Sindh Univ. Res. Jour. (Sci. Ser.) Vol.44 (1) 75-84 (2012)

SINDH UNIVERSITY RESEARCH JOURNAL (SCIENCE SERIES)

A quick review for rheological properties of polyolefin composites

A.U. CHAUDHRY, V. MITTAL AND M.I. HASHMI*

Chemical Engineering Department. The Petroleum Institute Abu Dhabi. United Arab Emirates.

*Correspondence author e-mail: cusman@pi.ac.ae (971) 056-7423183

Received 07th May 2011and Revised 2nd December 2012

Abstract: The search for alternative, cost effective and better properties' polymers is being continued to accomplish an increasing world wide demand in the field of materials. The hybridization of polymers and fillers is a quick and practical technique for development of new materials having improved properties. The discovery of nanomaterials has made possible to produce polymer composites having much lower filler concentrations with superior properties such as light weight, electrical, thermal and mechanical properties etc. Due to their high aspect ratio (surface/area ratio) and low density, they may be used as replacements for conventional fibers and fillers in polymer matrices. The following paper is a quick review for rheological properties of polyolefin composite using rheometer especially highlighted on graphene and carbon nanotubes nanocomposite

Keywords: Polyolefin, Graphene, Carbon, Nanotubes

1. INTRODUCTION

Polymer materials reinforced with nanofillers, such as layered silicate, graphite nanosheets, carbon nanotubes (CNTs), metal oxide nanoparticles .and layered titanate, have attracted much attention. Among them CNTs are ideal reinforcing fillers for a polymer matrix, because of their nanometer size, high aspect ratio and their excellent mechanical strength, and electrical and thermal conductivity (Song *et al.* 2010). The only major negative aspect of CNTs is their higher production cost. The best compensation of this factor lies in graphene sheets. **(Table 1)** gives the comparison of Tensile strength of graphene with different material (Kuilaa *et al.*, 2010).

Table 1 :Properties of Tensile strength of graphene, CNT, nanosized steel, and polymers

Materials	Tensile strength
Graphene	130 ± GPa
CNT	60-150 GPa
Nano sized steel	1769 MPa
Plastic (HDPE)	18-20 MPa
Rubber (Natural rubber)	20-30
Fiber (Kevlar)	3620 MPa

Rheological study of polymer composite plays a very vital role in order to know the complex behavior of system under stress. Polymer always showed this type of behavior due to deviation from Newtonian law of viscosity which is usually followed by normal liquids. These types of complex liquids neither follow hook's law of elasticity nor Newtonian law of viscosity but remain between them. This behavior is called viscoelastic and usually seen in polymer melts, polymer solutions and suspensions (Morrison 2001). **(Fig. 1)** classifies the different types of fluids based on behavior exhibit upon applied stress. The processing of polymers at industrial level could easily be predicted from measurement of rheological properties. This paper deals with a short overview of rheological properties of polyolefin composites.

2. Graphene and Carbon nanotubes

The allotrope of Carbon in form of carbon nanotubes were officially discovered in 1991and have exceptional potential properties such as electronic, thermal, optical, and mechanical. (Qinghua *et al.*, 2006, Thiébaud *et al.* 2010). The basic structure of carbon nanotube can be seen in fig 1 (Kim *et al.* 2010). It can be seen from the **(Fig. 1)** that single sheet of rolled graphene produces structure of single wall carbon nanotubes and in a

*Petroleum Engineering Department. The Petroleum Institute Abu Dhabi. United Arab Emirates.

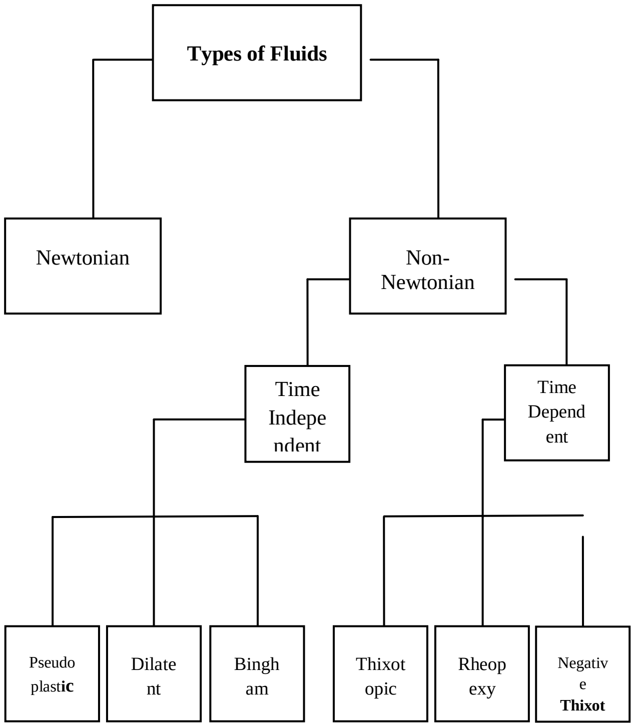

Fig 1. Classification of Fluids upon subjected to stress

analogous fashion two or more rolled graphene sheets produce multiwall carbon nanotubes. There are number of methods available to synthesis single and multiwalled carbon nanotubes including high temperature evaporation using arc-discharge (Ebbesen *et al.* 1992), laser ablation (Mittal 2010) chemical vapor deposition etc (Cheng *et al.* 1998).

