hybrid composites

Figure 2 (a-c), it is observed the loss modulus (G”) of the polypropylene hybrid composites at 230°C. The loss modulus characterizes the material’s viscous properties *i.e.,* the energy dissipation. From Figure 2(a), it was observed that the loss modulus (G") of PP/GF/WF hybrid composites decreases with the increase in wollastonite fiber weight fraction from 0 to 30% with exceptional composition. In Figure 2(b) for the compositions with grafted PP, the same results are obtained when wollastonite fiber weight fraction is increased from 0 to 20%. At 30% wollastonite fiber, it shows the highest loss modulus values, on the contrary.

For the "C" set of compositions *i.e.,* the compositions with both grafted PP and impact modifier, the results for loss modulus (G") are shown in Figure 2 (c). This figure shows the results similar to the "A" compositions. Also, it is observed that the loss modulus of the A3 (70/20/10) composites increases more significantly than the other compositions of "A". In Figure 2 (a) the loss modulus of B6 (65/0/30/5) composites increases more significantly at lower frequency and at higher frequency as well. But as explained in detail, the structure of polymer composites is more sensitively reflected on the storage modulus (G') than on the loss modulus (G").

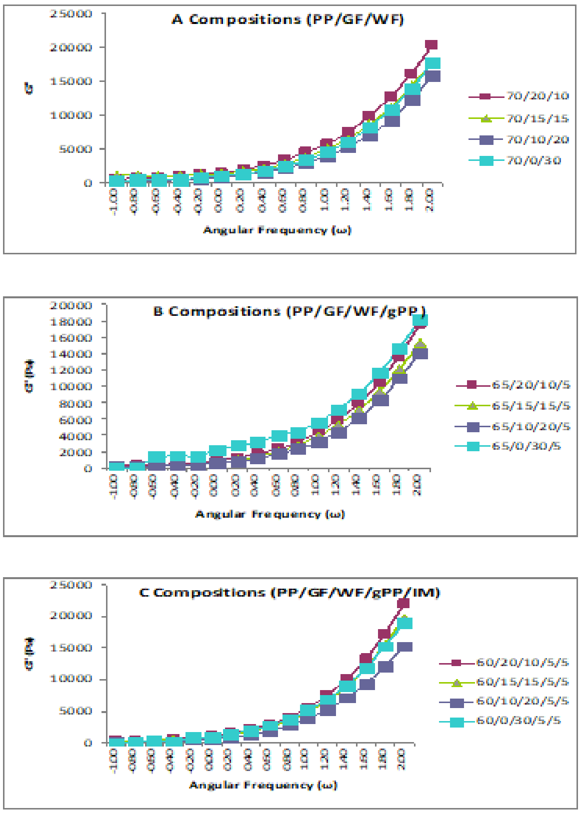

Figure 2. Loss modulus (G") of the PP hybrid composites at 230°C; (a) PP/GF/WF; (b) PP/GF/WF/gPP; (c) PP/GF/WF/gPP/IM composites

Storage modulus of PP/GF/WF, PP/GF/WF/gPP, PP/GF/WF/gPP/IM hybrid composites

Figure 3 (a-c) shows the storage modulus (G') of the Polypropylene hybrid composites at 230°C. As seen in the Figure 3 (a), the storage modulus of the composites is more than the virgin PP because of the intrinsic rigidity of the wollastonite fiber and glass fiber. The storage modulus and loss modulus of the PP composites were significantly improved relative to the PP matrix.

It is known that the polymer chains are fully relaxed and exhibit characteristic terminal flow behaviour with the power law relation of approximately $G' \sim \omega^2$ and $G'' \sim \omega$ for linearly homo dispersed polymer melts. The storage modulus is a measure for the elastic properties, and specifies the energy stored in the material.

