

SOME TENSILE PROPERTIES OF UNSATURATED POLYESTER RESIN REINFORCED WITH VARYING VOLUME FRACTIONS OF CARBON BLACK NANOPARTICLES

By

C.S. Obayi+, A.O. Odukwe+, D.O.N. Obikwelu*

+Department of Mechanical Engineering, University of Nigeria, Nsukka.

*Department of Materials and Metallurgical Engineering, University of Nigeria, Nsukka

+camilus.obayi@unn.edu.ng, daniel.obikwelu@unn.edu.ng

ABSTRACT

The recent emergence of nano science and nano technology has added another dimension to the staple of the modern composite technology. Instead of micron diameter fibres and particles, nano particles are being incorporated into polymer matrices to form a composite blend known as polymer nano composites (PNCs). This study investigated the tensile response of polyester composites reinforced with petroleum-based carbon black (CB) nano particles. The composites were prepared with 1 to 11% volume fractions of carbon black nanoparticles using manual and machine dispersion methods. Tensile samples of $165 \times 19.5 \times 3.2 \text{ mm}^3$ prepared using ASTM D638 Standard were tested in a Hounsfield (Monsato) testing unit. Results showed that tensile strength, percentage elongation and tensile toughness at fracture increased as the volume fractions of carbon black nanoparticles increased from 1% to 5% in both manual and machine prepared composites. It is important to note that the maximum tensile strength and percentage elongation at fracture occurred at 5% carbon black and as the volume fraction increased above this, tensile strength and elongation at fracture decreased. The machine mixed composite showed the highest improvement in the above tensile properties at this low volume fraction. The tensile modulus of manual mixed composite decreased as CB volume fraction increased. In contrast, modulus of machine mixed composite was constant from 1% to 5% but increased as volume fractions increased from 7% to 11%. The above findings corroborated earlier findings in previous works which noted that nanocomposites have advantage over micro composites at low volume fractions especially with better dispersion of nanoparticulates in polymer matrices.

Key words: Polyester; Carbon black; Nanoparticles; Volume fraction; Tensile properties.

1.0 INTRODUCTION

For ages, polymers were reinforced with a variety of micron scale particles to form polymer micro composites. These particles which include silicates (mica, talc, silica and fibre glass), metal oxides (titania, alumina), calcium carbonate and carbon black (CB), were successfully used as additives or reinforcements to improve various properties of polymers [1]. At the particle volume fractions, on the order of 15-40% [2], the conventional composites ordinarily improved rigidity, but they

sacrificed strength, elongation and toughness [1].

The recent emergence of nano science and nano technology has enabled the production of nanoscale particles and hence added another dimension to the staple of modern composite technology. It has also enabled the re-evaluation of the traditional nanosized particles such as carbon black and fumed silica and their uses as reinforcing phases in polymer nanocomposites (PNCs) [2]. PNCs are materials in which nanoscopic particles,

typically 1-100 nanometres (nm) in at least one dimension, are dispersed in an organic polymer matrix in order to improve the performance properties of the polymer.

Nanoscale particles or nanoparticles possess extremely small feature size (1-100 nm), high aspect ratio and high surface to volume ratio. As a result they exhibit remarkable physical, chemical, electrical, optical and even thermodynamic properties [3, 4, 5].

The latest technique in harnessing the extra-ordinary behaviour of nanoscale particles is to disperse individual particles completely in the polymer matrices. This configuration optimizes the number of available reinforcing particles and the bonding between the particles and polymer matrix. It also maximizes the amount of particle surface and hence the area available for interaction with the polymer leading to large improvement in physical and mechanical properties. Literature survey shows that these improvements are achieved with less than 10% volume additions of nanoscale particles (typically on the order of 1% to 5% for layered silicates and carbon nanotubes), which is in sharp contrast to conventional polymer fillers [2].

It was observed that complete dispersion was one of the fundamental challenges surrounding the development of PNCs because there were strong cohesive and van der Waals interactions at the nanoscale resulting in the tendency of the nanoscale particles to agglomerate [2, 6]. Another important challenging aspect of dispersing nanoparticles in polymers was the characterization of the particles and

their state of dispersion in PNCs [6]. Obikwelu [7] noted that these challenges were real but local researchers on Nanotechnology should not be deterred but should explore and benefit from this technological frontier of the 21st century.