The 2010 physics Nobel prize was awarded on the basis of discovery of free-standing single-layer graphene as shown in **(Fig. 2)** (Kim, *et al.* 2010).

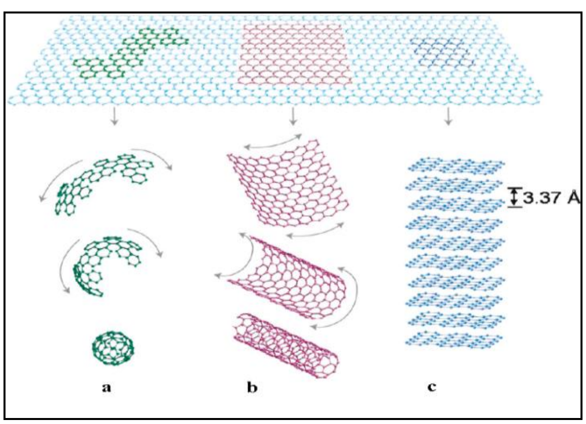

Fig 2. Graphene, the building block of all graphitic forms, can be wrapped to form (a) 0-D buckyballs (b) rolled to form the 1-D nanotubes (c) stacked to form the 3-D graphite. Reprinted with permission from reference (Kim, *et al.* 2010) Copyright 2010 American Chemical Society.

Graphene sheets are one-atom-thick two-dimensional layer of sp2-bonded carbon having a variety of remarkable properties and can enhance properties of polymers such as electrical and thermal conductivity, gas impermeability and the mechanical properties etc. It is the strongest material ever measured (Kim, *et al.* 2010).

There are many methods related to production of graphene mentioned in literature including thermal expansion of sulfuric acid-intercalated graphite, micromechanical exfoliation of graphite, chemical vapor decomposition, chemical reduction method of graphene oxide etc (Campos-Delgado *et al.*, 2008, Dixit *et al.*, 2010, Kuilaa, *et al.*, 2010, Stankovich *et al.*, 2007). The widely used method for the production of graphene is thermally expanded acid intercalated method (Kim *et al.* 2009). The parent material for graphene is graphite and excessive amount of graphite is available in nature and acceptable methods of graphene production have been invented. It would not be wrong to say that graphene is suitable to produce nanocomposites with polymers. It is cheaper and has the superior properties than CNT (Kim, *et al.*, 2010).

3 Polyolefin nanocomposites

Graphene can enhance the properties of polymers such as mechanical, thermal, gas barrier, electrical and flame retardance when in form of composites as compared to neat polymer (Ramanathan *et al.* 2008, Yanfei Xu 2009).

Interfacial bonding between the organic and inorganic phases plays significant role in improving physicochemical properties of nanocomposite (Zeng *et al.*, 2010). Graphene oxide is more attractable material rather than Pristine graphene in terms of building nanocomposite owing to the presence of hydroxyl, epooxide, diols, ketones and carboxyl functional groups which promotes the alteration of van der waals interactions and make it friendly with organic polymers (Kuilaa, *et al.*, 2010).

Polyolefin especially polyethylene and polypropylene having the largest tonnage in the world with respect to production. It is estimated that more than 60% of produced polyolefins (PE, PP) have been introduced to the market as compounds, while only about 23% of the volume of other thermoplastics have been used for compounding. The prominent properties including low cost, ability to be recycled, good processability, non-toxicity, bio-compatibility, and low production cost. These are the simplest and among the well studied polymers having wide range of applications including orthopedic implants, automobile parts, consumer goods, durable equipment and industrial machinery (Jancar 1999, Kanagaraj 2010). In case of polyethylene, there is a need to improve the properties such as stiffness, wear resistance, poor optical properties and rigidity for different applications (Incarnatoa *et al.* 2004, Jacobs *et al.* 2002, Kim, *et al.* 2009). Similarly for polypropylene, poor low-temperature impact behavior, shrinkage and relatively low stiffness are main deficiencies present in neat polymer which prohibit the replacement with other engineering polymers (Jancar 1999).

Several works using CNTs and graphene nanomaterials has been done on the enhancement of polyolefin's physical, mechanical and physicochemical properties such as elastic moduli, yield strength, fracture toughness, impact strength, creep, electrical and heat conductivity, EMI shielding capability, rheological behavior, flammability, UV stability, weathering, physical cross-linking, surface activity, adsorption characteristics and barrier (Kanagaraj 2010, Kuilaa, *et al.* 2010).

3.1 Polypropylene

The effect of multiwall carbon nanotubes on impact resistance of polypropylene was studied at a constant volume content of 1% having nanotubes with different size in length. The increment in notched charpy impact resistance was attributed to the nanotubes breakage, pullout and smaller spherulite size induced by nanotubes. (Zhang *et al.* 2007). In other work, it was showed that the tensile strength of polypropylene was slightly improved by melt mixing of silane surface improved multiwall carbon nanotubes rather than raw multiwall carbon nanotubes at about 1 wt % as shown in **(Fig. 3)** (Zhou *et al.* 2008).

