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Thermomechanical characteristics of KM2PLUS Kevlar nanocomposites

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ABSTRACT

Woven fabric laminates have proved to have grander properties compared to those of laminates made of unidirectional prepregs. Through control/ alteration of certain additives at the nanoscale level, it is possible to maximize property enhancement of selected polymer systems to meet or exceed the requirements of current applications. The current paper studies the thermal and mechanical properties of newly developed KM2PLUS woven Kevlar composites and the effect of mixing three different types of nanomaterials, namely SiC, Al_2O_3 and Carbone nanotubes to the composite. The mechanical properties for the composite materials samples were tested using three-point bending and nano-indentation tests. Thermal properties of the laminated samples were investigated using Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The results showed that 0.5% CNT added to the laminate system increased the stiffness and the load carrying capacity significantly. Thermal analysis showed that there was no major change in the thermal properties due to the addition of the nano fillers.

KEYWORDS

Nanofillers;
Thermal properties;
Nano fillers.

INTRODUCTION

The development of nanocomposites opened a new era of industrial applications due to their superior mechanical, thermal, chemical and electrical characteristics[1-5]. The addition of nano fillers as additives into polymer has resulted in polymer nanocomposites exhibiting multifunctional, high performance polymer characteristics beyond what traditional filled polymeric materials possess, which improves thermal resistance and/or flame resistance, moisture resistance, decreased permeability, charge dissipation, and chemical resistance[6]. Through control/alteration of the additives at the nano scale level, one is able to maximize property enhancement of selected polymer systems to meet or exceed the requirements of current military, aerospace, and commercial applications. The technical approach involves the incorporation of nano particles into selected polymer matrix systems[1]. These new nancomposite materials enabled the circumvention of classic material performance trade-offs by accessing new properties and exploiting unique synergies between materials.

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One of the important characteristics of nanocomposites that lead to their wide use in many industrial applications is their improved impact, mechanical and thermal properties. Woven roving fabric laminates have proved to have superior mechanical and impact energy absorbing properties to those of laminates made of unidirectional prepregs[7,8]. Woven fabrics are used in a number of engineering applications across various industries, including such products as automobile airbags; flexible structures like boat sails and parachutes; reinforcement in composites; architectural expressions in building roof structures; protective vests for military, police, and other security circles; and protective layers around the body in planes. Woven fabrics consist of yarns woven in the fill and the warp directions. Kevlar, which is a commercial name of aramid fiber, showed high performance in impact resistance tests and used in wide variety of applications such as military, aircraft, spacecraft etc.[2]. Different types of Kevlar have been developed in order to improve its properties and to fit various applications. One of the newly developed Kevlars KM2PLUS type. The current research studies the mechanical and thermal properties of laminated KM2PLUS kevlars and the role of three different types of nanofillers on further enhancing the thermal and mechanical properties of the laminated composite. The laminated composites were prepared manually, 10 plies of woven KM2PLUS kevlar were arranged in a symmetrical 0/45° alternation. A standard three-point bending testing apparatus was utilized to investigate the impact of the nano fillers on the flexure modulus. Nano indentation tests were carried out to further investigate the effect of the nanofillers on the hardness and the elastic modules of the lamina. The nanocomposite samples were tested using thermal gravitational analysis (TGA)[9] and differential scanning calorimetry (DSC)[10] to study the impact of the nanofillers on the thermal behavior of the laminated composte samples.

MATERIALS AND SAMPLE PREPARATION

Materials

Kevlar KM2PLUS

Woven aramid fibers produced under the commercial name of Kevlar by DuPont de Nemours were used in the current study. The chemical composition of Kevlar is poly para-phenyleneterephthalamide; it is more properly known as a para-aramid. Kevlar®, KM2Plus 600 denier was purchased from JPS Composite Materials Corporation (Anderson South Carolina). TABLE 1 summarizes the chemical and mechanical properties of Kevlar 29, Kevlar 49 & Kevlar 149[6].

Epoxy resin

ARALDITE® AY105, a medium viscosity unmodified epoxy resin based on bisphenol-A, was used in this study. Araldite®, which is a registered trademark of Huntsman LLC (The Woodlands, Texas), is used to bound the layers of the Kevlar fabrics together. The chemical properties of the epoxy resin used in this study are presented in TABLE 2.

