ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Fabrication and characterization of composite using carbon black-waste from petroleum products

***1Punyapriya Mishra & 2Tanushree Bera**

1.Department of Mechanical Engineering, VSSUT, Burla, Odisha
2.Department of Mechanical Engineering, CV Raman Institute of Technology Bhubaneswar, Odisha

Manuscript Info

Manuscript History:

Received: 15 May 2014
Final Accepted: 25 June 2014

Key words:
Polymer-matrix composite, Epoxy resin, carbon black reinforcement

Corresponding Author

1Punyapriya Mishra

Abstract

Carbon black dispersion during composite preparation and filler-matrix adhesion are major technical issues that need to be addressed in order to achieve the desired property enhancements in polymer-matrix composites. The successful use of filler reinforcement technology to improve the performance of epoxy resin would represent a major technical achievement in the development of high-temperature and tough advanced structural materials. In the present investigation, a novel technique has been undertaken to fabricate composite materials using epoxy resin and different percentages of carbon black reinforcement.
..

INTRODUCTION

In recent years the composites have attracted substantial importance as a potential structural material. The attractive features of composites are their low cost, light weights, high specific modulus, renewability and biodegradability. Increasingly enabled by the introduction of newer polymer resin matrix materials and high performance reinforcement fibres of glass, carbon and aramid, the penetration of these advanced materials has witnessed a steady expansion in uses and volume. The increased volume has resulted in an expected reduction in costs. Carbon black is a material produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking tar and a small amount from vegetable oil. Carbon black is a form of amorphous carbon that has a high surface area-to-volume ratio, although its surface area-to-volume ratio is low compared to that of activated carbon. It is dissimilar to soot in its much higher surface-area-to-volume ratio and significantly lower (negligible and non-bio available) PAH (polycyclic aromatic hydrocarbon) content. However, carbon black is widely used as a model compound for diesel soot for diesel oxidation experiments. Carbon black is used as a pigment and reinforcement in rubber and plastic products. The current International Agency for Research on Cancer (IARC) evaluation is that, "Carbon black is possibly carcinogenic to humans (Group 2B)" [1]. Short-term exposure to high concentrations of carbon black dust may produce discomfort to the upper respiratory tract, through mechanical irritation. Tire recycling has become a necessity because of the accumulation of discarded tires which has become a potential environmental risk. There are approximately 240 million waste tires generated annually in the United States [2]. The impact of using carbon black instead of zinc oxide as tire reinforcement is tremendous. The use of carbon black as a reinforcing agent for asphalt cement may result in a similar advantage [3].

Wu and Chung worked on Calorimetric study of the effect of carbon fillers on the curing of epoxy and found that the presence of a carbon filler in an epoxy resin with a linear amine curing agent increased the heat of the curing reaction, especially if the filler is ozone-treated carbon fiber (with oxygen-containing functional groups on its surface) [4]. Aderikha and Shapovalov has studied on effect of filler surface properties on structure, mechanical and tribological behavior of PTFE-carbon black composites and found that the mechanical characteristics to CB content showed that both families of PTFE composites reach ultimate tensile strength and relative elongation at break in a narrow range of filler content and their values are of the same magnitude or exceed those of the neat PTFE [5].

Evidence from literature suggest that carbon black dispersion during composite preparation and filler-matrix adhesion are major technical issues that need to be addressed in order to achieve the desired property enhancements in polymer-matrix composites [6-12]. The successful use of filler reinforcement technology to improve the performance of epoxy resin would represent a major technical achievement in the development of high-temperature and tough advanced structural materials.

Visualizing the increased rate of utilization of waste products, the present work has been undertaken to develop a polymer matrix composite (epoxy resin) using carbon black as reinforcement and its mechanical properties has been studied. The composites are prepared with different volume fraction of carbon black. Micro structural examinations (SEM) were made to ascertain the fracture behaviour of the composite.

MATERIALS AND METHODS

The carbon black (Vulcan XC72R GP-3820) is collected from Cabot Corp., Billerica, MA. It is a powder with an average particle size of 30 nm, a maximum ash content of 0.2% and a density of 1.7–1.9 g/cm^3. Carbon black has the highest specific surface area due to the smaller sizes of its particles.