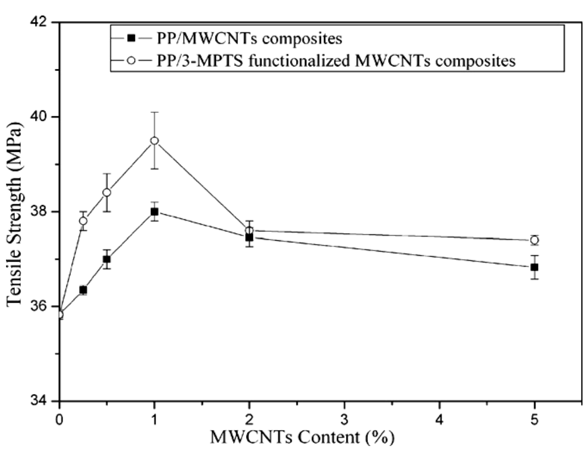

Fig 3. Effect of raw MWCNTs and 3-MPTS functionalized MWCNTs content on tensile strength of the PP composite. Reprinted from reference (Zhou, et al. 2008), Copyright (2010), with permission from Elsevier.

Similarly, melt mixed single-walled carbon nanotubes–polypropylene composites with maximum 0.75 wt% shown significantly enhanced tensile and mechanical properties and storage modulus as compared to the carbon black (Lo´pez Manchado *et al.* 2005).

The substitute of nano clay and carbon tubes having both layered structure and low cost is graphene. It is a newly discovered material and very less work on polyolefin nanocomposite has been done. In a work conducted by Kalaitzidou et. al (Kalaitzidou *et al.* 2007), using exfoliated graphite nanoplatelets of different diameters i.e. 1µm and 15 µm, it was shown that carbon black, VGCF and PAN carbon fibers and octadecylamine surface treated clays are inferior in terms of enhancing mechanical properties such as flexural strength, modulus, and impact strength of polypropylene nanocomposite. The flexural strength of both 1µm and 15µm diameter platelets reinforced PP composites increases at low concentrations up to certain amount. The better properties were seen in case of 1 µm owing to better dispersion. Similarly, Kalaitzidou *et. al.*, prepared nanocomposite polypropylene with exfoliated graphite nanoplatelets by using three different method i.e. melt mixing, polymer solution and a novel method called coating. It was observed that coating method is very much effective than solution and melt mixing method in terms of threshold percolation and other mechanical properties as shown in **(Fig. 4)** (Kalaitzidou *et al.* 2007).

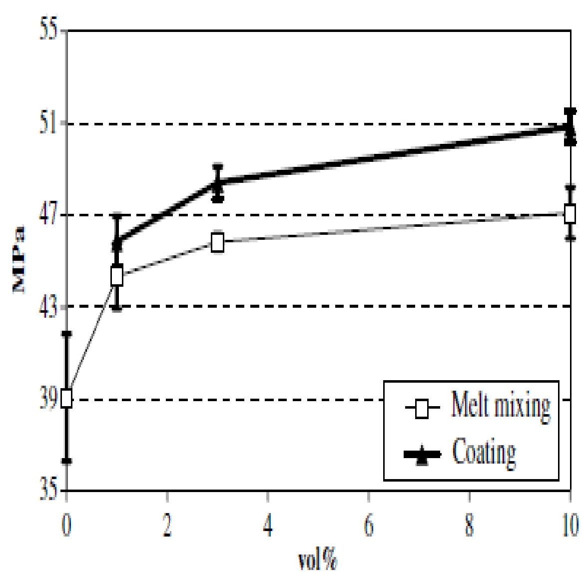

Fig 4. Effect of compounding on the flex strength of xGnP-15/PPComposites. Reprinted from reference (Kalaitzidou, *et al.* 2007) Copyright (2010), with permission from Elsevier.

The physiochemical such as thermal properties are very important for composite properties for applications such as lighting ballasts, transformer housings, microchip cooling, fuses, radiators, and barrier properties for packaging applications such as electronics, food or beverages is low permeability in small gas molecules such as O_2, CO_2 and H_2O. It was tried to reduce the coefficient of thermal expansion so that polymer could be activated thermally rather than neat one. It was seen that exfoliated graphene platelets reduce CTE in both longitudinal and transverse direction as compare to PAN and Vapor grown carbon fiber composites which mainly lessen only in direction. The superiority of exfoliated graphene platelets were also seen in barrier properties even at low loadings (Kalaitzidou *et al.* 2007)

3.2 Polyethylene

There was an attempt made to enhance the properties of HDPE, especially its stiffness, wear resistance and rigidity, CNT–HDPE composites were prepared. The effect of CNT on mechanical properties such as Young's Modulus, Ultimate Stress, and Toughness were observed in nanocomposites of HDPE and CNT dispersed by coating method followed by injection molding of samples. The composites up to 0.44% volume were prepared. It was seen that with increase in percentage of CNT the properties were also improving owing to good load transfer effect and interface link between CNT and polymer (Kanagaraj *et al.* 2007). Similarly, nanocomposite of HDPE and multi walled CNT prepared by an organic dispersant PEG which effected the improvement in mechanical properties. This phenomena was attributed to the deterioration effect of PEG on HDPE (Zou *et al.* 2004).