Epoxy resins are cured with the addition of a curing agent which is commonly called a hardener. Low viscosity cycloaliphatic polyamine - Hardener HY 2962 – Aradur 42 – from Huntsman LLC (The Woodlands, Texas), was used in this research. Ep-

TABLE 1 : Kevlar properties

	Kevlar 29	Kevlar 49	Kevlar 149
Density (g/cm^3)	1.44	1.44	1.44
Tensile Strength (GPa)	3.6	3.6 – 4.1	3.4
Young's Modulus (GPa)	83	131	186
Tensile Elongation (%)	4.0	2.8	2.0

TABLE 2 : Epoxy resin properties

Density @ 25°C (g/cm³)	Flash Point (°C)	Vapor Pressure @ 20°C (Pa)	Viscosity @ 25°C (mPa.s)
1.13	≥ 200	≤ 0.01	10000 - 12000

TABLE 3 : Hardener properties

Density @ 25°C (g/cm³)	Flash Point (°C)	Refractive Index @ 25°C	Viscosity @ 25°C (mPa.s)	H^+ Active Equivalent (g/eq)
0.92	≥ 110	1.4858 – 1.4878	10 - 20	42.5

TABLE 4 : Silicon carbide nano-

Fillers Properties	Molar Mass (g/mol)	Density (g/cm³)	Melting Point (°C)	Flexural Strength (MPa)	Elastic Modulus (GPa)	Hardness (kg/mm²)
Silicon Carbide	40.1	3.1	2730 (Decomposes)	550	410	2800

TABLE 5 : Aluminum oxide nano-fillers properties

Molar Mass (g/mol)	Density (g/cm³)	Melting Point (°C)	Boiling Point (°C)	Thermal conductivity ($W.m^{-1}.K^{-1}$)
101.96	3.95 – 4.1	2072	2977	30

oxy resins usually require the addition of the curing agent at a much higher ratio of resin to hardener. The ratio of resin to hardener, used in this study, is 5:1. The chemical properties of the hardener used in this study are presented in TABLE 3.

Nano-fillers

Silicon Carbide (SiC), Aluminum Oxide and Carbon Nanotubes were the nanofillers used in this study. The chemical and mechanical properties of the silicon carbide and Aluminum oxide (Al_2O_3)nanofillers are shown in TABLES 4 and 5 respectively.

Carbon Nanotubes (CNT's) were obtained from Nanolab (Newton, Massachusetts, USA), where the diameter of each single CNT range was 10 – 30 nm, with CNT length 5 – 20 μm, were added in three weight percentages of 0.25%, 0.5% and 1% of CNT to the epoxy to prepare three composite samples of 10 layers of Kevlar KM2Plus.

Sample preparation

Control sample

A piece of Kevlar KM2Plus cloth of 50 yard length and thickness of thickness 0.21 mm was cut into pieces using special type of scissors, 8" Serrated Kevlar Shears with Deluxe Comfort Grip. The control specimen was prepared from ten woven layers of Kevlar KM2Plus having a size of 20 cm x 20 cm stacked one on the top of the other at 0° angle. The weight of Kevlar layers was initially measured and recorded. Then the minimum amount of resin required for bounding the Kevlar piles was used. Medium viscosity unmodified epoxy resin based on bisphenol-A was used in order to bind the Kevlar plies. Low-viscosity cycloaliphatic polyamine hardener (Hardener HY 2962 – Aradur 42) was added to the epoxy resin to ensure and accelerate the curing where the weight ratio between the resin and the hardener was 5:1. Afterwards a mold of two aluminum plates (30 cm x 30 cm) were used in order to place the composite in between the plates. Once the resin was spread, another layer was placed on the top of the first Kevlar pile at 0° angle. Then a roller (Figure 1) was used to assure that the second ply is bounded to the first one and the air bubbles inside resin and cavities between the two Kevlar layers were eliminated.

Figure 1 : A roller to extract the air bubbles out of the laminates

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The same process was repeated for the rest of the ten Kevlar layers, where the Kevlar piles were stacked one on the top of the other. Upon completion of the ten layers, the other aluminum plate, which was again sprayed with a releasing agent, was placed on the top of the ten Kevlar piles. Once the layup of the specimen was completed, it was placed inside the hot press machine. The laminated composite was pressed inside the composite hot pressing machine for 15 minutes. The fiber volume fraction is usually greater than 60%[11]. Once the pressing process was completed, the total weight of the composite including the resin was measured. Hence, the weight of matrix phase, embedded inside the composite can be calculated based on Eq. 3.1 and the fiber and matrix percentages will be determined

$$m_{composite} = m_{fibre} + m_{matrix} \quad (1)$$

Laminated composites sample preparation with nano-fillers

The same procedure applied in the preparation of the control specimen was followed. The laminated In this case, different nano-fillers with different weight percentages were mixed with the the resin. Sonication process was applied at the maximum frequency (10 units) of Branson Sonifier 450 device to ensure the proper mixing of the mixture of the epoxy resin and the nanomaterial and achieve the homogeneous dispersion of the nanomaterial within the resin. The following steps were followed during the sonication process:

Heating resin up to 60°C till it becomes less viscous for ease of proper mixing due to high viscosity of the resin by using magnetic stirrer

Once the resin becomes less viscous, the nano material was added

The resin and the nano material mixture was sonicated for 20 minutes using sonication process with heat