The epoxy resins used in the present work is the diglycidyl ether of bisphenol A (DGEBA), a liquid epoxy resin which represents greater than 75% of the resin used in industrial applications. Diglycidyl ether of bisphenol-A (DGEBA) is a typical commercial epoxy resin and is synthesized by reacting bisphenol-A with epichlorohydrin in presence of a basic catalyst. The properties of the DGEBA resins depend on the value of n, which is the number of repeating units commonly known as degree of polymerization. The number of repeating units depends on the stoichiometry of synthesis reaction. Typically, n ranges from 0 to 25 in many commercial products.

Composite preparation

Epoxy resin and carbon black was heated separately inside a vacuum oven for 1hr at 60^{0}C [±2^{0}C]. Mixing of resin with carbon black was carried out by H.S.M (high-intensity mechanical liquid stirrer) at approximately 500 rpm speed and 60^{0}C [±2^{0}C] for 1hr. Curing agent was added to the mixture at predetermined parts per hundred ratio. The solution was gently mixed for 15-20 minutes to avoid introduction of any air bubbles due to mixing action. The final slurry, free from air bubbles, was poured into a preheated brass mould (165x165x3 mm) at 80^{0}C [±2^{0}C] and cured in the vacuum oven at -760mm of Hg for 1hr. Post curing was carried out in two phases: First at 120^{0}C [±2^{0}C] for 2hrs inside vacuum oven and then at room temperature for 48hrs. The above procedure will be repeated for different wt% (0-5%) of carbon black to get the sheets of composites.

CHARACTERIZATION

Tensile strength

Tensile tests were conducted on Universal Testing Machine Instron using laboratory dumb bell shaped specimens with 165mm X 165mm X 3mm dimensions of the working part at 1mm/min cross-head rate. The results were subjected to standard statistical treatment; the data presented are average values for a series of at least five measurements with standard deviation not exceeding 10%. Tensile modulus was estimated from the initial linear part of the stress–strain curve limited by ≈3% relative elongation.

Flexural Strength

The 3-point flexural test is the most common for polymers. Specimen deflection is usually measured by the crosshead position. The test specimens with 165mm X 165mm X 3mm dimensions were carried on Instron universal testing machine .The specimen was placed on the 3-point flexural test .The specimen was supported from both ends and load of [0.5 to 1KN] was applied on the mid-span of the specimen.

Impact strength

Low velocity instrumented impact tests are carried out on composite specimens. The tests are done as per ASTM using an impact tester. The charpy impact testing machine has been used for measuring impact strength.

RESULTS AND DISCUSSION

Tensile properties of all composites materials as a function of carbon black loading are given in figure 1. It was observed from figure that tensile strength values of composites increase steadily with carbon black loading. The tensile strength value of the neat epoxy resin increased from 39 MPa to 53 MPa with 4 % carbon black loading. There is steady improvement in the tensile strength values of neat epoxy resin with the addition of carbon black.

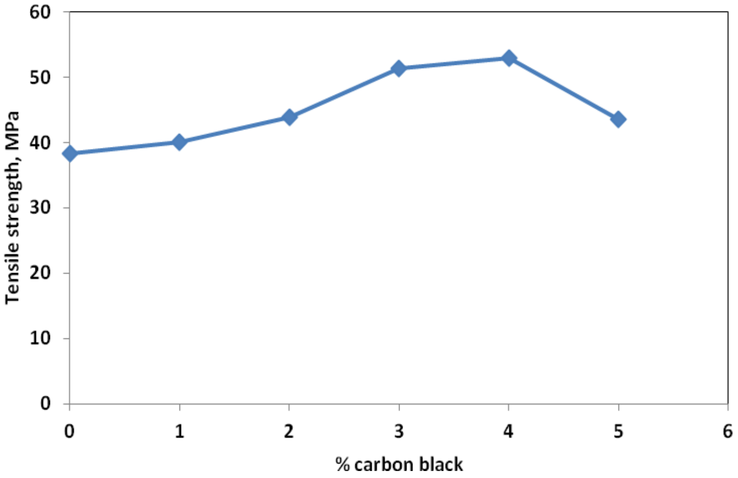


Fig 1 Tensile strength of CB-Epoxy composites for different weight percentage of CB

The tensile modulus of the composites shown in figure 2 has a maximum value with 4 wt% carbon black addition. At this carbon black loading, Young’s modulus value of composites is 23 % higher than that of pristine epoxy resin. This improvement in Young’s modulus can be attributed to exfoliation and good dispersion of the carbon black particles in the matrix as well as to the good interfacial adhesion between the carbon black particles and the epoxy matrix. Up to 4 wt% carbon black loading, mobility of the polymer chains can be restricted by well dispersed carbon black particles and by the adhesion at polymer-carbon black interface. So, composites resin becomes stiffer and leading to higher modulus.