"A process that decreases the agglomerate size of the small component to its eventual particle size" is called *Dispersive mixing (Martin 1998).* The dispersion of nanoparticles is attractable problem for researchers. Generally it is considered that better dispersion produce better properties. In a work, different method of dispersion of exfoliated graphene in LLDP were adopted and their effect on mechanical properties were reported. The method included solution mixing and melt mixing by co-, counter- and modifified co-rotating screw system. It was observed that solution mixing showed better properties than counter rotating co- and then modified co-rotating as shown **(Fig. 5)** and also it was proved by ESEM. Along with this it was also observed that with the increment in loading of graphene mechanical properties were also improved. Similarly in the same manner, the dynamic mechanical behavior of LLDPE and graphene was

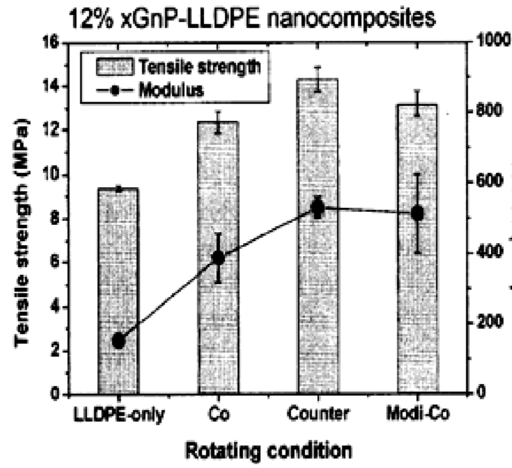

Fig 5. Tensile strength and modulus of 12% graphene/LLDP nanocomposite. (Kim *et al.* 2009) Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission

reported by the same author. It was observed that by adding 7 % wt of exfoliated graphite nanoplatelets, storage modulus was increased by 2.5 times as compared to neat LLPD (Kim*, et al.* 2009, Kim *et al.* 2009).

The discovery of nanocomposite has made possible to use lessen concentration of fillers of same chemical composition. There was comparison made between acid intercalated thermally expanded graphite with untreated graphite and it was reported that HDPE loaded with expanded graphite shown better properties such as electrical and mechanical properties at less concentration of filler rather than untreated graphite at higher concentration and in the same manner the viscosity was also increased which was endorsed to the higher surface to volume Ratio of expanded graphite (Zheng *et al.* 2004).

4. Rheological properties of Polyolefin composites

"*Polymers love shear*"(Vlachopoulos *et al.* 2003).

It is very important to know that how polymer materials respond under processing conditions because nearly all processing operations take place in the molten condition. Rheology performs as a relationship between molecular structure of polymer and processing behavior and then final end-use properties using rheological parameters i.e material functions. Some of the materials functions are viscosities, moduli, compliances, normal stresses and relaxation and retardation spectra (Brydson 1981). The measurement of material functions is called rheometry, it uses an experiment to produce defined kinematics in the definition of material functions which then make able to measure stress component needed (Morrison 2001).

Melt flow behavior tests, such as the MFR test, capillary rheometer and rotational rheometer are generally used to characterize the processibility of a material.

4.1 Using capillary rheometer

Capillary rheometer are capable to measure shear rate similar at which actual industry processes such as calandering, extrusion, injection, transfer molding etc occurred (Sholley 1985). It was observed in a work that rheological data from a capillary rheometer of polymers is appropriate to extruder (Klyosov 2007).The main advantage of capillary rheometers having similarity in flows just like to pipes and extrusion dies. Capillary rheometres are only adequate means of attaining data at shear rates greater than 10 s^{-1}. They are pressure driven and simple devices are capable to give accurate viscosity measurement (Macosko 1994)

The rheological properties of polymers have great influence on the processing such as injection molding and extrusion. The study of the melt flow properties of filled polymer systems is important to study the mechanism by which addition of fillers to polymers influences the original polymer and to determine those combinations in which such effects occur. These studies can then be utilized to establish better processing conditions and to develop optimum morphology to maximize products performance (Babbar *et al.* 1994). The viscoelasticity of polymer dictates that polymers have complex shear modulus i.e. elastic and viscous behavior. It was reported that generally nanofiller loading leads to increases in the shear viscosity (Song, *et al.* 2010).

In a paper (Yang *et al.* 2005) which describes the effect of filler size, filler ratio and composite preparation on apparent viscosity of isotactic polypropylene/ glass bead composite using capillary rheometer. The power law was used to describe the effect of apparent viscosity on filler content. It was shown that there was significant increment in apparent viscosity after adding 15 % wt of filler and after that it showed sudden drop of viscosity upon adding 30 % wt of filler as shown in **(Fig. 6)**.

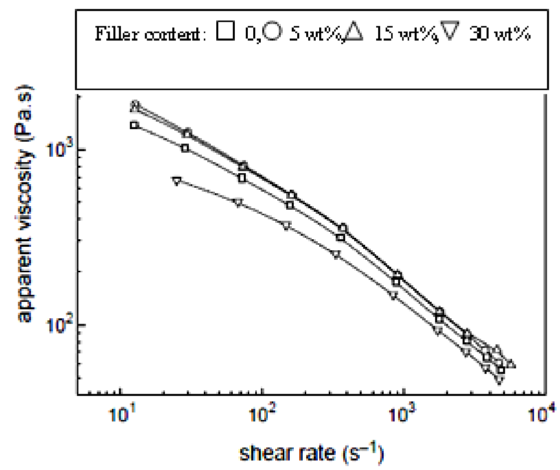

Fig 6. Flow properties of polypropylene composites filled with glass bead of different content (the size of the filled glass bead is 0.71 mm) at 230 °C. Reprinted from reference (Yang, *et al.* 2005) Copyright (2010), with permission from Elsevier.

