

Dynamic Shear Rheology of PC/MWCNT Composites Made from PC with Different Molecular Weights

Prakashan K.¹, Sung Cik Mun², Mokwon Kim², Hyuk Jin Jung²,
Younggon Son³ and O Ok Park²

¹ Gyeongsang National University, Jinju, Gyeongnam, Republic of Korea

² Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea

³ Kongju National University, Cheonan, Chungnam, Republic of Korea

ABSTRACT

The effect of MWCNT content on the viscoelastic properties of PC/MWCNT composites is strongly dependent on the molecular weight of matrix PC. MWCNT affects more significantly the rheological properties of low molecular weight PCs. This dependency is mainly attributed to the different levels of rheological properties of each pure PC.

INTRODUCTION

Dynamic shear rheology is an important tool in the characterization of polymer nanocomposites. It provides information on processing of these composites and most importantly it gives information on the state filler dispersion and its interaction with polymer matrix.

A large number of studies on polymer nanocomposites paid attention to the significant effect of nanoparticles on viscoelastic properties, particularly the appearance of a pseudo-solid like behavior above certain concentration of the nanofiller in the composite¹⁻¹¹. This phenomenon is widely known as rheological percolation and the filler content above which it occurs is termed rheological percolation threshold.

The origin of this phenomenon has not yet fully understood though different explanations are found in literature. Ren et al.³ have reported a pseudo-solid like behaviour for layered silicate based polymer

nanocomposites and attributed it to the mesoscopic structure of randomly oriented silicate layer tactoids that form a three-dimensional percolated network structure due to the anisotropy associated with these tactoids. Pötscheke et al.⁴ have attributed the pseudo-solid like behavior to formation of some kind of 'entanglements' between polymer chains and nanotubes or in other words formation of a combined nanotube-polymer chain network. The rheological percolation has been found to be depend on filler dispersion⁷, interfacial adhesion between nanofiller and polymer matrix⁷, aspect ratio⁸, alignment^{5,9}, and temperature^{4,10,11}.

The effect of temperature on the rheological percolation indicates the significant influence of chain relaxation or chain mobility on percolation phenomenon. In order to further explore the effect of chain mobility on percolation behaviour, in this paper, we study the dynamic shear rheology of PC / multiwalled carbon nanotube (PC/MWCNT) composites made from different PCs with varying molecular weights.

EXPERIMENTAL

Materials

The Table 1 lists the four different PCs used in this study along with their details of molecular weights and supplier name.

The four different PC samples are

Table 1. Details of different PCs used in this study

Sample Code	Supplier (Grade Name)	Molecular Weight Data (GPC)			Melt Flow Index at 250°C/10 kg (g/10 min)
		Mn (g/mol)	Mw (g/mol)	PDI	
PC4	LG-DOW, Korea (CALIBRE 200-3)	19000	35000	1.84	4
PC3	Teijin Kasei, Japan (PanliteL-1250WP)	14200	29300	2.06	12
PC2	Teijin Kasei, Japan (PanliteL-1225WX)	11800	23600	1.99	30
PC1	Teijin Kasei, Japan (Panlite CM-1000)	8900	17600	1.95	90

named as PC1, PC2, PC3 and PC4 in increasing order of their molecular weights. The MWCNT was Nanocyl[®] 7000 purchased from NANOCYL company, Belgium. It is produced by a catalytic carbon vapor deposition process and has carbon purity of 90%, average diameter of 9.5 nm, average length of 1.5 μm and aspect ratio ≈ 150 .

Composite Preparation

Composites were prepared by melt mixing in a Brabender internal mixer at a temperature of 250°C for 10 min with a 100 rpm rotor speed. The collected samples then pelletized and compression molded using a hot press at 260°C for preparing specimens for melt rheology. The compositions of the composites are varied as 0.5, 0.75, 1, 1.25, 1.5 and 2 wt% MWCNT for each PC and the nanocomposite series are named as PC1/MWCNT, PC2/MWCNT, PC3/MWCNT and PC4/MWCNT corresponding to the different PCs.

Dynamic Shear Rheology

Dynamic shear test were performed by ARES system from Rheometrics Scientific. Tests were performed on 25-mm parallel plate fixture at 200°C. The frequency window was 0.1–100 rad/s with a strain

within the linear viscoelastic regime in nitrogen atmosphere.