Beyond 4 wt% carbon black addition, the tensile modulus value of the composites decreased. This may have been resulted from lower degree of exfoliation. Un-exfoliated aggregates of carbon black layers can lead to reduction in the Young’s modulus value by splitting up under load. Moreover; addition of more than 5 wt% carbon black may also lower the cross-link density. Hence, composites resin may become less stiff and polymer chains can move more easily. Consequently, this leads to a decrease in Young’s modulus value. As a result, by the rule of mixture, resultant composites would have higher stiffness than pure epoxy resin. On the other hand, the increase in stiffness cannot be explained only by rule of mixture. There are some other factors affecting final composites properties. These are: aspect ratio of filler, volume ratio, direction of particles, adhesion between the carbon black and polymer.

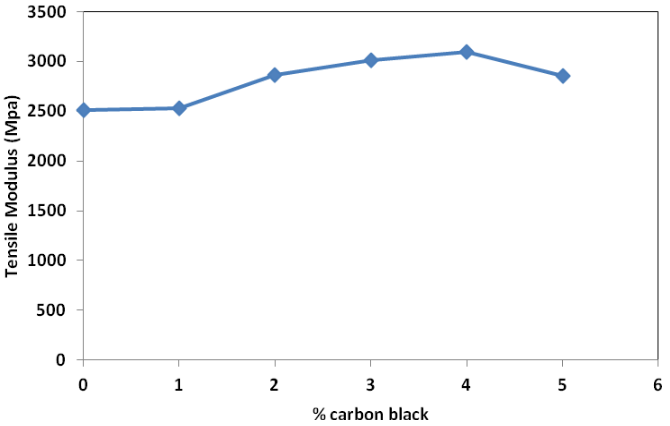


Fig 2 Tensile modulus of CB-Epoxy composites for different weight percentage of CB

The flexural strength, flexural modulus and flexural strain at break values of neat epoxy resin and epoxy/carbon black composites with different carbon black loading are shown in Figure 3. Flexural strength property exhibits similar trend with flexural strain property. They have a highest value at 4% carbon black loading. On the other hand, flexural modulus increases continuously. Figure shows the flexural strength values of composites with different carbon black contents. Flexural strength of the composites has a minimum value at 5% carbon black loading. The flexural strength values exhibit similar behavior as seen in the tensile strength. At 5% carbon black loading, flexural strength value is approximately 43% lower compared to the flexural strength of the 4wt% epoxy resin.

Beyond this point, little increase is observed in the flexural strength values of the composites, but they are still not so higher than those of pristine epoxy resin. Reduction in the flexural strength values can be attributed to the incompatibility between the epoxy resin and carbon black particles.

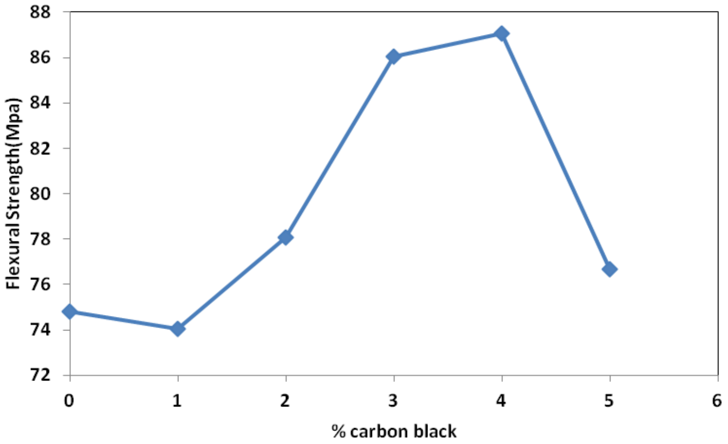


Fig 3 Flexural strength of CB-Epoxy composites for different weight percentage of CB

Figure 4 shows the behavior of flexural modulus with carbon black loading. It was observed that the flexural modulus of the epoxy/carbon black composites increased continuously with increasing carbon black content. Maximum improvement was achieved at 4 % carbon black content. At this point, flexural modulus value increased about 48 % compared to the pure epoxy resin. The increase in flexural modulus can be attributed to exfoliation of Cloisite 30B particles in the epoxy resin. Exfoliation of carbon black particles increases rigidity in the resultant composites. The increase in the rigidity may lead to high flexural modulus of composites resin.