In recent years, the successful use of nanoscale particles in PNCs enabled new combinations of mechanical, electrical, magnetic, optical, chemical and surface properties and their applications in many industries such as automotive, electronics, packaging, aerospace, information, pharmaceuticals, biomedical, energy, sports goods and personal care. Recent market surveys have estimated global consumption of PNCs at tens of millions of pounds, with a potential annual average growth rate of 24%, to almost 100 million pounds (45.4x10⁶ KG) in 2011, at a value exceeding 500-800 million dollars [2].

Carbon black is essentially elemental carbon in the form of extremely fine particles having a partially amorphous molecular structure. It is classified as aggregated traditional particle with nanoscopic dimension (1-100 nm) and high electrical conductivity but low aspect ratio [2]. Carbon black is among the nanoscale particles produced in commercial (tonne) quantities [4]. Depending on the method of production, average primary particle diameters in several commercially produced carbon blacks range from 10-500 nm, while average primary aggregate diameters range from 100-800 nm [8, 9, 10].

Carbon black was one of the long established nanotechnology applications and nanomaterial used to modify the

mechanical, electrical and other physical properties of polymers [4, 11]. Freedonia Research Group report [12], showed that carbon black was the dominant nano powder and in 2005 alone carbon black constituted the only nanomaterial for conductive applications.

2.0 OBJECTIVE OF THE STUDY

The objective of this work was to investigate the monotonic tensile properties of carbon black reinforced polyester, especially at low volume fractions of carbon black nanoparticles. This work is an attempt at nanostructure fabrication and to get into the mainstream of the technological frontiers of the 21st century.

3.
0
M



Fig. 3.1: Electron micrograph of a reinforcing grade carbon black (N330)

The matrix material used in this study was three-component unsaturated polyester resin system purchased from Nycil Nigeria Limited, Ikeja, Nigeria.. It consisted of polyester resin, catalyst [methyl ethyl ketone peroxide (MEKP) - Butanox HBO-50] and accelerator (cobalt), mixed in proportions of 64:2:1 respectively. The mould release agent was petroleum jelly (Vaseline) dissolved in paint thinner

ATERIALS AND METHODS

3.1 Materials

The carbon black used in this study was obtained from the Carbon Black Plant of Warri Refinery and Petrochemical Company Limited, Warri, Delta State of Nigeria. The carbon black was an already characterized nanoparticle in pellet form and of ASTM N330 grade. Figure 3.1 below shows the electron micrograph of a reinforcing grade carbon black (N330) while figure 3.2 is the same image obtained by numerical simulation [13].

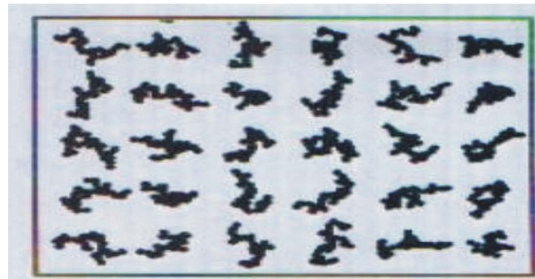


Fig. 3.2: Aggregates obtained by numerical simulation

(made by Henry Vester Ltd, Lagos, Nigeria).

3.2 METHODS

3.2.1 Composite Fabrication

Wooden mould, electric motor and stainless steel impeller blade, James Harris type [14] were used to disperse the carbon black particles and cast the tensile samples. The carbon black was dried in an electric oven

at a temperature of 200°C for 12 hours in the Solid State Laboratory of the Department of Physics and Astronomy, University of Nigeria, Nsukka. Volume fractions of unsaturated polyester resin, catalyst, accelerator and carbon black were measured out for compounding/mixing. Prior to the measuring out of the volume fractions of the constituents, the dried and pelletized carbon black were fractured or de-pelletized using a spatula.

Manual and Machine mixing methods were used for the composite preparation. Prior to mixing, cobalt accelerator was added to the unsaturated polyester resin and the moulds were uniformly rubbed with mould release agent and dried. The composites were prepared with 1, 3, 5, 7, 9, 11% volume fractions of carbon black. Tensile samples were cast with the moulds.

3.2.2 Manual Mixing

Carbon black was added carefully and gradually to the solution of pre-accelerated polyester resin to avoid the loss of carbon black. The composite mixture was stirred and observed to ensure that the carbon black mixed well with the matrix or until a homogeneous mixture was obtained. Measured volume of catalyst (MEKP) was added and stirred for 5 minutes. The mixture was cast in a wooden mould prepared according the ASTM standard D 638 and allowed to cure. The cured composite was later demoulded. The above procedure was followed in preparing the composites at the specified volume fractions of carbon black.

