# Chemical, mechanical, thermal analysis of a nano ceramic embedded novel composite material for automotive and industrial applications

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***Abstract***- Study describes the processing of nano ceramic/ polyester composite using a polyester matrix with different mixing ratios of nano-hydroxyapatite ceramic as the reinforcement and the filler. Processed products were analyzed to find out; physical, chemical, mechanical, thermal properties including reinforcement particle size distribution, composition, presence of functional groups, crystallography, surface morphology, structural features, thermal stability, a variation of glass transition temperatures and tensile properties. Results have shown high thermal stability, material stability with good mechanical properties in the processed nano-products. The study concluded, after incorporating polyester with nano-ceramic lead to have products with higher properties for automotive and industrial applications.

***Index Terms***- Hydroxyapatite, Solid state sintering, Polymer matrix composites, Automotive applications

## I. INTRODUCTION

Composites consist of two or more constituents that are not soluble in each other, in terms; those constituent materials are combined on a macroscopic scale to form a useful third material. The harder reinforcing phase available in the form of particles, flakes, woven mats, fibers or whiskers etc. imbedded in the matrix phase which may ductile and continuous. [1]

Specially, researchers have shown those lightweight composite materials offer a great potential for increasing efficiency of vehicles while requiring less energy, boosting the fuel economy, maintaining safety and reducing the exhaust emission with improved ride performance including reduction of noise, vibration, harshness etc. [14-18]

Considering that, we have processed a nano ceramic composite with polyester as the matrix material and a nano ceramic powder which inhouse synthesized material as the reinforcement. Used nano hydroxyapatite ceramic filler was solid state synthesized value-added product of Chloroapatite mineral that has several industrial applications due to its range of properties. [19-28] 101 Polyester (PA) was chosen as the light weight, low cost polyester matrix. It is a medium thixotropic, pre-accelerated, unsaturated, orthophthalic polyester resin with high wear resistance which is particularly suitable for molding casting and laminating in the manufacturing industries of boats, water tanks, bathtubs, portable, flower pots, chairs, trays etc. [29]

This study is fully aimed to process and analysis novel nano ceramic polyester composite which can be used for industrial applications including automotive structural applications for car bumpers, brakes, clutch plates etc.

## II. MATERIAL AND METHODS

### *A. Composite preparation*

Table 1. Masses of ceramic filler and polyester resin mixtures for composite samples

| Sample Name | Composition (Wt%) | |
|---|---|---|
| | Polyester mixture | Nano-hydroxyapatite ceramic |
| NP material (control) | 100 | 0 |
| SSHAp 5% composite | 95 | 5 |
| SSHAp 10% composite | 90 | 10 |
| SSHAp 15% composite | 85 | 15 |
| SSHAp 20% composite | 80 | 20 |
| SSHAp 25% composite | 75 | 25 |
| SSHAp 30% composite | 70 | 30 |
| SSHAp 35% composite | 65 | 35 |
| SSHAp 40% composite | 60 | 40 |
| SSHAp 45% composite | 55 | 45 |
| SSHAp 50% composite | 50 | 50 |
| SSHAp 55% composite | 45 | 55 |
| SSHAp 60% composite | 40 | 60 |
| SSHAp 65% composite | 35 | 65 |
| SSHAp 70% composite | 30 | 70 |
| SSHAp 75% composite | 25 | 75 |
| SSHAp 80% composite | 20 | 80 |
| SSHAp 85% composite | 15 | 85 |
| SSHAp 90% composite | 10 | 90 |
| SSHAp 95% composite | 5 | 95 |

First solid-state synthesized ceramic was ball milled using a planetary ball mill (TENCAN, XQM-0.4A) over 24 hrs to obtain

more fine particles. Resulted nano-hydroxyapatite powder was taken as the ceramic filler material. [19, 20]
Next masses of the filler and polyester resin mixture were mixed according Table 1 below to process the series of nano-ceramic incorporated polyester composite samples.