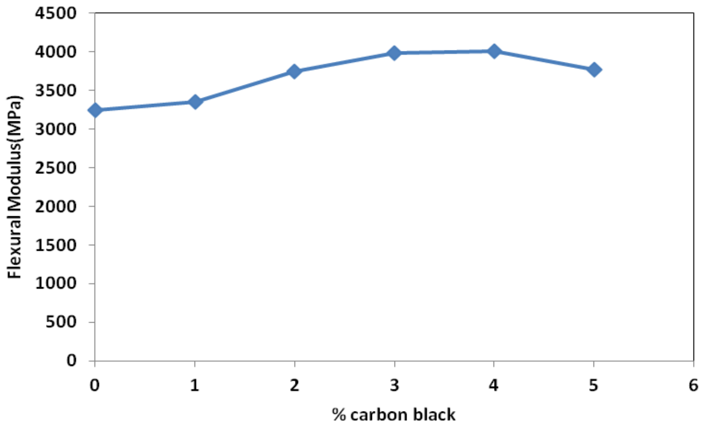


Fig 4 Flexural modulus of CB-Epoxy composites for different weight percentage of CB

Impact strength values of the neat epoxy and epoxy/carbon black composites with different carbon black loadings are shown in figure 5. Impact strength of the composites has similar behavior as their flexural strength.

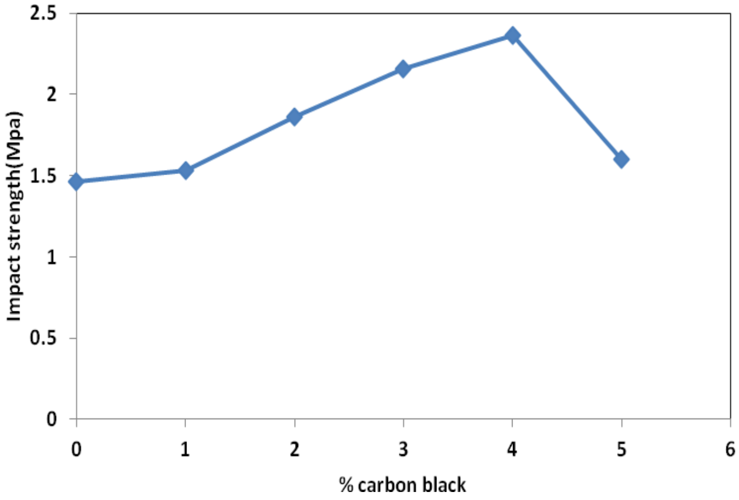


Fig 5 Impact strength of CB-Epoxy composites for different weight percentage of CB

Impact strength of the neat epoxy resin increased continuously up to 4wt% carbon black loading. At this carbon black content, a minimum of 60% increase in impact energy was obtained. Beyond this point, the impact energy showed a decreasing trend. The impact strength value with 5 wt% carbon black content was almost equal to that of the neat epoxy resin. The neat epoxy resin has the maximum impact strength1.5kJ/m^2. In this study, good improvement in impact strength was achieved by the addition carbon black.

THERMAL ANALYSIS

Differential scanning calorimetry (DSC)

The glass transition temperatures (Tg) of neat epoxy resin and epoxy/carbon black composites were determined by differential scanning calorimeter (DSC). Figure 6 presents effects of the carbon black on the Tg of the developed composites. DSC analyses indicated that Tg of the cured composites resins increased continuously with carbon black loading. On the other hand, in previous studies both reduction and increase have been observed in the Tg for different resin systems (Table 1). The neat epoxy resin has Tg of 68°C. Addition of 4% carbon black into the epoxy resin has an effect of increasing Tg to 90°C. The increase in the Tg with carbon black addition may be attributed to consumption of un-reacted monomers on the surface of the carbon black particles. Hence, crosslink density increases by increasing carbon black loading of the resin. Finally, increase in the crosslink density may result in higher Tg. Also, consumption of the free radicals may lead to excess un-reacted curing agent in resin system. The excess curing agent has the plasticization effect on the resin system. This may lead to a reduction in Tg value beyond 4% of filler loading. Consumption of un-reacted monomers in the galleries and entanglements can lead to reduction in Tg. DSC graphs of neat resin and 2, 3, 4 wt % composites are given.