3.2.3 Machine Mixing

The same procedure was followed as in the manual mixing except that the initial mixing of the pre-accelerated polyester resin and carbon black was done with a motorized stirrer. The mixture was stirred at an impeller speed of 1200 r.p.m for 15 minutes. The impeller speed was less than the speed of 1780 r.p.m used in an earlier work by James Harris [14]. This was followed by addition of measured volume of catalyst and manual stirring of the mixture for 5 minutes, pouring of the mixture into the mould and allowing it to cure. This procedure was repeated for different volume fractions of carbon black.

3.3 TENSILE TESTING OF THE COMPOSITE SAMPLES

The cured polyester- carbon black composites were cut into tensile samples according to the ASTM standard D 638 for further analysis and studies. The tensile test pieces were parallel-sided strips, 165mm long, 19.5mm wide and 3.2mm thick. A minimum of ten samples were tested in each case and the tests were carried out several days after curing. Hounsfield (Monsanto) Tensometer (serial no: 8889) was used in performing the tensile tests.

4.0 RESULTS AND DISCUSSION RESULTS

4.1

The test values presented below were averages. For each volume fraction, ten samples were tested. Figures 4.1-4.4 show the values and graphs of the tensile strength, tensile modulus, percentage elongation at fracture and tensile toughness of the manual and machine mixed

composites versus the carbon black volume fractions.

Fig.4.1:Tensile Strength vs CB Volume Fraction

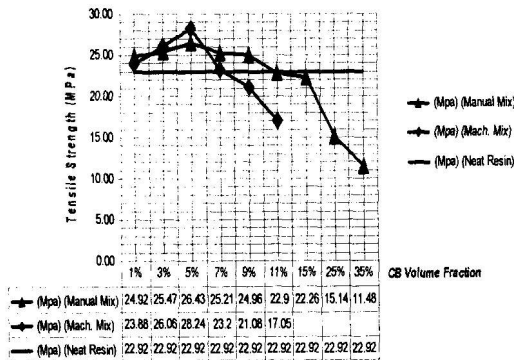


Fig.4.2:Tensile Modulus vs CB Volume Fraction

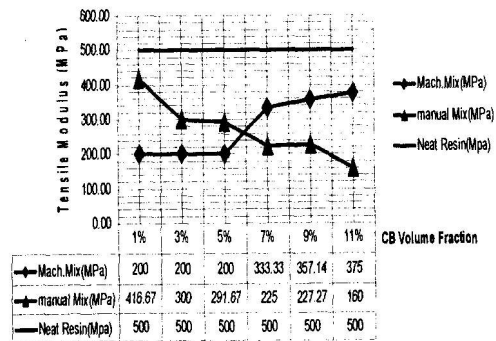


Fig. 4.3:

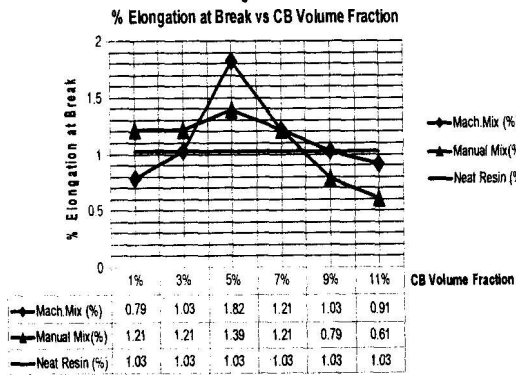
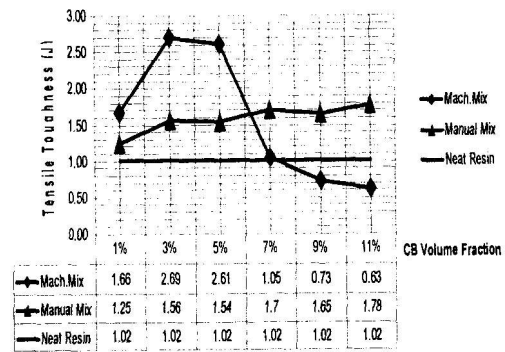