The masses of the 101PA, unsaturated polyester resin was calculated according to the required volume of cast, the Cobalt naphthalate accelerator and the MEKP, hardener was added as weight % with an amount of 0.05% and 1 % respectively.
Using an overhead stirrer, nearly for 150 rpm stirring rate, weighed amounts of polyester resin, hardener, filler and the catalyst were mixed together thoroughly for nearly 30 minutes at the room temperature continuously and slowly to avoid bubbling during mixing. After that, the mixture was uniformly poured from one corner into the molds until the required level of filling (to avoid bubbles formation which may led to cast damage).
Then the mixture was left in the mold for 24 hrs at room temperature to solidify. Finally, after placing them inside a dryer oven for 48 hrs at (60-75) °C to reveal complete polymerization, best coherency, and to relieve residual stresses; samples were taken out from the molds to do further analysis.

*B. Composite analysis*

Solid state sintered ball milled hydroxyapatite powder was analyzed under Malvern nano- particle analyzer (MAL1184267) to find out its particle size distribution. Then the NP material, crosslinked pure polyester matrix material without reinforcement was taken as "control" and series of ceramic filler added polyester matrix composites were analyzed with Fourier transform infra-red spectroscopy (Bruker – Alpha [FTIR] spectroscopy) over the region 400–4000 $cm^{-1}$ using KBr pellet technique with the resolution of 4 $cm^{-1}$ to obtain composition, mainly the presence of functional groups. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM with EDS) (Hitachi SU6600 with AZtec software) was carried out to examine elementary composition, presence of impurities and surface morphology micro/nano structural features of all processed composites. Also, the sample mixtures of all new nano-hydroxyapatite ceramic polyester composites were studied using X-ray diffractometer (Rigaku – Ultima. IV diffractometer) in reflection mode with CuKα1: 0.154 nm radiation, scanned speed of 1.5° $min^{-1}$ within 15°–80° ranged angles as 2θ values to determine their crystallographic phases. Differential scanning colorimetry was done for the processed composites using DSC PT1000 (DSC_A_7016_17_0) instrument with N environment, 100 $^0C$ $min^{-1}$ heating rate up to 650 $^0C$ maximum temperature to find out their variation of glass transition temperatures (Tg values). After that, Thermo gravimetric analysis (TGA) was done only for contro, SSHAp 15% and SSHAp 50% composite samples using a thermal analyzer (SDT Q600) with N environment, 20 °C $min^{-1}$ heating rate and 1450 °C maximum temperature to find out the thermal stability of composite with the addition of filler. At last, Tensile test was performed at room temperature using Tensile Strength Tester (Testometric M500-50CT) for all composite samples including control to find out best mixing ratio of filler and the polyester matrix having highest tensile properties. For that, ASTM E 8/E 8M - 08 standard sample specimens were used.

## III. RESULTS AND DISCUSSION

*A. Nano particle Analysis*

Particle analysis was performed for hydroxyapatite ceramic filler samples to find out its distribution of size. Results have shown diameter of filler particle, distributed around average value of 419.7 nm with a standard deviation of 56.85 nm. It has proven that the filler particles in nano meter range which tend to be in spherical shape.

*B. EDS Analysis*

Table 2. Comparison of EDS results between NP material, SSHAp 15% and SSHAp 50% composites

| Element % | NP material | | SSHAp 15% composite | | SSHAp 50% composite | |
|---|---|---|---|---|---|---|
| | Avg | SD | Avg | SD | Avg | SD |
| C | 76.9 | 0.91 | 65.4 | 0.31 | 66.7 | 0.42 |
| O | 22.8 | 1.01 | 33.7 | 0.65 | 32.4 | 0.73 |
| Ca | - | - | 0.6 | 0.25 | 0.6 | 0.22 |
| P | - | - | 0.2 | 0.13 | 0.2 | 0.12 |
| Si | 0.3 | 0.12 | 0.1 | 0 | 0.1 | 0 |

Avg - Average value SD - Standard Deviation

As indicated in Table 2 it can be clearly stated that NP material is only comprised of normal polyester resin, hardener and accelerator consists of C, O and Si elements. Comparing it's result with SSHAp 15% and SSHAp 50% polyester composites results show that; after the addition of nano-hydroxyapatite as the ceramic filler, Ca and P elements have added to the polyester composites. Also, Avg and the SD values describe that the repetition of values is more consistent.