The Tg of the composites systems are affected by both the bulk epoxy properties and epoxy-carbon black interaction. In the case of conventional composites, Tg of the system is the same as the Tg of the bulk matrix system. But in composites, motion of the epoxy monomers is restricted by carbon black layers. So, the Tg values with epoxy carbon black interaction are different. Well exfoliated carbon black layers lead to the same or higher Tg values than the neat resin, but intercalated carbon black layers result with lower Tg values. The Tg of the composites system will be affected by the epoxy-carbon black interaction.

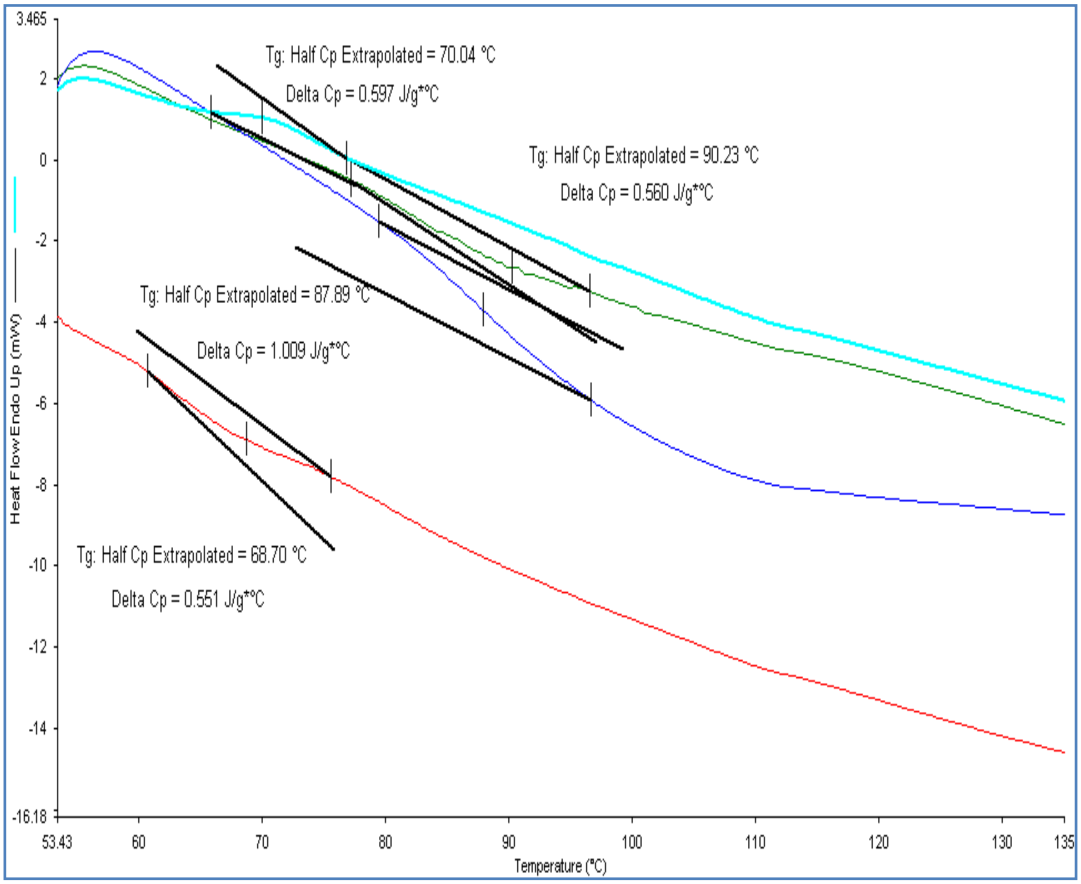


Fig 6 DSC thermogram of CB-Epoxy composites for different weight % of CB

Table-1 Glass transition temperature (T_g) of epoxy carbon black composites

Composite Samples	Tg (°C)
Neat Epoxy	68.70
Epoxy + 2 wt% CB	70.04
Epoxy + 3 wt% CB	87.89
Epoxy + 4 wt% CB	90.23