Fig.4.4: Tensile Toughness vs CB Volume Fraction



4.2 DISCUSSION

Figure 4.1 shows the graph of tensile strength of the composites at different volume fractions of carbon black. Results showed that the tensile strength increased as the volume fractions increased from 1 to 5%, but decreased as the volume fraction increased beyond 5%. However, the tensile strength of the cast neat resin was lower compared to the composites at low volume fractions of 1 to 7%. This demonstrated that addition of carbon black nano particles improved the tensile strength of the

composites at low volume fraction but degraded/lowered the tensile strength at higher volume fraction. Tensile strength recorded optimum at 5% volume fraction of carbon black for both manual and machine prepared composites. However, the machine prepared composite showed the highest tensile strength of 28.24 MPa compared to 26.43 MPa obtained for manual prepared composite. The tensile strength continued to decrease at higher volume fraction of 15 to 35%. The higher tensile strength at volume fraction range

might be attributed to better dispersion of carbon black in the polyester resin matrix, better wettability and interfacial bond. The lower tensile strength of the composites at higher volume fraction could be due to a number of reasons such as weak interfacial bonding at carbon black and polyester matrix interfaces, agglomeration of carbon black particles, process-related defects such as observed porosity [15]. The decrease of tensile properties at higher volume fraction had been observed in previous studies [16, 17, 18, and 19]. Agglomeration and incorporation between particles and matrix were the main factor for the trend. The adsorption of the carbon filler limited wettability in the polyester matrix phase resulting in poor interface adhesion of carbon black particles to the polyester resin matrix and inefficient stress transfer between the particle-matrix interface as load was applied [20, 18, 17]

Figure 4.2 shows the graph of tensile modulus of the composites at different volume fractions. Tensile modulus of manual mixed composite decreased as the filler loading increased from 1-11%. In contrast, the tensile modulus of the machine mixed composite was virtually constant between 1-5% but increased as the filler loading increased from 5-11%. The tensile modulus values for both composites were far below that of the cast resin at this filler range. The highest modulus of machine mixed composite was obtained at 11% filler loading (375 MPa) while that of the manual mixed type was highest at 1% filler loading (416.67MPa). The tensile modulus was mainly influenced by the shape factor (structure) than particle size of carbon

black. Essentially spherical aggregates loaded in a polymer would inhibit the elasticity of the polymer to a degree, but when these aggregates had a certain shape factor (long dimension), they acted as if they were short fibres and interfered with the elastic mobility of the polymer in which they were dispersed. The variation in tensile modulus responses of the manual and machine mixed composites might be attributed to the extent of dispersion of carbon black particles in the matrix phase.

Figure 4.3 shows the plot of percentage elongation at fracture of the composites versus the volume fraction. The values of elongation at fracture of both composites generally increased as the volume fraction increased from 1 to 5% compared to elongation at fracture of the cast resin (1.03%). However, elongation at fracture of both composites peaked at 5% volume fraction and decreased as the volume fraction increased beyond 5%. The machine mixed composite exhibited a more significant increase in elongation at fracture (1.82%) at this peak than that of the manual mixed composite (1.39%). The high improvement of the composites' elongation can be attributed to the effect of adhesion between the fillers and polyester matrix at this low volume fraction range [16] and better dispersion especially for the machine mixed composite [6].

A plot of tensile toughness versus filler loading is shown in figure 4.4. Machine mixed composite showed higher toughness than the manual mixed composite. The highest toughness value of 2.69 J for the machine mixed composite was recorded at 3% volume fraction while

the highest for manual mixed composite was 1.78 J at 11% volume fraction. The machine mixed composite was tougher than the cast neat resin from 1 to 7% and fell below that of the cast neat resin between 9 and 11% volume fraction. Manual mixed composite proved tougher than cast neat resin from 1 to 11% volume fraction.

Since toughness is a measure of energy needed to deform a material to failure, the result demonstrated that higher energy was required to break samples of the machine mixed composite from 1 to 5% volume fraction while lesser energy was needed to break the manual mixed samples from 1 to 11% volume fraction. This behaviour could be attributed to the mixing methods. An earlier study by Françoise, et al [13] indicated that physical properties of carbon black filled composite, even composites apparently consisting of similar matrices and similar carbon black might behave differently when prepared by different mixing methods.

5.0 CONCLUSION

The results of the study showed that tensile strength, percentage elongation and tensile toughness at fracture increased as the carbon black volume fraction increased at the low particle volume range (1 to 5%) for both manual and machine prepared polyester resin/carbon black composites above that of the cast neat resin. Machine mixed composite showed the highest improvement in the above tensile properties at the low filler range (1-5%). It is important to note that the maximum tensile strength and percentage elongation at break occurred at 5% filler loading and as filler

loading increased both tensile properties decreased. Tensile modulus of the manual mixed composite decreased as the filler loading increased. In contrast, the tensile modulus of the machine mixed composite was constant from 1-5% filler loading but increased as the filler loading from 7-11%.