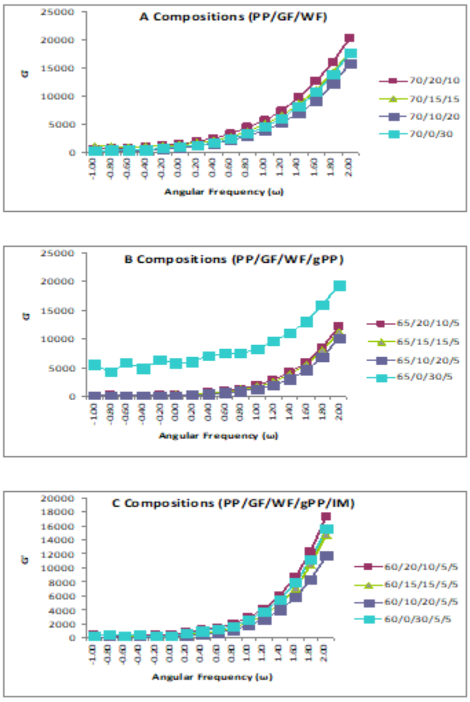

Figure 3. Storage modulus (G') of the PP hybrid composites at 230°C; (a) PP/GF/WF; (b) PP/GF/WF/gPP; (c) PP/GF/WF/gPP/IM composites

From Figure 3 (a), the storage modulus (G') of PP/GF/WF hybrid composites shows almost similar values for both the compositions A3 and A4 with 10 and 15% wollastonite fiber respectively. When wollastonite fiber increases further *i.e.,* 20% the values of storage modulus decrease. At 30% wollastonite the values of storage modulus w.r.t angular frequency shows an increase. Figure 3 (b) shows the values of storage modulus of the "B" composition with grafted PP added.

The G' values increase in this case with the increase in wollastonite fiber from 0 to 20%. At 30% wollastonite storage modulus increases very sharply showing the highest values for the storage modulus. The values for the storage modulus for "C" set of compositions are shown in Figure 3 (c). With the increase in the weight fraction of wollastonite from 0 to 20% the values for the storage modulus decrease. While in case of the hybrid composites with 30% wollastonite, increase in the storage modulus takes place.

Loss factor (tan δ) of PP/GF/WF, PP/GF/WF/gPP, PP/GF/WF/gPP hybrid composites

The loss factor tan (δ) describes whether the sample is more viscous or elastic. It should be noted that this parameter is independent of the material's stiffness and hence is an important parameter when the differences in viscoelastic response of the material are desired. This state depends on the temperature. The loss factor tan (δ) is calculated as ratio of loss modulus and storage modulus which is equivalent to:

tan (δ)=G"/G'=Viscous portion/Elastic portion=flexibility/stiffness

Variation of loss factor with the angular frequency for the PP composites is shown in the Figure 4 (a-c). While observing the graph we conclude that damping factor is highest for the compositions A5 (10% GF 20% WF). Thus, it may be concluded that in the A set of compositions, this composition has the more viscous properties. The composition with 20% GF shows the lowest value for the loss modulus, indicating this composition to be improved elastic properties at this composition.

It has been found by observing the plot 4 (b) that the addition of grafted PP to the hybrid composites has slightly increased value of loss factor indicating more viscous properties of this "B" set of compositions.

Among all the hybrid composites under this category, it was observed that the graph showed a flattened section below 10 rad/sec ω. The flattened section in this curve indicates the relaxation of the fibers. Composition B4 (15% GF 15% WF) showed the highest value of loss factor while the composition B6 with 30% wollastonite shows the least values for the same. Thus, we may conclude that this composition B6 (30% wollastonite) shows the good elastic properties among all the compositions with grafted PP.

Figure 4 (c) explains the variation of loss factor with angular frequency for the PP/GF/WF/gPP/IM compositions. Here also a flattened section is observed till 10 rad/sec ω explaining the relaxation of the fillers. We observe that the composition with 30% wollastonite fiber showed the least value for the loss factor at lower frequency, explaining the better elastic properties of this compositions as compared to that of other having both grafted PP and impact modifier.