The mixture was subjected to normal mixing for 15 minutes using sonication process without heating to assure proper mixing & homogeneity between

TABLE 6 : Sample description

Sample #	Sample Description	Fiber Weight %	Resin Weight %
K	Control Sample	86.5	13.5
S1	Kevlar + 1% SiC	83.5	16.5
S2	Kevlar + 2% SiC	82.2	17.8
S3	Kevlar + 3% SiC	81.7	18.3
A1	Kevlar + 1% Al_2O_3	84.5	15.5
A2	Kevlar + 2% Al_2O_3	84.2	15.8
A3	Kevlar + 3% Al_2O_3	84.1	15.9
C1	Kevlar + 0.25% CNT	81.1	18.9
C2	Kevlar + 0.5% CNT	79.7	20.3
C3	Kevlar + 1% CNT	79.1	20.9

TABLE 7 : Summary of the three point test results

Sample	Peak Load (N)	Ultimate Tensile Strength (MPa)	Young Modulus (GPa)
K	190.997	118.1	6.07
S1	142.664	80.8	6.12
S2	252.996	185.9	8.16
S3	305.995	198.6	8.34
A1	259.996	158.5	6.23
A2	236.996	129.6	8.27
A3	214.597	130.8	10.12
C1	333.495	156.3	8.26
C2	341.995	233.3	9.62
C3	330.370	215.6	8.73

resin and nano material

The hardener HY 2962 – Aradur 42 was added to the resin-nanomaterial mixture and then stirred properly to ensure and accelerate the curing, where the weight ratio of the resin to the hardener is 5:1.

TABLE 6 shows a description of all the samples with their fiber and matrix weight percentages.

Mechanical Analysis

The mechanical characteristics of the NC Kevlar composites were investigated using three different tests; namely, a three point bending, micro hardness and nano indentation tests. These tests are described below.

Three point bending test

The objective of this test was to study the effect of nanofillers addition on the flexure stiffness and the load carrying capaciry of the nanocomposite samples. The three point bending tests were carried out according to the ASTM D790 standard[1]. Five samples were tested for each group. The load-deflection behavior was recorded for all samples, and the elastic modulus, *E*, was calculated using the flexural modulus formula. TABLE 7 summarizes the results of the tested samples. It is clear from Figure 2 that the addition of nanofillers increased the stiffness of the nanocomposite samples. The highest increase was for A3 sample with approximately 58% increase in the stiffness. The C samples were the best ones in terms of load carrying capacity. C2 sample showed 80% increase in the load carrying capacity, Figure 3.

Nano hardness

Nano indentation tests were performed on the Micro Materials Ltd., Wrexham, UK testing platform. This platform is equipped with a three sided pyramid diamond indenter tip of the Berkovich type. Five indents were performed for each sample. The distance between indentations was 50 µm to avoid interaction. The hardness and the elastic modulus