Thermogravemetric Analysis (TGA)

Thermal stability of epoxy/carbon black composites with different carbon black loadings were determined by thermo-gravimetric analysis (TGA) as shown in Figure 7. Thermal stability is related with degradation of carbon black and epoxy resin. The initial decomposition temperature of pure epoxy resin was increased in the order of 5-10°C by carbon black loading. Degradation resistance of epoxy resin was slightly improved by the addition of the carbon black up to 4% as shown in Table 2. The initial decomposition temperature of the neat epoxy resin increased from 302°C to 310°C with 4% carbon black loading. This slight improvement may have been achieved by the barrier properties of the layered filler and the tortuous path for the removal of volatile decomposition products preventing the diffusion out of decomposition products. Also, carbon black particles act as insulator reducing conduction heat transfer within the composites.

Table-2 Dynamic Mechanical Analysis (DMA) Of Carbon black Epoxy composite

Content of MWCNT	TanDelta (MPa)	Loss modulus (MPa)	Tg (^{0}C)	Tg (^{0}C)Loss
Neat Epoxy	0.7152	400.3	90.52	77.65
2% CB	0.9596	128.6	100.68	84.26
3% CB	0.7274	404.3	104.54	83.35
4% CB	1.012	311.4	90.97	71.30

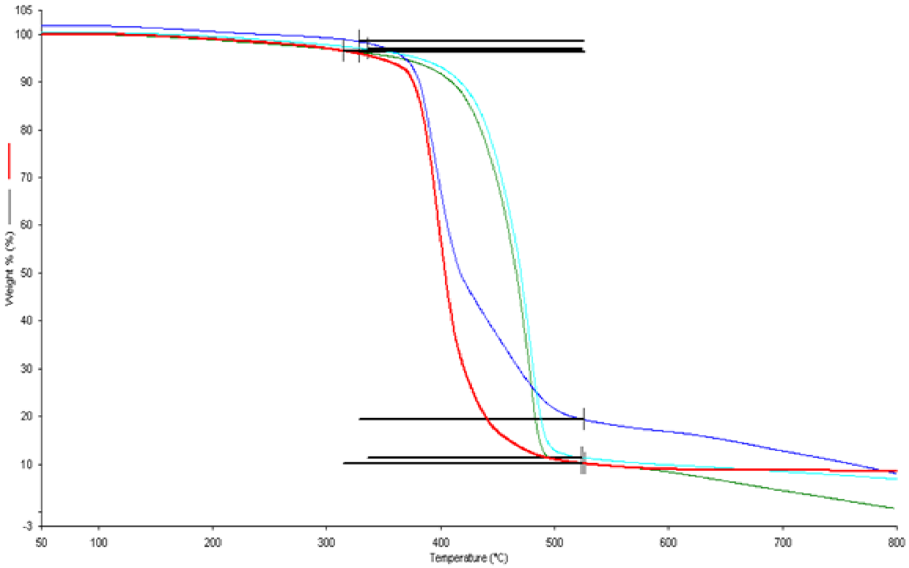


Fig 4.7 Percentage weight loss due to heating in presence of N_2 atmosphere

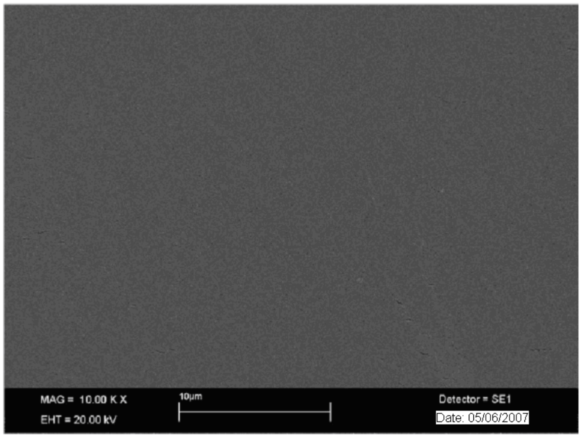
Initial decomposition temperature and the weight remaining after decomposition are shown in Table 3. After the decomposition of the epoxy/carbon black composites, char formation takes place. The weight remained shows the char formation after decomposition. Char acts as an insulator material and enhances decomposition temperature of the composites material. Carbon black loading has an effect of increasing the char formation. Neat epoxy resin has char formation of 4.94% whilst char formation is 11.68 % for composites with 4% carbon black content. The amount of char formation increases continuously with carbon black loading.