Die swell and entry pressure losses play an important role during extrusion of polymeric materials. It effects the final size and shape of the extrudate and consequently helpful for die design and process control during extrusion. The addition of filler could reduce the extrudate swell. It was observed during the processing of propylene/glass bead composite using capillary rheometer that with the increase in volume fraction of filler die swell was decreasing nonlinearly but there was insignificant effect on entry pressure as shown in **(Fig. 7)** (Liang 2002). This effect was attributed towards the restriction of movement of molecular chains hence preventing the elastic recovery of the shear deformation.

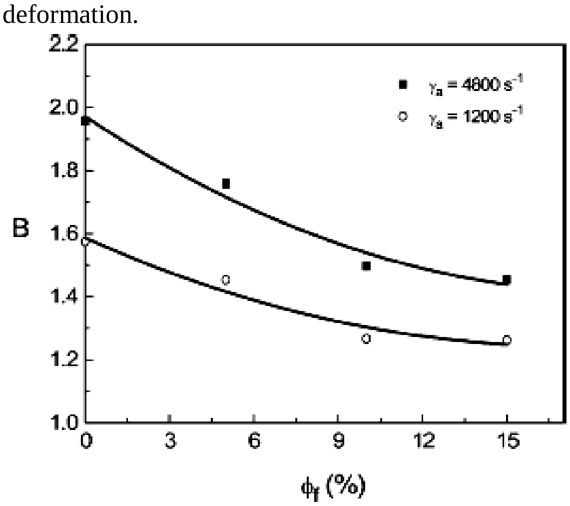

Fig 7. *B* as a function of filler fraction. Reprinted from reference (Liang 2002) Copyright (2010),with permission from Elsevier.

Similarly, in another paper, no significant changes were observed in shear viscosity and shear stress with addition of nanoclay (1 and 2%) to polypropylene at different shear rates (50 to 10000 sec^{-1}). However, the power law index (n) indicates that the polymer melt becomes less shear thinning with increasing nanoclay loading (Dixit, *et al.* 2010).

The dependence of composite viscosity on fiber loading and fiber length at lower shear rate than at higher shear rate were observed in composites of pineapple fiber reinforced low density polyethylene. It was shown that increasing the fiber loading leads the increment in viscosity and in case of improved interfacial adhesion achieved by treating fibers with different materials also increase the viscosity of the system as shown in **(Fig. 8)**. This phenomena was attributed to the fiber-matrix interaction (George *et al.* 1996).

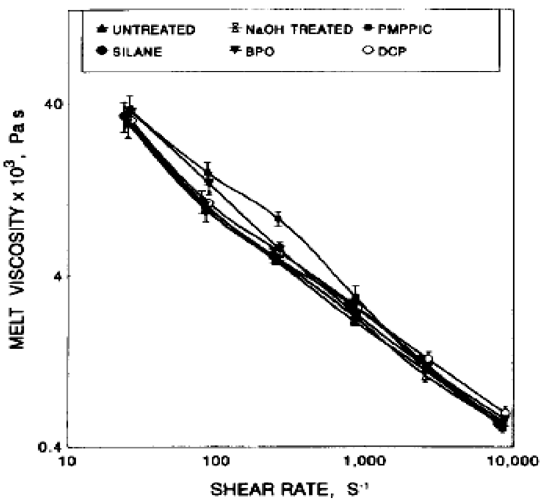

Fig 8. Variation of melt viscosity with shear rate of PALF LDPE composites for different fibre treatments. Fibre length 6mm and temperature 125°C. Reprinted from reference (George, *et al.* 1996) Copyright (2010), with permission from Elsevier.

It is very important to take an account of melt flow instabilities for the processing of commodity polymers such as polyolefin. Commonly, three types of melt instabilities i.e. sharkskin, spurt and gross melt fracture are shear rate and polymer microstructure dependent. Nano materials such as CNTs at lower loading than conventional fillers could be used to reduce the effect of above mentioned instabilities in polymers processing. During a research work on CNTs nanocomposite with two types of polyethylene i.e. LHDPE with low amount of long chain polyethylene and PE ethylene copolymer with 1-octene short chain branching, the effect of ratio of Single wall CNT and multiwalled CNT on melt instabilities was observed with help of novel capillary rheometer having three high sensitive pressure transducer inside the slit. Overall It was shown that the addition of fillers improves the melt stabilities of polymer melts (Palza *et al.* 2010). Similarly in a paper related to MWCNT/polypropylene nanocomposite, the processing behaviour of these nanocomposite were seen at the conditions analogues to injection moulding and extrusion process at industry level i.e. 10^2 to 10^4 shear rate range. It was reported that the viscosity of composite was decreased adding 1 phr MWCNT attributed to the flow favoring orientation by CNTs as shown in **(Fig. 9)**. It was also observed that beyond this ratio the melt viscosity was increased with the increasing of the MWCNT content owing to the increased MWCNT–MWCNT interaction(Chih-Chun *et al.* 2008).