*C. FTIR analysis*

According to the Figure 1; all ceramic added polyester composites consists of 560 $cm^{-1}$,640 $cm^{-1}$,963$cm^{-1}$,1028 $cm^{-1}$,1110 $cm^{-1}$ and 3572 $cm^{-1}$ peaks related to the hydroxyapatite ceramic. That may occur with the addition of ceramic filler. Further the 560 $cm^{-1}$,640 $cm^{-1}$, 963 $cm^{-1}$, 1110 $cm^{-1}$ and 1028 $cm^{-1}$peaks related with the presence of $PO_4^{-3}$ groups and the 3572 $cm^{-1}$ peak exhibits the characteristic $OH^-$ peak in the hydroxyapatite.
Also, some peaks nearly 1117 $cm^{-1}$, 1286 $cm^{-1}$, 1726 $cm^{-1}$ and 2986 $cm^{-1}$ can be found within NP material as well as in all ceramic filler added polyester composites. Those peaks directly related to the polyester group of the mixture. Normally, 1117 $cm^{-1}$, 1286 $cm^{-1}$, 1726 $cm^{-1}$ and 2986 $cm^{-1}$ related with the C-O, C=O and C-H (alkyl) stretches accordingly. [19, 20]

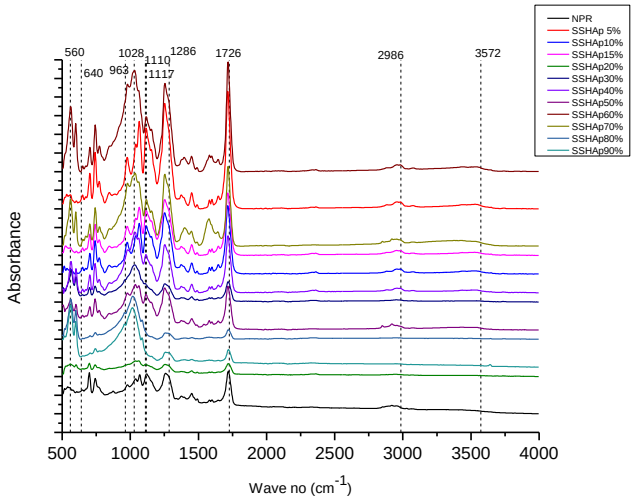


Figure 1. Resulted FTIR curves for processed composites

*D. XRD analysis*

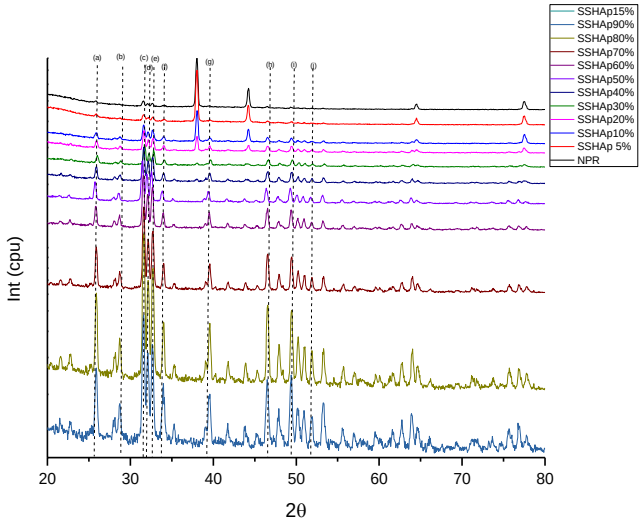


Figure 2. Resulted XRD patterns for processed composites

As mentioned in the Figure 2, when consider (a) - (j) peaks which are mentioned in the resulted XRD patterns for processed ceramic polyester composites apart from NP material related to the 002, 210, 211, 112, 300, 202, 310, 222, 213 and 004 crystallographic phases of hexagonal hydroxyapatite ceramic filler in order. Both peaks which occurred in the processed ceramic polyester composites as well as the NP material may occur due to the polyester. Also considering the XRD pattern it can be concluded that the processed composites contain crystalline properties. [19, 20]

*E. DSC analysis and Tensile test*

Table 3 & Figure 3 have shown; with the addition of ceramic up to 15%, processed composites' Tg values have increased due to the increasement of crosslinked density or with the increasement of number of cross links between polyester molecules and internal heat transfer.[30] As that, tensile strength /mechanical and thermal properties of the composites are increased parallelly. With the excess addition of ceramic than 15% Tg value has decreased that may sue to the free volume occupied, agglomerations and the sample degradation etc. The highest average value for tensile strength can be found within SSHAp 15% composite samples. Therefore, it can be concluded 15% ceramic filler added polyester composites is the best mixing ratio.