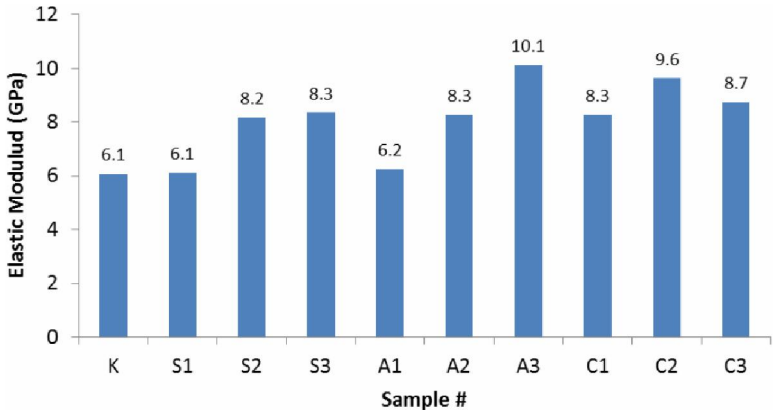

Figure 2 : Young modulus of Kevlar composite samples

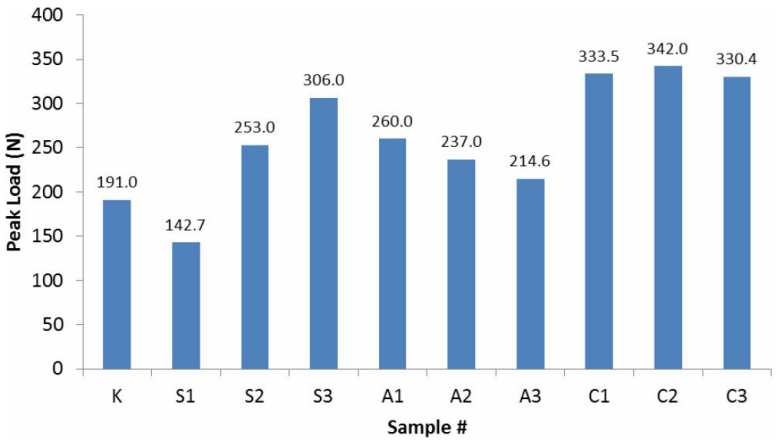

Figure 3 : Maximum load of Kevlar composite samples

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were calculated from the load–displacement data. As the indenter was allowed to penetrate into the specimen, both elastic and plastic deformation occurred and only the elastic portion of the displacement was recovered during unloading. By adopting the Oliver-Pharr method[12], the slope *S* at the maximum load point, characterized by $dp/dh = 0$, is the experimentally measured stiffness of the upper portion of the unloading data. The slope S thus calculated be used to calculate the reduced modulus of elasticity E_r as follows

$$E_r = S\sqrt{\pi}/(2\beta\sqrt{A_p}) \quad (1)$$

Where A_p is the area of the indentation at the contact depth, β is a constant that depends on the geometry of the indenter (β = 1.034 for a Berkovich indenter). The reduced modulus E_r reflects the effect of the sample material and indenter elastic deformations[13, 14]. The effect of non-rigid indenters on the load-displacement behavior is taken into considerations by defining the reduced modulus through Equation 2.

$$\frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i} \quad (2)$$

where E_s and υ_s are, respectively, the Young's modulus and Poisson's ratio for the sample; E_i and ν_i are, respectively, those of the indenter. Equation 4 is used to calculate the sample Young's Modulus from the reduced modulus as obtained from Equation 3. The Poisson's ratio of the sample is taken to be *0.35* for Vinylester while that of the diamond indenter used in the tests is taken to be *0.07*; the Young's modulus for the diamond indenter is taken to be *1140 GPa.*

The nano hardness results are shown in Figure 4 where it can be seen that the hardness increased for nearly all the composites by the addition of the nanofillers. The maximum increase was for the A3 samples. The results reported in TABLE 8 represent the average of five cycles of loading and unloading curves. Figure 5 shows the effect of the

TABLE 8 : Summary of the nanoindentation test results

Sample	Maximum Depth (nm)	Hardness (GPa)	Reduced Modulus (GPa)
K	1509.79	0.242	5.037
S1	1467.28	0.263	4.95
S2	1497.27	0.314	6.675
S3	1111.43	0.502	7.625
A1	1309.87	0.347	6.405
A2	1234.94	0.388	6.566
A3	1102.61	0.507	8.07
C1	1469.29	0.28	5.11
C2	1412.44	0.303	5.769
C3	1290.14	0.372	6.33

