

MECHANICAL PROPERTIES OF POLYESTER AS HYBRID COMPOSITES

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Abstract:

The aim of this work is to study the effect of zirconia, boron carbide, and their mixture with unsaturated polyester (hybrid composites) on mechanical and thermal properties of unsaturated polyester. Results show an improvement in the hardness by 41, 38, and 21% at 5% ZrO_2 , B_4C , and $ZrO_2 + B_4C$ respectively, bending increasing by 193, 146, and 121% at 1% additives from ZrO_2 , B_4C , and $ZrO_2 + B_4C$ respectively. Also results show an increasing in the compression strength when added 5% from above additives and the improvement percent was 29, 22, and 19% respectively. The additives materials show a less effect in thermal conductivity comparing with mechanical properties, this due to that, the reinforcement materials has a low thermal conductivity. An addition 5% of $ZrO_2 + B_4C$ shows an improvement in the weight loss by 33%. It is concluded that ZrO_2 has the ability to improve the general properties of polymer such as, hardness, bending, and compression strength, this mechanical properties which is the highly demanded property in the polymer applications as well as B_4C improves the polymer properties less than ZrO_2 .

الخواص الميكانيكية للبولي استر الغير مشبع كمادة مركبة هجينة

الخلاصة:

الهدف من البحث الحالي هو دراسة تأثير الزركونيا وكاربيد البورون والخليط منهما مع البولي استر الغير مشبع (كمادة مركبة هجينة) على الخواص الميكانيكية والحرارية للبولي استر الغير مشبع. بينت النتائج تحسن في الصلادة بمقدار 41 و 38 و 21% عند إضافة 5% من الزركونيا وكاربيد البورون والخليط منهما على التوالي، مقاومة الانحناء ازداد بمقدار 193 و 146 و 121% عند إضافة 1% من الزركونيا وكاربيد البورون والخليط منهما على التوالي. النتائج أظهرت أيضا تحسن في مقاومة الانضغاط عند إضافة 5% من المضافات أعلاه فكانت نسبة التحسن 29 و 22 و 19% على التوالي. المضافات أظهرت اقل تأثير على الموصلية الحرارية بالمقارنة مع الخواص الميكانيكية ، يرجع ذلك إلى انخفاض الموصلية الحرارية لمواد التقوية المستخدمة. إضافة 5% من الزركونيا وكاربيد البورون كخليط اظهر تحسن في مقدار فقدان الوزن 33%. يمكن ان نستنتج بان الزركونيا لها القابلية على تحسين الخواص العامة للبولىمر مثل الصلادة ومقاومة الانحناء ومقاومة الانضغاط و تعتبر هذه الخواص كثيرة الأهمية في التطبيقات البوليمرية، بالإضافة إلى تحسن تلك الخواص عند إضافة كاربيد البورون ولكن بنسبة اقل من الزركونيا.

Introduction:

The word composite has a modern ring. But using the high strength of fibers to stiffen and strength cheap matrix materials is probably older than the wheel. The composites it has grown rapidly in the past 30 years with the development of fibrous composites. Composites need not be made of fibers, plywood is a lamellar composite, particular composites are made by blending silica flour, glass beads, even sand into a polymer during processing⁽¹⁾.

There are several researchers who have investigated the effect of reinforcement materials on polymer properties. The structural integrity of combinations of graphite and glass fibers with a toughened epoxy matrix under dynamic impact loading were studied by Christors and Levon ⁽²⁾. Zhang used boron carbide as nanowires with uniform carbon nitride coating on a silicon substrate using a simple thermal process ⁽³⁾. Huang studied the bioactive and dielectric properties of zirconia thin films ⁽⁴⁾. Burdick studied the thermal expansion, thermal diffusivity and elasticity measurements, over a range of temperatures, were made for zirconia bodies modified by additions of MgO, Al₂O₃, CeO₂, CaO, Ti, and Zr ⁽⁵⁾. A study of lattice dielectric and thermodynamic properties of yttria stabilized zirconia (YSZ) crystals as a function of yttria concentration is reported by Kah ⁽⁶⁾.

Materials used:

Zirconia ZrO₂:

Zirconia ceramics have a martensite-type transformation mechanism of stress induces, giving the ability to absorb great amounts of stress relative to other ceramic materials. It exhibits the highest mechanical strength and toughness at room temperature. Zirconia has excellent wear, chemical and corrosion resistance and low thermal conductivity. Zirconia is an extremely refractory material. It offers chemical and corrosion inertness to temperatures well above the melting point of alumina. The material has low thermal conductivity. It is electrically conductive above 600°C and is used in oxygen sensor cells and as the susceptor (heater) in high temperature induction furnaces. With the attachment of platinum leads, nernst glowers used in spectrometers can be made as a light emitting filament which operates in air.

Pure zirconia exists in three crystal phases at different temperatures. At very high temperatures (>2370°C) the material has a cubic structure. At intermediate temperatures (1170 to 2370°C) it has a tetragonal structure. At low temperatures (below 1170°C) the material transforms to the monoclinic structure. The transformation from tetragonal to monoclinic is rapid and is accompanied by a 3 to 5 percent volume increase that causes extensive cracking in the material. This behavior affects the mechanical properties of fabricated components during cooling and makes pure zirconia useless for any structural or mechanical application.