Table 3. DSC and Tensile analyzed results for all processed composites

| Sample Name | Glass transition temperature Tg ($^0$C) | Maximum Tensile Strength $\sigma_{Max}$ (MPa) | |
|---|---|---|---|
| | | Avg value | SD value |
| NP material (control) | 72.5 | 14.3 | 0.08 |
| SSHAp 5% composite | 74.9 | 14.1 | 0.79 |
| SSHAp 10% composite | 75.8 | 13.5 | 0.83 |
| SSHAp 15% composite | 77.9 | 18.7 | 1.25 |
| SSHAp 20% composite | 76.7 | 15.6 | 1.84 |
| SSHAp 30% composite | 74.8 | 12.7 | 1.15 |
| SSHAp 40% composite | 70.0 | 10.4 | 0.76 |
| SSHAp 50% composite | 71.9 | 5.9 | 1.17 |
| SSHAp 60% composite | 71.7 | 9.2 | 1.23 |
| SSHAp 70% composite | 68.9 | 3.8 | 0.98 |

Avg -Average value SD-Standard Deviation
*** 80%, 85%, 90% and 95% ceramic filler added polyester composites are too much brittle. Therefore, there DSC and Tensile results have not included in the table.

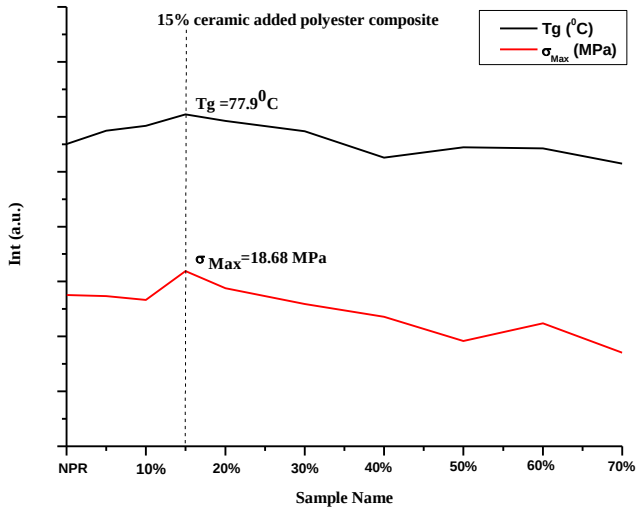


Figure 3. Comparison of Tg and $\sigma_{Max}$ values of processed composites

*F. TGA analysis*

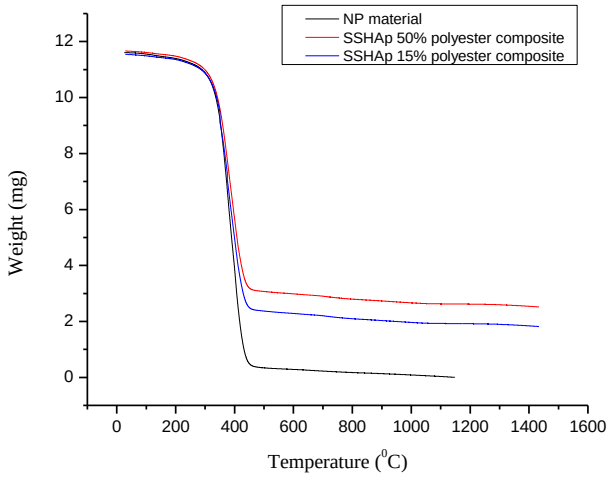


Figure 4. Comparison of TGA results between NP material, SSHAp 15% and SSHAp 50% composites

Similar pattern of weight loss can be found within all three curves in the Figure 4. With the addition of hydroxyapatite ceramic filler, composites overall weight loss has decreased than the control, which may occur due to higher heat absorbance of hydroxyapatite ceramic than the polyester. Therefore, it can be concluded that amount of weight loss of control has reduced after incorporating nano hydroxyapatite ceramic as the reinforcement as well as the filler and the ceramic filler added polyester composites perform good thermal stability and good material stability in nature and applications than the pure crosslinked polyester material without reinforcement.