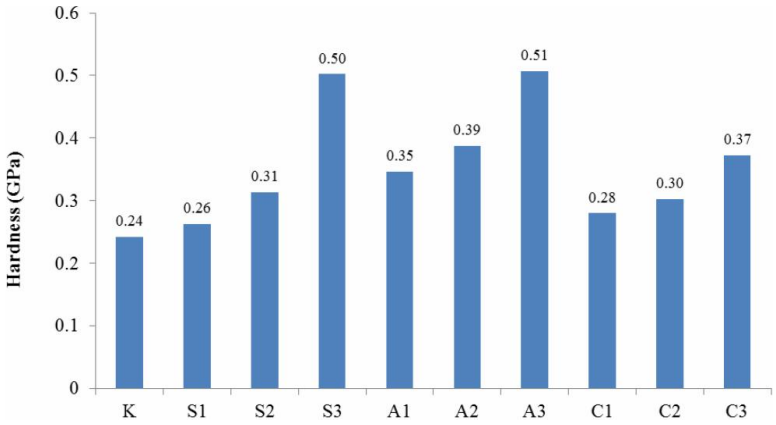

Figure 4 : Hardness of Kevlar composite samples

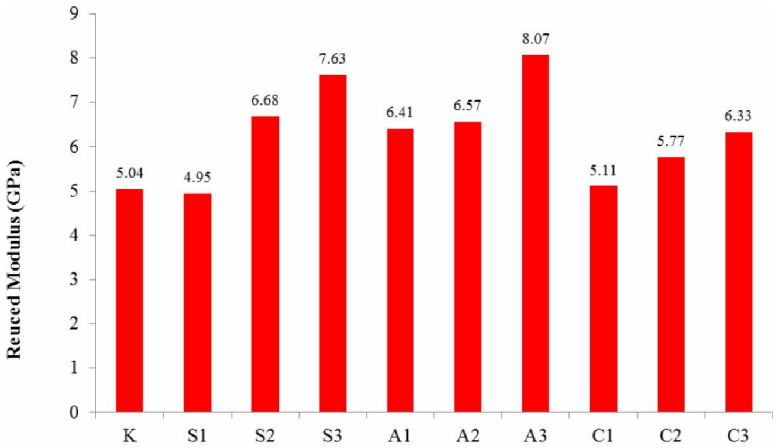

Figure 5 : Hardness of Kevlar composite samples

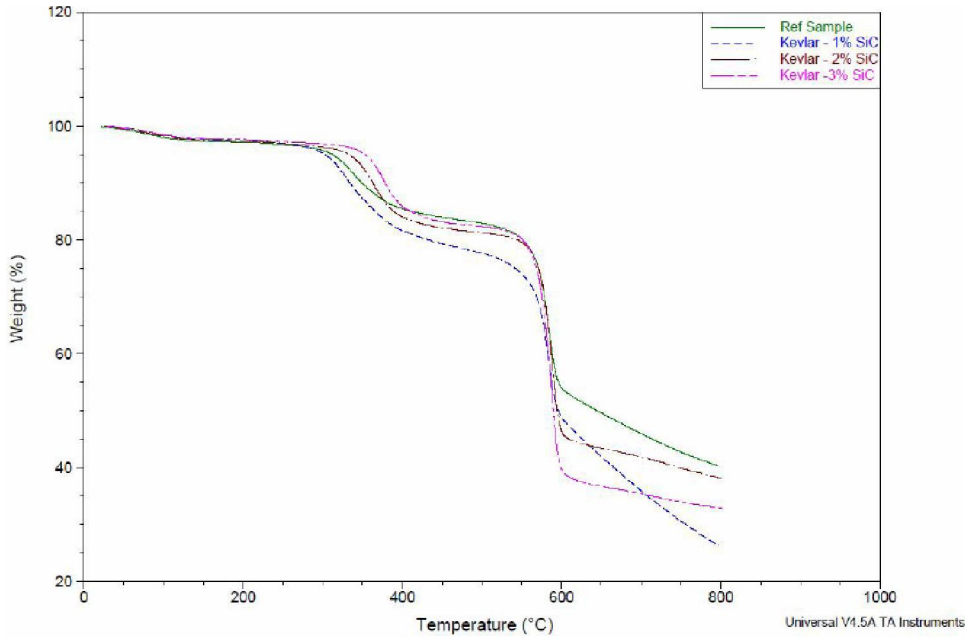

Figure 6 : TGA curves of Kevlar composite enhanced with SiC sample

nanofillers on the sample reduced modulus of Kevlar composites deduced by nano indentation. It can be noticed that the sample modulus increased with the addition of nanofillers. This result is consistent with that obtained by the three point bending test shown in TABLE 2.

THERMAL ANALYSIS

Thermal gravimetric analysis (TGA)

Thermal Gravimetric Analysis (TGA) Q50 Device from TA Instruments (New Castle, Delaware) was utilized to study the thermal weight-change of the NC/ Vinylester samples. The Thermo gravimetric analyzer measures the amount and rate of weight change in a material, either as a function of increasing temperature, or isothermally as a function of time, in a controlled atmosphere. It can be used to characterize any material that exhibits a weight change and to detect phase changes due to decomposition, oxidation, or dehydration. This information helps us identify the percentage weight change and correlate chemical structure, processing, and end-use performance[14]. The TGA measurements were performed under nitrogen atmosphere with balance purge flow of 40 mL/min and sample purge flow of 60 mL/min. About 10 mg of the composites samples were used each time. The measurements were done with a heating rate of 20°C/min in the temperature range of (0-

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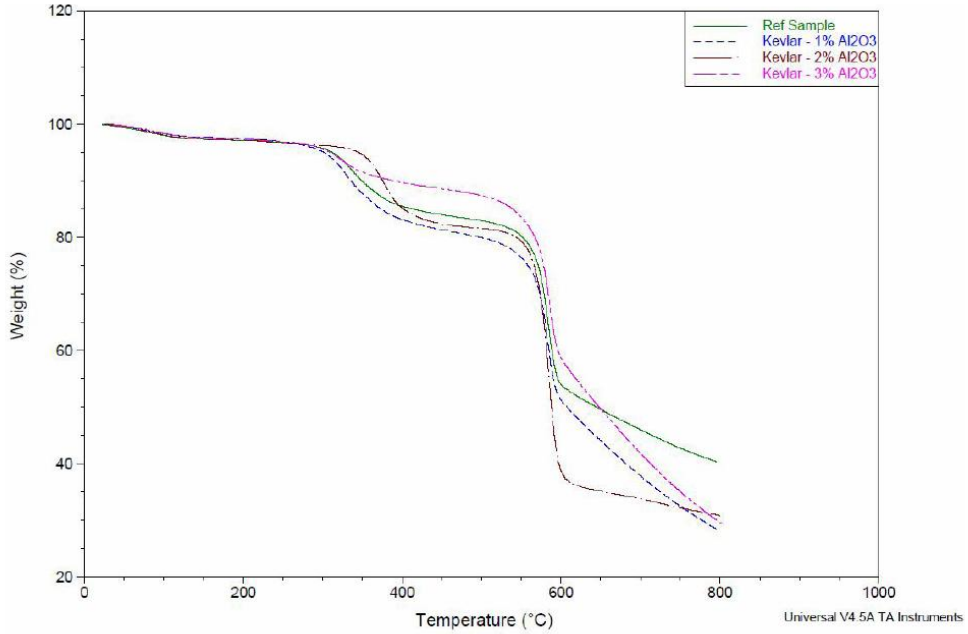