Table-3 Thermo gravimetric analysis

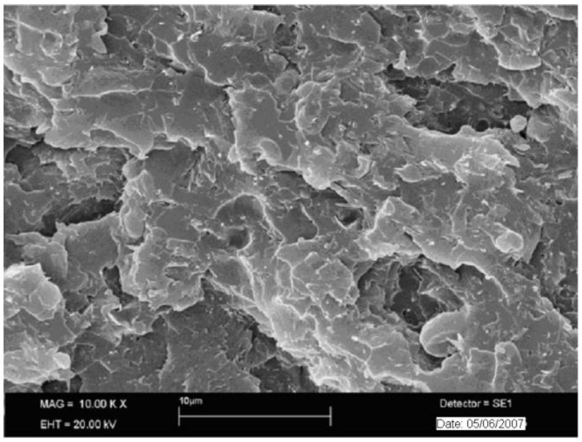
Sl.No.	Sample	T_{onset}	T_{end}	T_{peak}	$T_{10\%}$	$T_{30\%}$	$T_{50\%}$	$T_{90\%}$
1	Neat Epoxy	302.67	402.44	364.04	361.75	388.93	402.57	600
2	2% CB	308.50	409.75	366.12	362.94	390.84	414.90	610
3	3% CB	309.25	410.63	365.11	357.20	387.65	460.47	478.30
4	4% CB	304.64	406.81	364.64	364	389.17	466.83	481.34

Scanning Electron Microscopy (SEM)

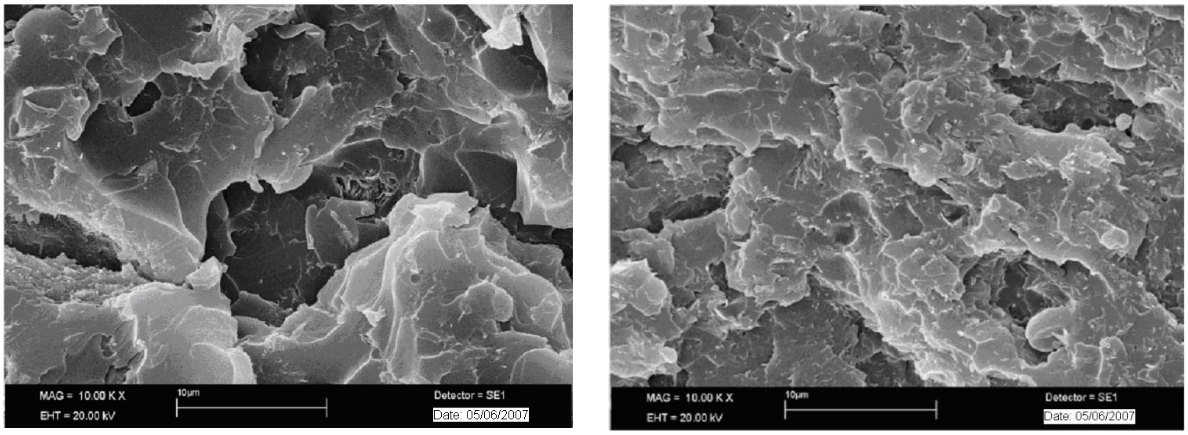
From the SEM image as shown in Figure 8, the carbon black was shown as micro-ribbon with about several microns in length and about 200 nm in width. It was not hard to imagine when this kind of micro-ribbon was evenly distributed across the matrix, it would inter-lock and entangle with the polymer chains in the matrix. For the ease of comparison, except the SEM image of carbon black , the SEM images of 0 wt%, 2-4 wt% each of carbon black , epoxy samples were all focused to a magnification of 10,000•. For the 2-4 wt% Carbon black epoxy sample as shown in the SEM image in figure 8 (b-d), the cleavage surface were a big different from that of pure epoxy sample in figure 8 (a). The cleavage surface showed fracture pieces with smooth white facture borders.