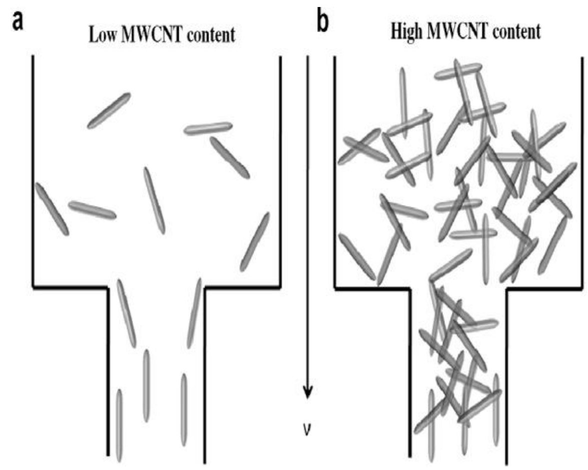

Fig 9. The flow model proposed showing the flow of MWCNT/PP composite by adding various MWCNT contents in capillary rheometer. Reprinted from reference (Teng *et al.* 2008) Copyright (2010),with permission from Elsevier.

4.2 Using rotational rheometer

In general, rotational rheometer are used to measure the rheological properties with the shear rate range around 1–10^2 s^{-1} and along with shear moduli i.e. storage modulus G' and loss modulus G''. These moduli are useful for calculating service properties of a polymer (Teng *et al.* 2008). This type of rheometer usually deal with the shearing of polymer melt between the rotating plates and torque is measured across the shear stress (Brydson 1981). Seo et al. studied the effect of multiwalled carbon nanotubes ratio on complex viscosity with polypropylene composite. It was observed that with an increase in ratio of nanotubes, complex viscosity was also increased. This effect was significant at lower frequency and become weaken at higher frequency owing to shear thinning. Similar effect was also seen in case of storage and loss modulus (Min-Kang *et al.* 2004). Rheological properties can be used to ensure the dispersion of reinforcement as these are sensitive to the structure, particle size, shape and surface properties of the dispersed phase (Prashantha *et al.* 2008). The major problem associated with CNTs is their dispersion in host matrix. Many work have been to done to study the effect of different treatment on dispersion of CNTs. Zhang et al. studied the effect of dispersion of SWCNTs in high density polyethylene by treating SWCNTs with 2% sodium dodecylsulfate as a surfactant and sprinkled this aqueous suspension on polymer powder followed by extrusion. It was reported that surfactant treated SWCNTs have insignificant influence on complex viscosity of composite (Zhang *et al.* 2006). Similar observations were seen in case of SWCNTs and ultrahigh molecular weight polyethylene composites (Qinghua, *et al.* 2006). In another work where low density polyethylene was used with MWCNTs as reinforcement, the composite steady state viscosity rapidly decreased with increase in shear rate at higher content on carbon i.e. up to 10%. It was also observed that with the increment of nanotubes ratio system became more elastic as tan delta peak diminished (Xiao *et al.* 2007). Using expanded graphite and unexpanded graphite with high density polyethylene, it was reported that with increase in surface area in case of expanded graphite, increment in viscosity was seen. This behavior was attributed towards the deformation hindrance owing to the enhancement in intercalation between HDPE and expanded graphite (Zheng, *et al.* 2004).

1. CONCLUSION

Graphene and carbon nanotubes are remarkable materials for making nanocomposite with polyolefin to enhance their properties. There is a need to improve the dispersion and interfacial adhesion of the materials so that even better properties could be attained. There are many methods available e.g. solution mixing, melt mixing, in situ polymerization and coating method. Although solution method has shown better results but presence of solvent is a major obstacle. Melt and in situ polymerization are preferable. Capillary rheometer has industrial importance and the rheological properties are important for processing and mostly depend on many factors such as filler concentration, filler-filler interaction and filler-polymer interaction, filler dispersion, orientation and size etc. Rotational rheometers are useful for measuring service properties of polymers. Different routes could be used to enhance theses interactions and there effect on rheological properties could be studied using capillary and rotational rheometer. The factors such as die swell, viscosity increment, melt instabilities, optimization of shear rate and stress must be explain for graphene based nanocomposite of polyolefin.

REFERENCES:

Babbar, I. and G.N. Mathur, (1994) Rheological properties of blends of polycarbonate with poly(acrylonitrile-butadiene-styrene). Polymer. 35 **(12):** 2631–2635.

Brydson, J. A., (1981) Flow properties of polymer melts. 2nd Edition, Godwin in association with the Plastics and Rubber Institute, London.

Campos-Delgado, J., J. M. Romo-Herrera, J. Xiaoting, A.C. David, M. Hiroyuki, A. K. Yoong, H. Takuya, R. Zhifeng, J.S. David, O. Yu, O. Tomonori, K. Hirofumi, K. Katsumi, E. Morinobu, T. Humberto, S. D. Mildred and T. Mauricio, (2008) Bulk Production of a New Form of sp2 Carbon: Crystalline Graphene Nanoribbons. Nano Letter. 8 **(9):** 2773-2778.

Cheng, H.M. , F. Li, G. Su, H.Y. Pan, L.L. He, X. Sun and M.S. Dresselhaus, (1998) Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbons. Applied Physics Letters. 72 **(25):** 3282-3284.

Chih-Chun, T., Chen-Chi. M. M. Yen-Wei. H. Siu-Ming. Y. Cheng-Chih. W. Cheng-Ho. C. and Shun-Fua. S. (2008) Effect of MWCNT content on rheological and dynamic mechanical properties of multiwalled carbon nanotube/polypropylene composites. Composites: Part A : Applied Science and Manufacturing 39 **(12):** 1869–1875.