Figure 7 : TGA curves of Kevlar composite enhanced with Al_2O_3 sample

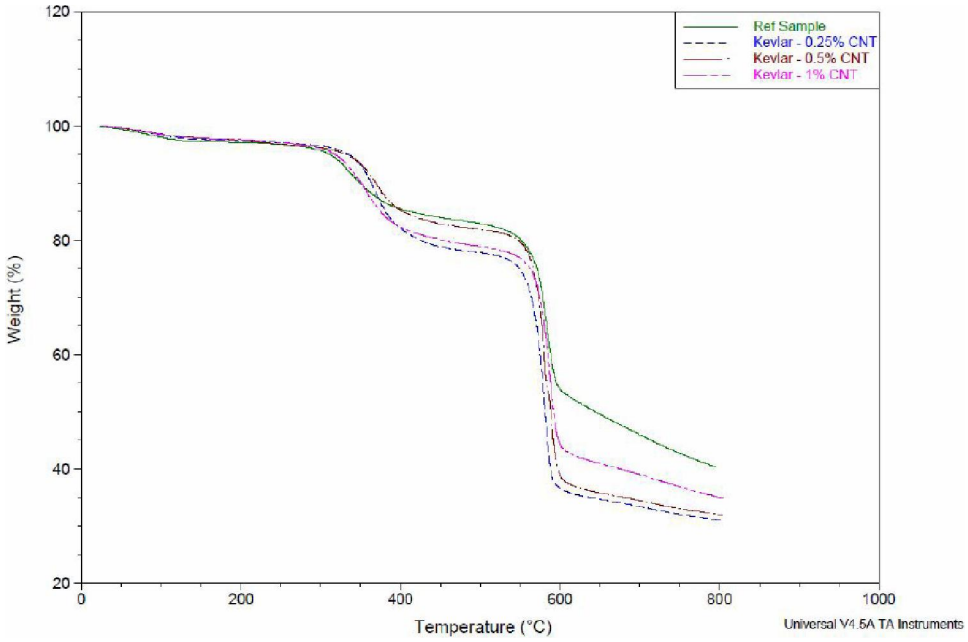

Figure 8 : TGA curves of Kevlar composite enhanced with CNT sample

600 °C). Figures 6 - 8 show the TGA results for all samples compared to the control sample where the onset slope method was used to evaluate the exact value of decomposition temperature.

TABLE 9 summarizes the TGA readings, including decomposition temperature (Td).

There was no major change in the decomposition temperature due to the nanofillers addition. The maximum change was for the S3 sample with approximately 4.5% increase in the decomposition temperature.

Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermal analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and the reference are maintained at nearly the same temperature throughout the experiment. The basic principle

TABLE 9 : Summary of TGA results

Sample	Decomposition Temperature (°C)
K	525.33
S1	541.04
S2	548.36
S3	549.67
A1	529.26
A2	537.11
A3	533.19
C1	533
C2	534.68
C3	535

underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will be needed to flow to the sample compared to the reference to maintain both at the same temperature[15]. The DSC measurements were performed using a TA instrument (New Castle, Delaware) DSC 200 under nitrogen atmosphere with a sample purge flow of 50 mL/min. 10 mg of the composites samples were used each time in a sealed aluminum pan. The samples were heated to 250°C at a rate of 10°C/min to eliminate the heating history. Then they were cooled below 0°C at a