Epoxy+Hardener



2% CB



3% CB **4% CB**

Fig 8 SEM photograph of different weight percentage of CB-Epoxy composites

In general, for the SEM images of 2 wt% each of carbon black epoxy samples as shown in figure 8 (b-d) respectively, there was a trend that the cleavage surface broken with smaller and rougher fracture pieces. Sometimes, some tiny white lines, which believed to be the carbon black, were found coming out from the fracture surfaces. Therefore, the carbon black introduced inside the epoxy acted like the grid lines of a net. When generalizing the pictures of SEM images with tensile test results, the addition of this kind of ‘‘micro-ribbon’’ into the epoxy matrix, the micro-ribbon would interlock with the epoxy network chains. With the addition of higher carbon black content, the interlocking mechanism seemed prevail more comprehensively. Therefore, it seemed that increase in proportion of this kind of carbon black would make the sample less brittle, or on the other way of saying, the ductility increased with the addition of this kind of carbon black. The more the addition of Carbon black inside the epoxy, the less is the brittleness of the samples. Therefore, it can be concluded that the ribbon-like carbon black hindered the linking up of epoxy chains network, making the carbon black epoxy samples less brittle, but it did make the carbon black epoxy samples stronger and harder in a certain extent.

CONCLUSION

The following conclusions are drawn from the above studies.

- The carbon black, an underutilized waste material can successfully be utilized to produce composite by suitably bonding with resin for value added product.
- The addition of carbon black enhances the thermal properties of epoxy matrix.
- The degradation starts at higher temperature and char formation mechanism is enhanced when adding filler particles.
- For higher CB content, the interaction between the polymer matrix and the filler particles play an important role and the degradation process become slower.
- From TGA measurement it was found that the addition of CB increases the % of char in epoxy when it is heated above the glass transition temperature (Tg).
- From the SEM studies it was found that the interaction between the filler particles and the epoxy matrix seem to play an important role on the thermal properties on molecular dynamics mechanisms.

REFERENCES

[1] Kuempel, Eileen D. and Sorahan, Tom (2010). "Identification of Research Needs to Resolve the Carcinogenicity of High-priority IARC Carcinogens" (PDF). Views and Expert Opinions of an IARC/NORA Expert Group Meeting, Lyon, France, 30 June - 2 July 2009. IARC Technical Publication No. 42. Lyon, France: International Agency for Research on Cancer 42: 61–72. Retrieved August 30, 2012.

[2] Amirkhanian S. N. (1993) "Utilization of scrap tires in flexible pavements—Review of existing technology", ASTMSTP 1193.

[3] Rostler F. S, White R. M, Dannenberg E. M (1977), "Carbon black as a reinforcing Agent for asphalt", Association of asphalt paving technologists, vol. 46, pp376-401.

[4] Wu, Junhua and Chung, D.D.L. (2004),“Calorimetric study of the effect of carbon fillers on the curing of epoxy”, Letters to the Editor / Carbon, 42, pp. 3003–3042.

[5] Aderikha, V. N. and Shapovalov, V. A. (2011), “Tribological behavior of polytetrafluoroethylene-silica composites”, Journal of Friction and Wear, 32 (2), pp 124-132.

[6] Manocha, L.M. and Bansel, A.R.(1980), “Advances in composite materials”, Pergamon Press, Oxford, 2, pp. 1233 - 1240.

[7] Jartiz, A.E., Design 1965, pp.18.

[8] Kelly, A. (1967), Sci. American 217(B), pp. 161.

[9] Berghezan, A. Nucleus (1966), Nucleus A Editeur,1,rhe,Chalgrin,Paris, 8(5).

[10] Van, Suchetclan and Repts, Philips Res, (1972), “Study of mechanical properties of hybrid natural fiber composite”, 27, pp. 28.

[11] Agarwal, B.D. and Broutman, L.J. (1980), “Analysis and performance of fiber composites”, John Wiley & Sons, New York, pp. 3-12.

[12] Chand, N. and Rohatgi P.K. (1994), “Natural fibers and their composites”, Publishers, Periodical Experts, Delhi.