REFERENCES

1. Tony Nguyen. "Clay Loading and Dispersion Effects on the Rheological Properties of Unsaturated Polymer Nanocomposites". *Journal of Undergraduate Research*, Vol.5, Issue 3, 2003.
2. Karen I. Winey, Richard A. Vaia. "Polymer Nanocomposites." *Materials Research Society Journal*, 32(4), pp.314-319, 2007.
3. Steven A. Edwards. "Nanotech Pioneers: Where are they Taking Us." John Wiley and Sons Ltd, Weinheim, pp.1-14, 2006.
4. Pritchard, D.K., Dr.R.K.Wharton. "Literature Review-Explosion Hazards Associated with Nanopowders." *Health and Safety Laboratory*, Vol.12, pp.1-17, 2004.
5. Jaebem Lee, Nicholas A. Kotov. "Thermometer Design at the Nanoscale." *Nanotoday Journal*, 2(1), 2007.
6. Ramanan Krishnamoorti. "Strategies for Dispersing Nanoparticles in Polymers." *Materials Research Society Journal*, 32(4), pp.314-347, 2007.
7. D.O.N. Obikwelu. "The Story of Nanoscience and Nanotechnology

- and Nanostudies at the University of Nigeria". Presented at the US/Africa International Workshop on Nanotechnology and Nanosciences Education at University of Nigeria, Nsukka, April, 20-23, 2008.
8. International Agency for Research on Cancer (IARC). "Summary and Evaluation- Carbon Black." Vol.65, p.149, 1996.
 9. Occupational Safety and Health (OSH). "Basic Information on Carbon Black." Dec., 1997.
 10. Peter J.F. Harris. "Carbon Nanotubes and Related Structures." Cambridge University Press, UK, 1999.
 11. Meng-Jao Wang, Charles A. Gray, Steve A. Reznick, Khaled Mahmud, Yakov Kutsovsky. "Carbon Black" Wiley InterScience, 2003.
 12. Freedonia Research Group. "Nanocomposites." Research Report #2042, Electronic.ca Publication, Mar., 2006.
 13. Francoise, E.D., Manuela, H.B., Erik, G., Cyrille, R., Francoise, B., Frederic, L. "Role of Fractal Features in the Structure-Property Relationships of Carbon Black Filled Polymers." Materials Research Society Symposium, Vol. 661, pp.kk7.4.1-kk7.4.9, 2001.
 14. James Harris. "Electrically Conductive Latex-Based Composites." Presented at the 3rd Texas Institute for Intelligent Bio-nano Materials and Structures for Aerospace Vehicles, Annual Review and Conference, Airlington, Aug., 2-3, 2005
 15. Asma Yasmin, Jyi-Jiin Luo, Isaac M.Daniel. "Processing of Expanded Graphite Reinforced Polymer Nanocomposites". Composites Science and Technology, Vol.66, pp. 1179-1186, 2006.
 16. Standard Methods of Evaluating the Properties of Wood-based Fibre and Particle Panel Materials. ASTM D-1037-99. American Society of Testing & Materials, Philadelphia, PA, 1999.
 17. Hu, Z, Srivivivasan, M.P., "Mesoporous High-surface-area Activated Carbon". Microporous and Mesoporous Materials, Vol.43, PP.267-275, 2001.
 18. H.P.S. Abdul Khalil, N.Z. Noriman, M.N. Ahmad, M.M. Ratnam "Polyester Composites Filled Carbon Black and Activated Carbon from Bamboo (*Gigantochloa Scortechinii*): Physical and Mechanical Properties." Journal of Reinforced Plastics and Composites, 26(3), pp.305-320, 2007.
 19. Luyi Sun, Min Xiao, Peng Xiao, Jianhua Song, Weixing Wang, Yafeng Zhang, Kecheng Gong. "A Preliminary Study on Rice Husk Filled Polypropylene Composite." Materials Research Society Symposium, Vol. 661, pp.kk.5.14.1-kk.5.14.5, 2001.
 20. Ismail, H., Suryadiansyah, A. "Effects of Filler Loading on Properties of Polypropylene-Natural Rubber-Recycle Rubber Powder

(PP-NR-RPP) Composites.” Journal of Reinforced Plastics and Composites, 23(6), pp.639-650, 2004.