Dixit, T., V. Das, V. Nigam and A. K. Pandeyb, (2010) Effect of Shear Rate and Nanoclay Content on the Die Swell of Polypropylene Nanocomposites Extruded Under Capillary Flow. "International Conference On Advanced Nanomaterials And Nanotechnology, AIP Conf. Proc., (Giri, P. K. , eds.) 288-293.

Ebbesen, T.W. and P.M. Ajayan, (1992) Large-scale synthesis of carbon nanotubes. Nature nanotechnology. **(358):** 220-222.

George, J., R. Janardhan, J. S. Anand, S. S. Bhagawan, V. Sarabhai and S. Thomas, (1996) Melt rheological behaviour of short pineapple fibre reinforced low density polyethylene composites. Polymer. 37 **(24):** 5421 5431.

Incarnatoa, L., P. Scarfatoa, L. Scatteiab and D. Acierno, (2004) Rheological behavior of new melt compounded copolyamide nanocomposites. Polymer. 45 **(10):** 3487–3496.

Jacobs, O., M. Kazancib, D. Cohnb and G. Marom, (2002) Creep and wear behaviour of ethylene–butene copolymers reinforced by ultra-high molecular weight polyethylene fibres. Wear. 253 **(5):** 618-625.

Jancar, Josef, (1999) Structure-Property Relationships in Thermoplastic Matrices. in Mineral Fillers in Thermoplastics I Raw Materials and Processing. Springer-Verlag Berlin Heidelberg New York, 57Pp.

Kalaitzidou, K., H. Fukushima and Lawrence T. D., (2007) Multifunctional polypropylene composites producedby incorporation of exfoliated graphite nanoplatelets. Carbon. 45 **(7):** 1446–1452.

Kalaitzidou, K., H. Fukushima and Lawrence T. D., (2007) A new compounding method for exfoliated graphite–polypropylene nanocomposites with enhanced flexural properties and lower percolation threshold. Composites Science and Technology. 67 **(10):** 2045–2051.

Kalaitzidou, K., H. Fukushima and T. D. Lawrence, (2007) Mechanical properties and morphological characterization of exfoliated graphite–polypropylene nanocomposites. Composites: Part A. 38 **(4):** 1675–1682.

Kanagaraj, S., (2010) Polyethylene Nanotube Nanocomposites. in Polymer Nanotube Nanocomposites Synthesis, Properties, and Applications. Scrivener Publishing LLC, USA, 113-136.

Kanagaraj, S., R. V. Fa´tima, V. Z. Tatiana, S.A.O. Mo´nica and Jose´ A.O.S., (2007) Mechanical properties of high density polyethylene/carbon nanotube composites. Composites Science and Technology. 67 **(16):** 3071–3077.

Kim, H., A. A. Abdala and C.W. Macosko, (2010) Graphene/Polymer Nanocomposites. Macromolecules. 43 **(16):** 6515–6530.

Kim, S., I. Do and L.T. Drzal, (2009) Multifunctional xGnP/LLDPE nanocomposites prepared by solution compounding using various screw rotating systems. Macromolecular Material Engineering 294 **(3):** 196-205.

Kim, S., I. Do and L.T. Drzal, (2009) Multifunctional xGnP/LLDPE nanocomposites prepared by solution compounding using various screw rotating systems. Macromolecular Material Engineering. 294 **(3):** 196-205.

Kim, S., I. Do and L.T. Drzal, (2009) Thermal stability and dynamic mechanical behavior of exfoliated graphite nanoplatelets-LLDPE nanocomposites. Polymer Composites. 31 **(5):** 755–61.

Klyosov, Anatole A., (2007) Wood-plastic composites John Wiley and sons Inc., 643Pp.

Kuilaa, Tapas, B. Sambhu, Y. Dahu, N.H. Kim, B. Saswata and L. Joong Hee, (2010) Recent advances in graphene based polymer composites. Progress in polymer Composite. 35 **(11):** 1350-1375 .

Liang, Ji-Z., (2002) The melt elastic behavior of polypropylene/glass bead composites in capillary flow. Polymer Testing 21 **(8):** 927–931.

Liang, Ji-Z., (2002) The melt elastic behavior of polypropylene/glass bead composites in capillary flow. Polymer Testing. 21 **(8)**: 927–931.

Lo´pez Manchado, M.A. , L. Valentini, J. Biagiotti and J.M. Kenny, (2005) Thermal and mechanical properties of single-walled carbon nanotubes–polypropylene composites prepared by melt processing. Carbon. 43 **(7):** 1499–1505.

Macosko, C.W., (1994) Rheology: Principles, Measurements and Applications. Wiley-VCH, inc. New York, 238Pp.

Martin, G., (1998) Compounding with Single-Screw Extruders. Advances in Polymer Technology. **16** (4): 251–262.

Min-Kang, S. and P. Soo-Jin, (2004) Electrical resistivity and rheological behaviors of carbon nanotubes-filled polypropylene composites. Chemical Physics Letters 395 **(1-3):** 44–48.

Mittal, Vikas, (2010) Carbon Nanotubes: An Introduction. in Polymer Nanotube Nanocomposites Synthesis, Properties, and Applications. Scrivener Publishing LLC, USA, 1-12.