In all the compositions *i.e.,* "A", "B" and "C", it is observed that at high frequency region, the decrease of tan δ with increasing frequency was attributed to the partial orientation of polymer chains caused by shear deformation.

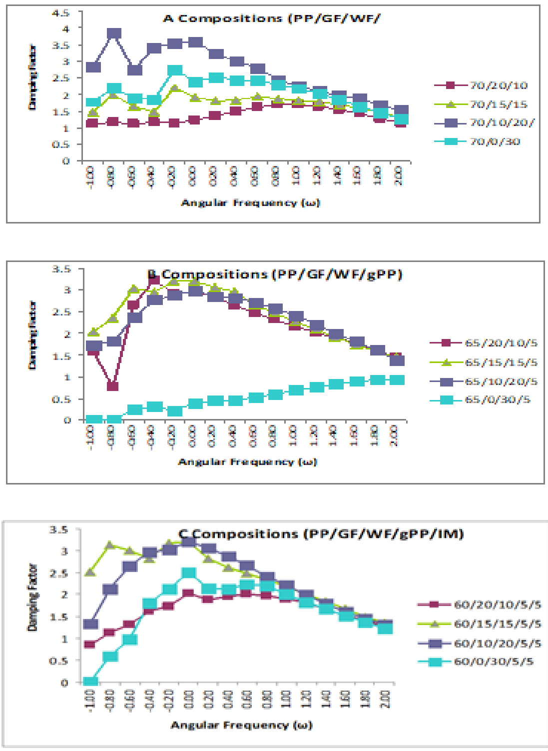

Figure 4. Loss factor (tan(δ)) of the PP hybrid composites at 230°C. (a) PP/GF/WF; (b) PP/GF/WF/Gpp; (c) PP/GF/WF/gPP/IM composites

Complex viscosity of PP/GF/WF, PP/GF/WF/gPP, PP/GF/WF/gPP hybrid composites

The relation between the moduli and frequency can be expressed as complex viscosity. Figure 5 (a-c) shows the complex viscosity η^* of the PP hybrid composites at 230°C. It is well established that the addition of filler into the polymer matrix increases the viscosity of the melt. Viscous flow, the irreversible bulk deformation of polymeric material, is associated with irreversible slippage of molecular chains past one another. The most important structural variable determining the flow properties of polymers is molecular weight. The increase of the viscosity depends on the concentration, particle size, particle size distribution and shape of the filler. From Figure 5 (a-c), the values of complex viscosity show significant difference at the low frequency region as compared to that in the high frequency region. For the “A” compositions Figure 5 (a) explains that at low frequency region the A4 (70/15/15) composite possess the highest viscosity. But at higher angular frequencies, the values for complex viscosities are almost same. On the addition of grafted PP to the compositions, the variation in the values of complex viscosities is given in graph 5 (b). In these compositions also, there is a significant difference in values of complex viscosity at lower frequency region, composition with 30% wollastonite shows the highest complex viscosity.

As can be seen from Figure 5 (b) the highest complex viscosity is related to the polypropylene containing 30% wollastonite fiber. It seems that the effect of gPP on the smaller size of wollastonite fiber is more than glass fiber which means better interaction between wollastonite fiber and PP matrix, so the melt samples containing higher wollastonite fiber content is more homogeneous and shows higher viscosity. In addition, the presence of some wollastonite fiber agglomerates causes resistance against the flow and increase viscosity of samples.

On the other hand, due to orientation of glass fiber in flow direction the flow ability sample containing glass fiber is easier. While at high frequency region all values are similar. Figure 5 (c) shows the complex viscosity for hybrid composites with grafted PP and impact modifier for the composition with 20% GF. Difference in the composites exists at lower angular frequency region. The composition C3 with 20% GF and 10% WF exhibits the highest complex viscosity.