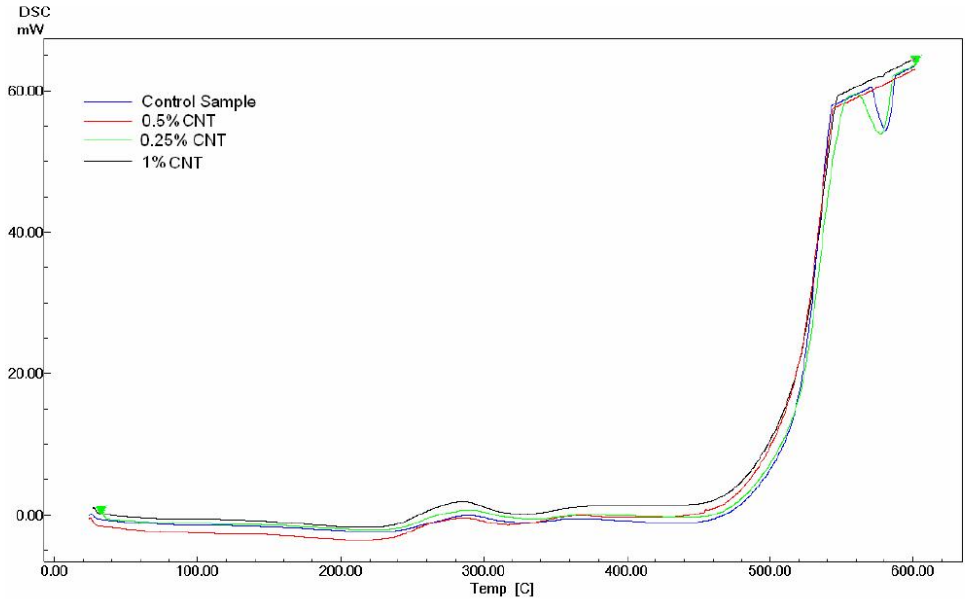

Figure 9 : DSC curves of Kevlar composite enhanced with SiC sample

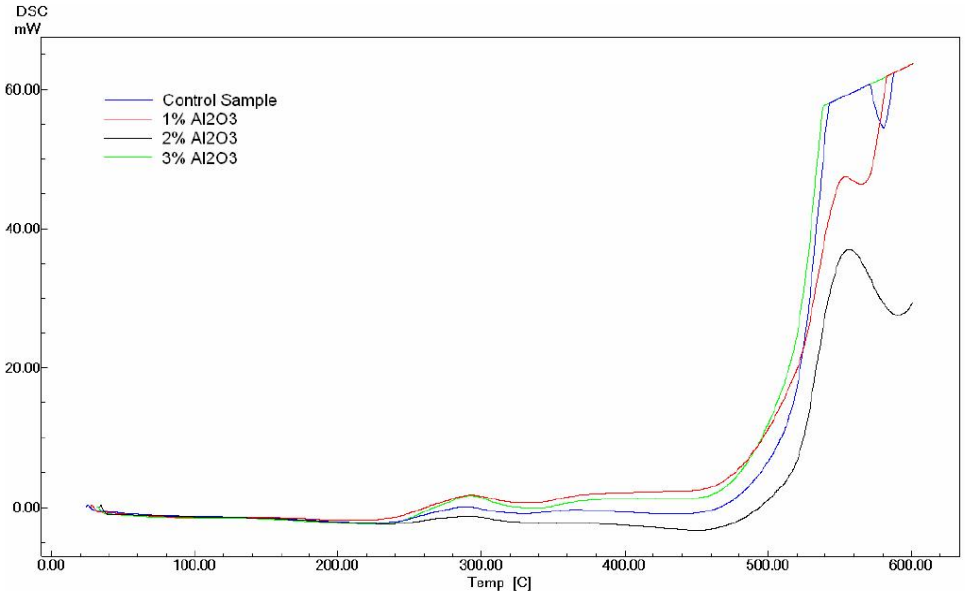

Figure 10 : TGA curves of Kevlar composite enhanced with Al_2O_3 sample

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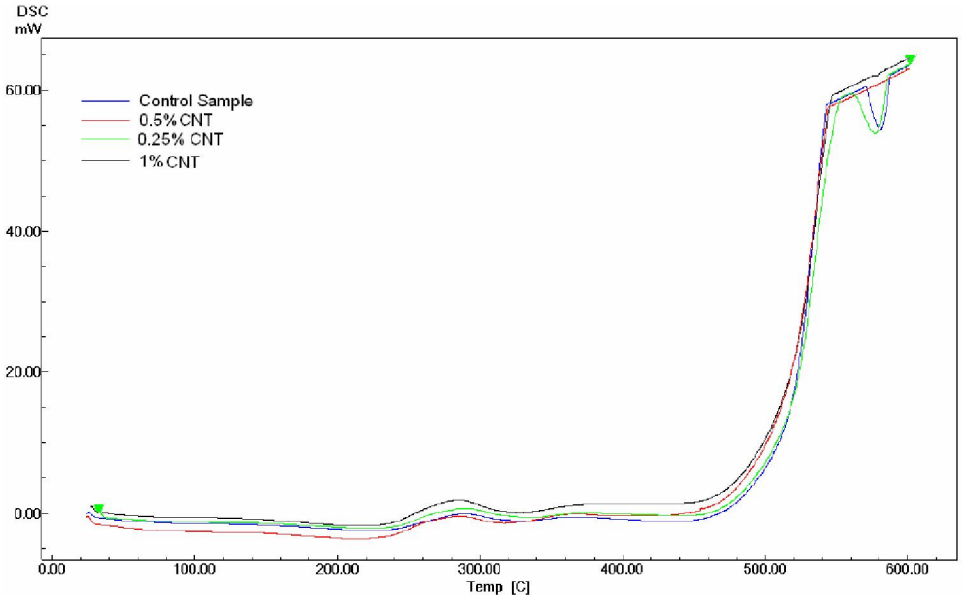

Figure 11 : DSC curves of kevlar composite enhanced with CNT sample

TABLE 10 : DSC results

Sample	Glass Transition Temperature (°C)
K	222.81
S1	212.67
S2	216.96
S3	221.56
A1	218.76
A2	223.46
A3	228.18
C1	223.33
C2	214.8
C3	211.73

rate of 10°C/min and then heated at the same rate to a temperature of 500°C.