RESULTS AND DISCUSSIONS

The complex viscosity versus frequency plot for all the series of nanocomposites are shown in Fig. 1. The complex viscosity increases with increase in filler content in all the four composites series. The increase in complex viscosity was more pronounced in for PC1/MWCNT and PC2/MWCNT compared to PC3/MWCNT and PC4/MWCNT. The effect of increase in viscosity becomes less pronounced as the molecular weight of the matrix increased. The Newtonian plateau of the pure polymer in the low frequency region gradually changed to a non-Newtonian shear thinning slope for the nanocomposites with increasing MWCNT content. This effect is also varied with the molecular weight of PC of these composites. At the low frequency, the Newtonian plateau changed to a non-Newtonian shear thinning slope as increasing MWCNT content. This change was more significant for PC1 and PC2 as compared with other high molecular weight PCs.

The storage moduli of these composites are shown in Fig. 2. All the PCs except the low molecular weight PC1 show a typical

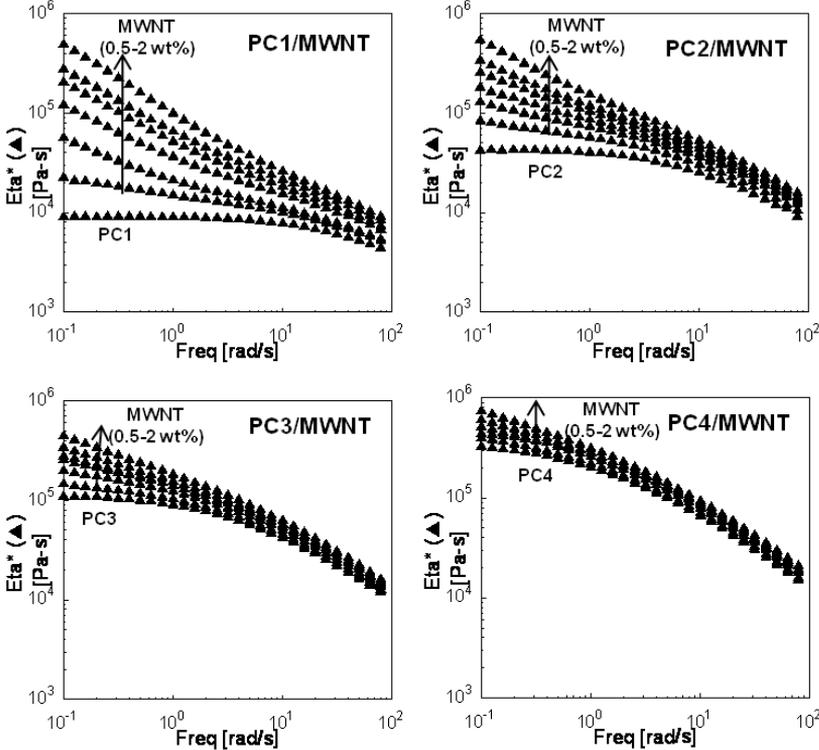


Figure 1. Complex viscosity (Eta^*) versus frequency plots for PC1/MWCNT, PC2/MWCNT, PC3/MWCNT and PC4/MWCNT composite series

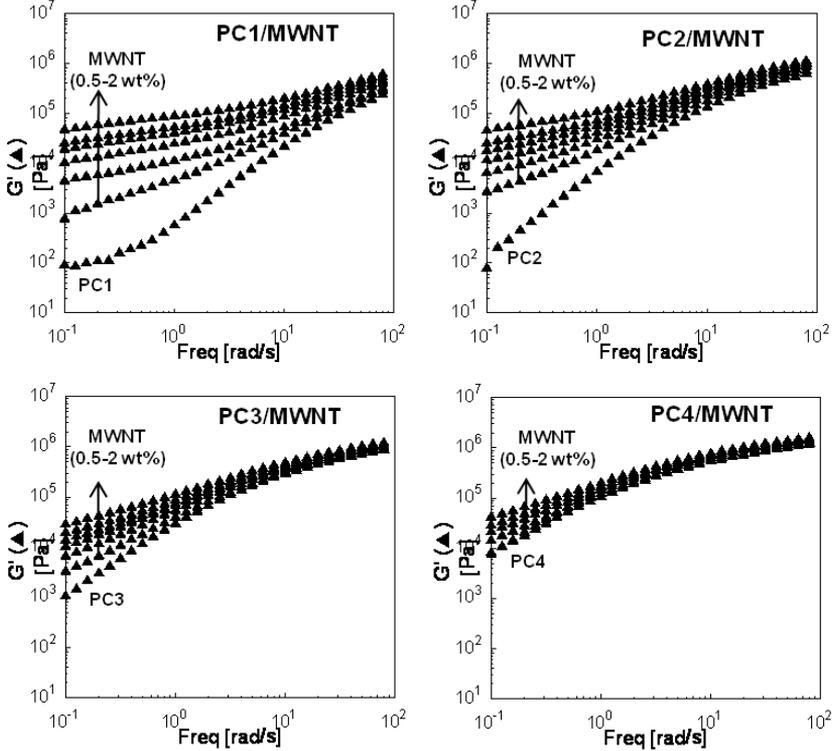


Figure 2. Storage modulus (G') versus frequency plots for PC1/MWCNT, PC2/MWCNT, PC3/MWCNT and PC4/MWCNT composite series