Comparison was made for the complex viscosity of all three types of compositions *i.e*. “A”, “B” and “C”, the values for “B” set having grafted PP is lower as compared to the rest two set of composites. This might be due to the continuous thermomechanical degradation process caused by chain scissions. The highest molecular weight chains are preferentially broken during the degradation and the scissions may be located close to the macromolecule centre. In all the compositions of “A”, “B” and “C” loss modulus (G'') is found to be higher than the storage modulus (G'), which indicated that the viscous behaviour dominates over the elastic behaviour. The sample shows the character of a liquid. The only exception is B6 (70/0/30/5/5). Here G’>G. In this range the elastic behaviour dominates over the viscous behaviour and the sample behaves as a solid or as a gel, and shows form stability.

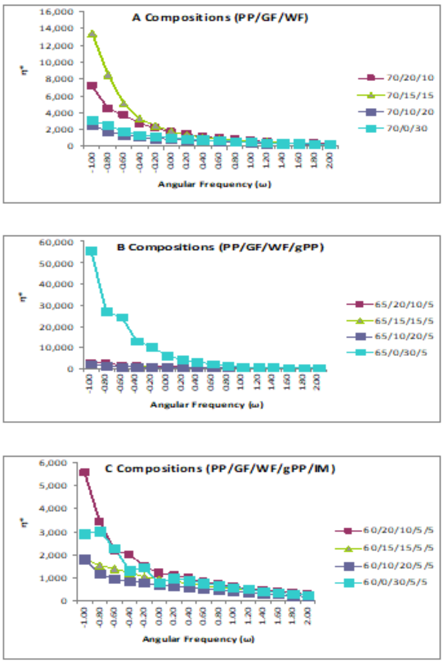

Figure 5. Complex viscosity of the PP hybrid composites at 230°C. (a) PP/GF/WF; (b) PP/GF/WF/gPP; (c) PP/GF/WF/gPP/IM

CONCLUSION

Rheological studies are presented for all the hybrid composites of PP. The values for loss modulus, storage modulus, loss factor and complex viscosity with respect to angular frequency are obtained and the results are analysed. All the composites show long term stabilities as observed in the graphical presentations of loss modulus, storage modulus, loss factor and complex viscosity values. Loss modulus is highest for the composition C3 (60/20/10/5/5) having both grafted PP and impact modifier at high frequency. Hybrid composites have greater values of storage modulus than neat PP indicating the increased stiffness of the composites than the polymer. The values of complex viscosity show significant difference at the low frequency region. C3 (60/20/10/5/5) and B6 (65/0/30/5) shows the highest values for the complex viscosity.

Acknowledgements

The author is acknowledged to Prof. Anup K. Ghosh H.O.D, CPSE (IIT, Delhi) for kind supervision and Anton Paar for their contributions to provide the facilities.

REFERENCES

1. Dealy, J.M., et al. Structure and rheology of molten polymers. *Carl. Hanser. Verlag*. **2006** 17(5): 258-259.
2. Mezger, T.G., et al. The Rheology Handbook. 2nd Edition. Vincentz Network. Germany. **2006**.
3. Lauger, J., et al. From sample changer to the robotic rheometer: Automation and high throughput screening in rotational rheometry. InAIP conference proceedings, Monterey, California, 3-8 August. **2008** 1027(1): 1198-1201.
4. Breedveld, V., et al. Micro rheology as a tool for high throughput screening. *J. Mater. Sci*. **2003** 38(22): 4461.
5. Finegan, C., et al., Recent research on enhancement of damping in polymer composites. *Compos. Struct.* **1999** 44(2-3): 89
6. Patil, Y.P., et al. Rheological characterization of asphalt in a temperature gradient combinatorial squeeze flow setup. *Rheologica. acta*. **2007** 46: 1075-1082
7. Potschke, P., et al. Rheological behavior of multiwalled carbon nanotube/polycarbonate composites. *Polymer*. **2002** 43(11): 3247-3255
8. Mitchell, C.A., et al. Dispersion of functionalized carbon nanotubes in polystyrene. *Macromolecules*. **2002** 35(23): 8825-8830
9. Shenoy, A.V., et al. Rheology of highly filled polymer systems. 1st Edition. Kluwer Academic, London. **1999**.