*G. SEM analysis*

Considering Figure 5-8 SEM images of all processed composites; 100k images have shown that all composites have unique continuous surface in the 500nm range. Those images contain boundaries or cracks that may occur due to the gold coating of samples while analyzing samples under the SEM. When examine the 5k images; they have clearly exhibited that free volume has reduced with the addition of nano ceramic filler within SSHAp 15% and SSHAp 50% samples and with the excess addition of nano ceramic filler, sample lead to have some porous structure which improve the brittleness of structure as shown in SSHAp 90%. Those results coincided with the Tensile & DSC results as well.

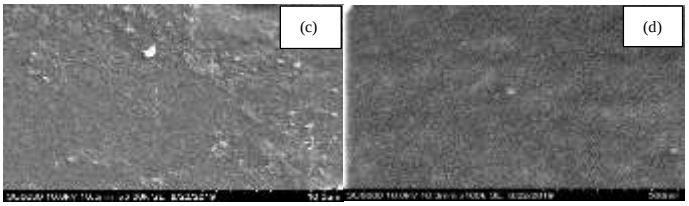


Figure 5. SEM images of NP material; 10kv, (c)5k (d)100k

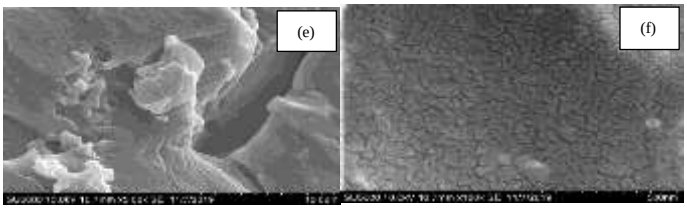


Figure 6. SEM images of SSHAp 15% composite; 10kv, (e)5k (f)100k

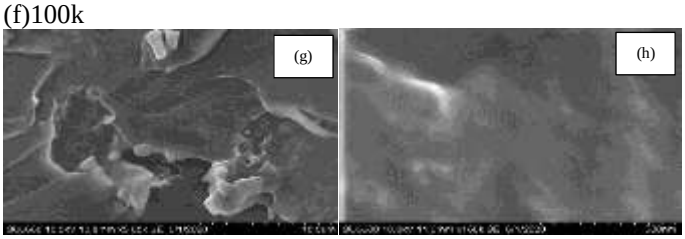


Figure 7. SEM images of SSHAp 50% composite; 10kv, (g)5k (h) 100k

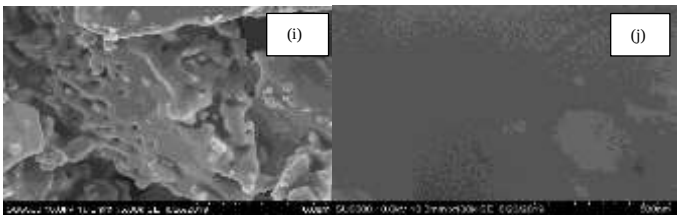


Figure 8. SEM images of SSHAp 90% composite; 10kv, (i)5k (j)100k

## IV. CONCLUSION

Finally, the study concludes that processed nano-hydroxyapatite ceramic filler added polyester composites can be used for automotive applications such as car bumpers, brake pads/liners, internal and external structural parts etc. Also, it can be used for other industrial applications such as for structural parts in building constructions, bridge repairing, for sports ware - cricket baseball etc. [31,32] considering its better tensile properties good material stability and thermal stability in nature than the pure polyester crosslinked material without reinforcement.

Hydroxyapatite ceramic has a higher melting point nearly 1670 $^0$C and with that it's ability of absorbing more heat energy lead to process nano-hydroxyapatite incorporated polyester composites with better thermal and material properties than the pure polyester resin. Amongst them SSHAp 15% composite has shown highest Tg value and higher tensile properties. At, 15% Hydroxyapatite nano-composite has increased its crosslink density due to high thermal absorption of nano ceramic with high heat conductivity and higher surface area due to nano particle size; beyond that maximum tensile peek has passed and oxidative degradation starts during fully cured composites.

Resulted nano hydroxyapatite ceramic added polyester composites consisted of unique continuous composite surface and excess addition of ceramic, above 75% increases brittleness. That may occur due to the decrease of free volume, decrease of polyester and ceramic bonding capacity with the addition of ceramic as mentioned in the SEM images. Therefore, excess

addition of ceramic, above 75% more porous, brittle structure can be found within processed ceramic polyester composites.

## V. ACKNOWLEDGEMENT

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