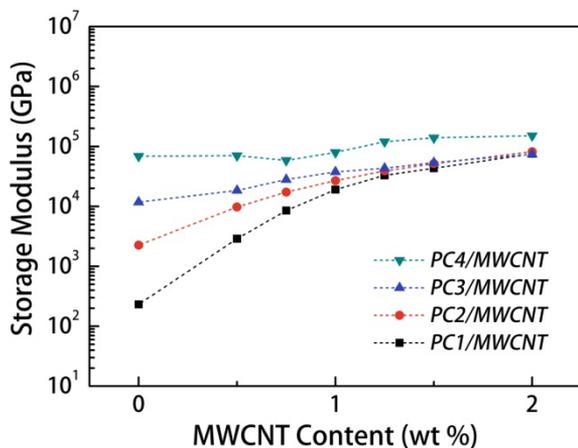


Figure 3. Storage modulus (G') versus MWCNT content plot for PC1/MWCNT, PC2/MWCNT, PC3/MWCNT and PC4/MWCNT composite series

terminal dependency ($G' \sim \omega^2$) for the fully relaxed polymer chains. But for the PC1 sample the observed terminal dependency at the low frequency is unreasonable for a pure polymer. This is attributed the error of measurement arising from low viscosity that violates a limitation of the minimum torque of the instrument.

The storage modulus increases of the composites increases with filler content and the effect was more pronounced in low molecular weight matrix, similar to the tendency observed in complex viscosity data. The terminal behaviour of the polymer changed to a pseudo-solid like plateau in PC1/MWCNT and PC2/MWCNT composites as incorporating more MWCNT into PCs. However, the low frequency plateau is not seen for PC3/MWCNT and PC4/MWCNT until adding 2 wt% of filler content.

There have been a few approaches to analyze the phenomenon by means of rheological percolation threshold defined as the onset content of nano-sized fillers that enables a sudden transition to solid-like viscoelastic behaviour. Du et al.⁵ suggested determining the threshold at a certain frequency (for example, 0.5 rad/s or 1.0 rad/s) by using a power law relation as presented in Eq. 1.

$$G' \propto (w - w_c)^\beta \quad (1)$$

where G' is the storage modulus, w is the weight fraction of nano-sized fillers, w_c is the rheological percolation threshold, and β is the power law constant. Although this power law relation is a fabulous approach to explain the rheological percolation phenomenon, it is hard to utilize this relation in the system adopted in this paper, as inferred from Fig. 3.

Storage moduli of PC/MWCNT composites at a frequency of 0.5 rad/s as a function of MWCNT content are presented in Fig. 3. All the PC/MWCNT composites show gradual increases in storage moduli as embedding more MWCNT. However, there exists no such a sudden change that deserved to be called a percolation threshold, especially in high molecular PCs.

The dominant reason that PC4/MWCNT does not show a considerable increase in storage modulus is primarily due to high storage modulus of pure PC4. For this system, it is almost impossible to apply the power law relation between storage moduli and filler content. For this reason, it is imperative to adopt another definition to determine a rheological percolation threshold when dealing with the system using different polymer matrices. The percolation threshold was herein arbitrarily determined as the weight percentage of MWCNT at which the G' versus frequency curve crossed over the G'' versus frequency curve, first at the low frequency region over 10^{-1} rad/s.