Figures 9-11 shows the DSC results of K, S, A and C samples compared to the control one. TABLE 10 summarizes these results. It can be seen from these figures that the addition of nanofillers did not significantly affect the glass transition temperature.

CONCLUSIONS

The nano indentation results showed higher elastic modulus than the three point bending results, this was due to the difference in local and bulk properties, the nano particles expected to affect polymer chain mobility and kinetics in their near vicinity.

The enhancement in mechanical properties of the nano-fillers Kevlar composites didn't accompany considerable changes in the thermal properties. The Decomposition temperature of pure epoxy resin was increased by the addition of the nano-additive. The resin/Kevlar nano-composites experienced direct decomposition without melting. The effect of the weight percentage of the nano-material on the glass transition temperature of the epoxy resin/Nano-material composite was not significant; the results show small variation in the glass transition and decomposition temperatures for all composites.

REFERENCES

[1] Saud Aldajah, Yousef Haik; "Transverse strength enhancement of carbon fiber reinforced polymer composites by means of magnetically aligned carbon nanotubes", Materials & Design, **34**, 379-383, February, **(2012)**.

[2] Kamal Moustafa, Saud Aldajah, Saleh Hayek, Ammar Alomari, Yousef Haik; "Role of nanofillers in low speed impact enhancement of composites", Journal of Composite Materials, Accepted, **(2013)**.

[3] Yousef Haik, Saud Aldajah, Kamal Moustafa, Ammar Alomar; "Thermal characterization of nanoclay nanocomposites", GJRE-A, **14(2)** Version 1.0, 39-44 **(2014)**.

[4] AAlomari, S.Aldajah, S.Hayek, K.Moustafa, Y.Haik; "Experimental investigation of the low speed impact characteristics of nanocomposites", Materials

& Design, **47**, 836-841 **(2013)**.

[5] Saud Aldajah, Ghydaa Alawsi, Safaa Abdul Rahmaan; "Impact of sea and tap water exposure on the durability of GFRP laminates" Materials & Design, **30(5)**, 1835-1840, May **(2009)**.

[6] J.K.Chen, Firooz A.Allahdadi, Theodore C.Carneyb; "High-velocity impact of graphite/epoxy composite laminates", Composite Science and Technology, **57**, 1369-1379, **(1997)**.

[7] Ercan Sevkat, Benjamin Liaw, Feridun Delale, Basavaraju B.Raju; "A combined experimental and numerical approach to study ballistic impact response of S2-glass fiber/toughened epoxy composite beams", Composites Science and Technology, **69**, 965–982 **(2009)**.

[8] Hyonny Kim, Douglas A.Welch, Keith T.Kedward; "Experimental investigation of high velocity ice impacts on woven carbon/epoxy composite panels", Composites: Part A, **34**, 25–41 **(2003)**.

[9] S.R. Reid, G.Zhou; "Impact behavior of fiber-reinforced composite materials and structures", Florida, CRC Press LLC, **(2000)**.

[10] ASTM international, "Test method for measuring the damage resistance of a fiber-reinforced polymer matrix composite to a drop-weight impact event", American Society for Testing and Materials D 7136, West Conshohocken, PA, **(2000)**.

[11] M.Sadighi, R.C.Alderliesten, R.Benedictus; "Impact resistance of fiber-metal laminates: A review", International Journal of Impact Engineering, **49**, 77–90 **(2012)**.

[12] W.C.Oliver, G.M.Pharr; "A new improved technique for determining hardness and elastic modulus using load and sensing indentation experiments", Journal of Materials Research, **7**, 1564-1582 **(1992)**.

[13] D.J.Shuman, A.L.M.Costa, Andrade; "Calculating the elastic modulus from nanoindentation and microindentation reload curves", Materials Characterization, **58**, 380-389 **(2007)**.

[14] W.C.Oliver, G.M.Pharr; "Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology", Journal of Materials Research, **19**, 3-20 **(2004)**.

[15] Q Series Manual, "TGA Thermogravimetric Analyzer", TA Instruments, Waters LLC, **(2006)**.

[16] Q Series Manual, "DSC Differential Scanning Calorimeter", TA Instruments, Waters LLC, **(2007)**.