Morrison, F.A., (2001) Understanding Rheology. Oxford University Press, Inc. New york, 382Pp.

Palza, H., B. Reznik, M. Kappes, F. Hennrich, I.F.C. Naue and M. Wilhelm, (2010) Characterization of melt flow instabilities in polyethylene/carbon nanotube composites. Polymer. 51 **(16):** 3753-3761.

Prashantha, K., J. Soulestin, M. F. Lacrampe, M. Claes, G. Dupin and P. Krawczak, (2008) Multi-walled carbon nanotube filled polypropylene nanocomposites based on masterbatch route: Improvement of dispersion and mechanical properties through PP-g-MA addition. Polymer Letters. 2 **(10)**: 735–745.

Qinghua, Z., R.L. Dirk and R. Sanjay, (2006) Dispersion and Rheological Aspects of SWNTs in Ultrahigh Molecular Weight Polyethylene. Macromolecules 39 **(2):** 658-666.

Ramanathan, T. , A. A. Abdala, S. Stankovich, D. A. Dikin, M. Herrera-Alonso, R. D. Piner, D. H. Adamson, H. C. Schniepp, D. Chen, R. S. Ruoff, S. T. Nguyen, I. A. Aksay, R. K. Prud'homme and L. C. Brinson, (2008) Functionalized graphene sheets for polymer nanocomposites. Nature Nanotechnology. 3 **(210):** 1247-1254.

Sholley, Charlene K., (1985) Use of the Automatic capillary rheometer in quality control. in Quality Assurance of Polymeric Materials and Products. American society for testing and materials STP **(846):** 73Pp.

Song, M. and J. Jin, (2010) Rheological Behavior of Polymer Nanocomposites. in Optimization of Polymer Nanocomposite Properties. Wiley-Vch Verlag GmbH and Co Kgaa, Weinheim, 93-119.

Stankovich, S., A.D. Dmitriy, D. P. Richard, A. K. Kevin, K Alfred, J. Yuanyuan, W. Yue, T. N. SonBinh and S.R. Rodney, (2007) Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon. 45 **(7):** 1558–1565.

Teng, Chih-Chun, Chen-Chi M. Ma, Yen-Wei Huang, Siu-Ming Yuen, Cheng-Chih Wenga, Cheng-Ho Che and B. Shun-Fua Su (2008) Effect of MWCNT content on rheological and dynamic mechanical properties of multiwalled carbon nanotube/polypropylene composites. Composites: Part A: Applied Science and Manufacturing **(39):** 1869–1875.

Teng, Chih-Chun, Chen-Chi M. Ma, Yen-Wei Huang, Siu-Ming Yuen, Cheng-Chih Wenga, Cheng-Ho Che and Shun-Fua Su b, (2008) Effect of MWCNT content on rheological and dynamic mechanical properties of multiwalled carbon nanotube/polypropylene composites. Composites: Part A: Applied Science and Manufacturing. **(39):** 1869–1875.

Thiébaud, F. and J.C. Gelin, (2010) Characterization of rheological behaviors of polypropylene/carbon nanotubes composites and modeling their flow in a twin-screw mixer. Composites Science and Technology. 70 **(4):** 647–656.

Xiao, K.Q., L.C. Zhang and I. Zarudi, (2007) Mechanical and rheological properties of carbon nanotube-reinforced polyethylene composites. Composites Science and Technology. 67 **(2):** 177–182.

Yanfei X., Y. Wang, J. Liang, Y. Huang, Y. M. Xiangjian Wan, Y. Chen, (2009) A Hybrid Material of Graphene and Poly (3,4-ethyldioxythiophene) with High Conductivity, Flexibility, and Transparency. Nano Research. **(2):** 343-348.

Yang, W., L. Zheng-Ying, S. Gui-Fang, L. Zhong-Ming, X. Xie and Y. Ming-Bo, (2005) Study on the melt flow behavior of glass bead filled polypropylene. Polymer Testing. 24 **(4):** 490-497.

Zeng, Q. and A. Yu, (2010) Prediction of the Mechanical Properties of Nanocomposites. in Optimization of Polymer Nanocomposite Properties. WILEY-VCH Verlag GmbH and Co. KGaA, Weinheim, 323Pp.

Zhang, H. and Z. Zhang, (2007) Impact behaviour of polypropylene filled with multi-walled carbon nanotubes. European Polymer Journal Macromolecular Nanotechnology. **(43):** 3197–3207.

Zhang, Q., S. Rastogi, D. Chen, D. Lippits and P. J. Lemstra, (2006) Low percolation threshold in single-walled carbon nanotube/high density polyethylene composites prepared by melt processing technique. Carbon. **(44):** 778–785.

Zheng, W., X. Lu and S.C. Wong, (2004) Electrical and mechanical properties of expanded graphite-reinforced high-density polyethylene. Journal of Applied Polymer Science. 91 **(5):** 2781–2788.

Zhou, Z., S. Wang, L. Lu, Y. Zhang and Y. Zhang, (2008) Functionalization of multi-wall carbon nanotubes with silane and its reinforcement on polypropylene composites. Composites Science and Technology. **(68):** 1727–1733.

Zou, Y., Y. Feng, L. Wang and X. Liu, (2004) Processing and properties of MWNT/HDPE composites. Carbon. **(42):** 271–277.

.