The storage modulus (G') and loss modulus (G'') of the PC1/MWCNT composites are plotted against frequency in Fig. 4. Other PC/MWCNT composites were also observed in the same way but not presented as figures in this paper. It showed the pseudo-solid like behaviour ($G' > G''$) in the low frequency region first appeared at 0.75 wt% of MWCNT and it gradually pronounced with the further increase in

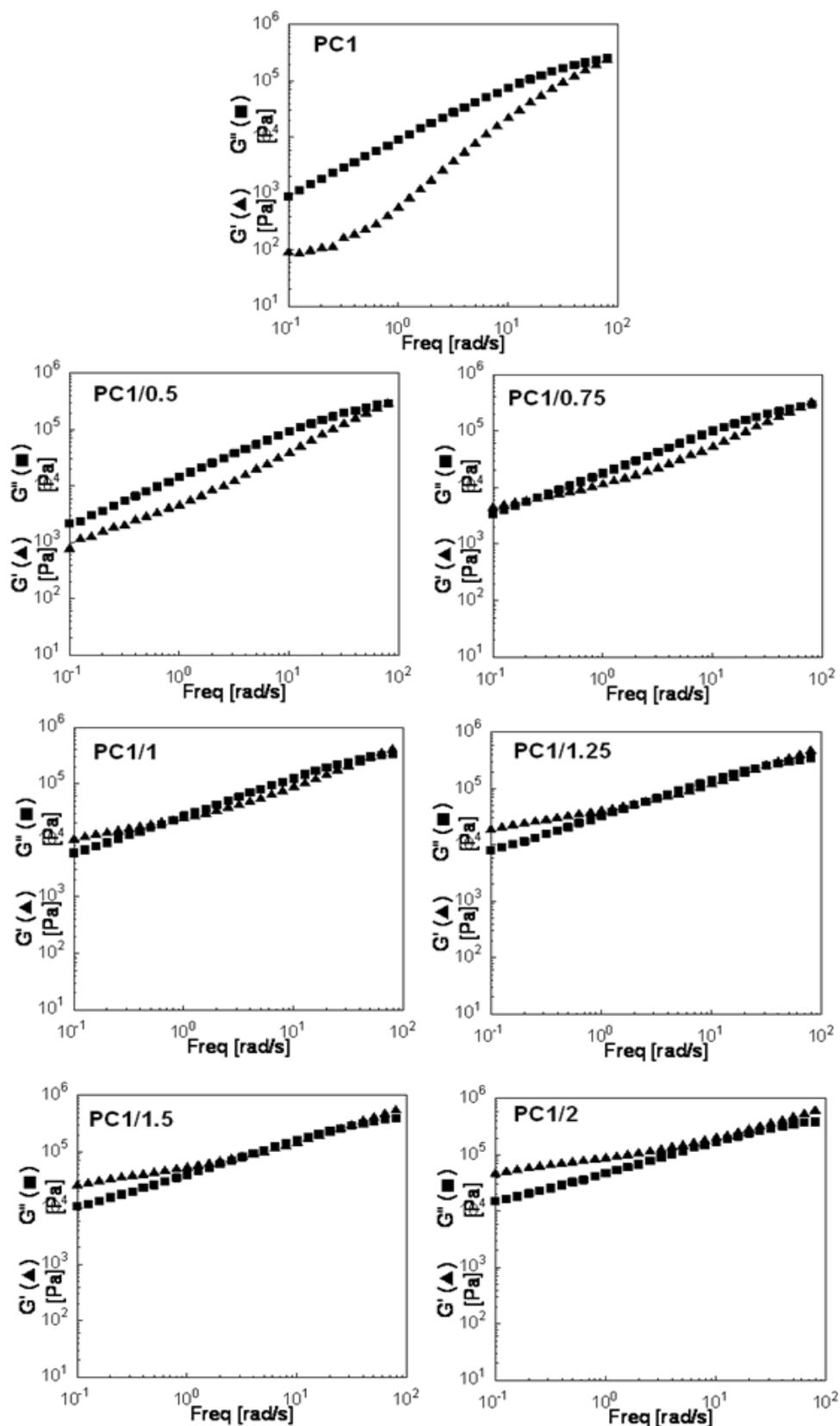


Figure 4. Plots of storage modulus (G') and loss modulus (G'') versus frequency for PC1/MWCNT composites

MWCNT content for PC1/MWCNT composites. The pseudo-solid like behaviour ($G' > G''$) occurred only at a higher filler content of MWCNT (1.25 wt%) in PC2/MWCNT while no such pseudo-solid like behaviour is seen for PC3/MWCNT and PC4/MWCNT at the MWCNT content less than 2 wt% (i.e. the rheological percolation threshold of PC3/MWCNT and PC4/MWCNT are above 2 wt%).

It is clear that the effect of MWCNT on the rheological properties varied with molecular weight of the PC matrices. This tendency is mainly attributed to the different level of rheological properties of each pure PC, varying with its molecular weight. A low molecular weight PC, for instance, has very low level of storage modulus and viscosity so that it may readily change to a pseudo-solid by adding relatively small amount (< 2 wt%) of MWCNT. Meanwhile, a high molecular weight PC has very high storage modulus and viscosity without fillers. It means it does not enable pure PC to show a rapid transition to pseudo-solid like behaviour by embedding MWCNT.

Other than this, MWCNT dispersion, the chain mobility, and relaxation behaviour of the composites are also expected to vary with the molecular weight. Therefore, the authors believe that the effect from these factors also might have contributed to the observed decrease in percolation threshold with decreasing the molecular weight of the matrix. It is similar to the decrease in percolation threshold with increasing temperature (increasing the chain relaxation) reported in other studies on polymer-nanotube composites^{4,10,11}.

CONCLUSIONS

The effect of MWCNT on the complex viscosity and storage modulus was more pronounced in the case of composites made from low molecular weight PC as compared to the high molecular weight PCs. The percolation threshold determined as the

weight percentage of MWCNT at which the G' versus frequency curve crossed over the G'' versus frequency curve in the low frequency region, was significantly varied in the composites. The percolation threshold of the composites decreased with the decrease in molecular weight of PC in the composites. This decrease in percolation threshold was primarily attributed to the different level of the rheological properties of each pure PC varying with its molecular weight. The authors believe that the increased chain mobility or relaxation behaviour of the PCs in low molecular weight PC might also have contributed to this. More studies are required to confirm the effect of chain relaxation on percolation keeping the effect of dispersion constant or isolated for these composites

REFERENCES

1. Krishnamoorti, R. and Giannelis, E.P. (1993), "Rheology of End-tethered Polymer-layered Silicate Nanocomposites", *Macromolecules*, **30**, 4097-4102.
2. Potschke, P., Fornes, T.D. and Paul, D.R. (2002), "Rheological Behavior of Multiwalled Carbon Nanotube-Polycarbonate Composites", *Polymer*, **43**, 3247-3255.
3. Ren, J., Silva, A.S. and Krishnamoorti, R. (2000), "Linear Viscoelasticity of Disordered Polystyrene-Polyisoprene Block Copolymer Based Layered-silicate Nanocomposites", *Macromolecules*, **33**, 3739-3746.
4. Pötschke, P., Abdel-Goad, M., Alig, I., Dudkin, S. and Lellinger, D. (2004), "Rheological and Dielectrical Characterization of Melt Mixed Polycarbonate-Multiwalled Carbon Nanotube Composites", *Polymer*, **45**, 8863-8870.
5. Du, F., Scogna, R.C., Zhou, W., Brand, S., Fischer, J. E. and Winey, K.

- I. (2004), "Nanotube Networks in Polymer Nanocomposites: Rheology and Electrical Conductivity", *Macromolecules*, **37**, 9048-9055.
6. Chapartegui, M., Markaide, N., Florez, S., Elizetxea, C., Fernandez, M. and Santamaría, A. (2010), "Specific Rheological and Electrical Features of Carbon Nanotube Dispersions in an Epoxy Matrix", *Comp. Sci and Technol.*, **70**, 879-884.
7. Mitchell, C.A., Bahr, J.L., Arepalli, S., Tour, J.M. and Krishnamoorti, R. (2002), "Dispersion of Functionalized Carbon Nanotubes in Polystyrene", *Macromolecules*, **35**, 8825-8830.
8. Wu, D., Wu, L., Zhou, W., Sun, Y. and Zhang, M. (2010), "Relations between the Aspect Ratio of Carbon Nanotubes and the Formation of Percolation Networks in Biodegradable Polylactide/Carbon Nanotube Composites", *J. Polym. Sci. Part B: Polym. Phy.*, **48**, 479-489.
9. Abbasi, S., Carreau, P.J. and Derdouri, A. (2010), "Flow Induced Orientation of Multiwalled Carbon Nanotubes in Polycarbonate Nanocomposites: Rheology, Conductivity and Mechanical Properties", *Polymer*, **51**, 922-935.
10. Wu, D., Wu, L., Sun, Y. and Zhang, M. (2007), "Rheological Properties and Crystallization Behavior of Multi-walled Carbon Nanotube/poly(ϵ -caprolactone) Composites", *J Polym. Sci. Part B: Polym. Phy.*, **45**, 3137-3147.
11. Abbasi, S., Carreau, P.J. and Derdouri, A., Moan, M. (2009), "Rheological Properties and Percolation in Suspensions of Multiwalled Carbon Nanotubes in Polycarbonate", *Rheol Acta*, **48**, 943-959.