Common applications include extrusion dies, wire and pipe extension, guide and other wear rollers, pressure valves, and bearing materials. Table (1) shows the main properties of zirconia ⁽⁷⁾.

Table (1) Typical properties of zirconia.

Density (g.cm ⁻³)	6.04
Use temperatures up to (°C)	2400
Hardness (Knoop 100g) (kg.mm ⁻²)	1600
Fracture Toughness (MPa.m ^{-1/2})	13
Young's Modulus (GPa)	207
Dielectric Strength (kV/mm)	9
Thermal Conductivity (at 25°C) (W/m.K)	2.7
Thermal Expansion Co-eff. x10 ⁻⁶ (°C)	11
Thermal neutron capture cross section (barn)	-----

Boron Carbide:

A compound of boron and carbon, especially B_4C , an extremely hard, black crystalline compound or solid solution. It is used in control rods for nuclear reactors, and as a reinforcing filament in composite structural materials.

Boron Carbide is a well reputed abrasive material. Its hardness is just below diamond and for this reason it is extensively used as a lapping agent in place of diamond. In the finishing of semiprecious gems such as ruby, synthetic corundum etc. Boron carbide powder achieves 60% of the efficiency of diamond paste. It is also used for polishing high speed steel and carbide tip tools and wire drawing dies. It is reported in the literature that the development of hard metal cutting tools and high speed steels could not have been possible without the availability of boron carbide as a grinding and tapping medium. Table (2) shows the main properties of boron Carbide ⁽⁷⁾.

Table (2) Typical properties of boron carbide.

Density ($g.cm^{-3}$)	2.52
Melting Point ($^{\circ}C$)	2445
Hardness (Knoop 100g) ($kg.mm^{-2}$)	2900-3580
Fracture Toughness ($MPa.m^{-1/2}$)	2.9 - 3.7
Young's Modulus (GPa)	450 - 470
Electrical Conductivity (at $25^{\circ}C$) (S)	140
Thermal Conductivity (at $25^{\circ}C$) ($W/m.K$)	30 - 42
Thermal Expansion Co-eff. $\times 10^{-6}$ ($^{\circ}C$)	5
Thermal neutron capture cross section (barn)	600

Unsaturated polyester:

Unsaturated polyester consists of unsaturated material maleic anhydride and ethylene glycol there are dissolved in a reactive monomer (styrene) as shown in figure (1), when catalyst is added (Methyl Ethyl Ktone Peroxide MEKP) and accelerator (Cobalt Naphanate) the double bonds open and an addition reaction leads to the formation of a highly cross – linked network ^(8,9).

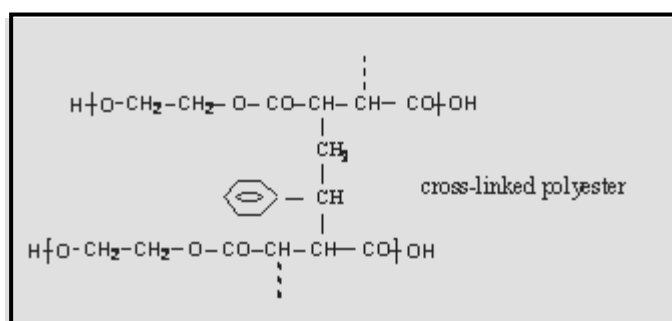


Figure (1): Unsaturated polyester structure.

Unsaturated polyester was used as the matrix available locally without detail specifications. The mixing ratio used was 100g of UPE resin with 0.5g accelerator (Cobalt naphthenate) and 2g hardener (Methyl Ethyl Ketone peroxide).

Experimental Procedure:

Zirconia Fiber Preparation:

The route of ceramic fibers involves the preparation of a concentrated solution with which to impregnate a conventional rayon or cotton thread chosen for its wicking rate. During heating two processes occur; the first, solution is rapidly crystallized when solvent molecules are flash- evaporated, and the second cotton is pyrolysed, leaving behind a skeleton of the relevant oxide. This pyrolysis has to be undertaken carefully to avoid disruption, and is responsible for the hollow tube morphology. The evaporation stage remove solution from the surface to cause a degree of back-wicking leaving a center core with no solution. The more rapidly the evaporation can be achieved, the smaller will be the cross section of the hollow tube.

The manufacturing process of Zirconia fiber is proprietary, although certain details have been made available which outline the general fabrication route as illustrated in Fig (2). The innovation fabrication technique involves the use of an organic precursor fiber, rayon as an internal former. The organic fiber is impregnated with an aqueous solution of zirconium chloride. During drying the metallic salts are deposited within the organic fiber which can be burnt off by controlled oxidation.

The fabrication process was achieved by these steps:

1. Preparation the solution of the Zirconium oxychloride in a concentration of 1-M solution.
2. Selection cotton as a substrate.
3. Impregnation of the cotton from the solution 3 day and extraction the cotton from the drying in furnace at 100°C.
4. Heat treatment was achieved at two stages, heat treated to a temperature 350°C slowly, need 4 hrs. to reaching this temperature then raised the temperature to 600°C and leave the cotton at this temperature to 1 hr. then slowly cooled at furnace⁽¹⁰⁾.

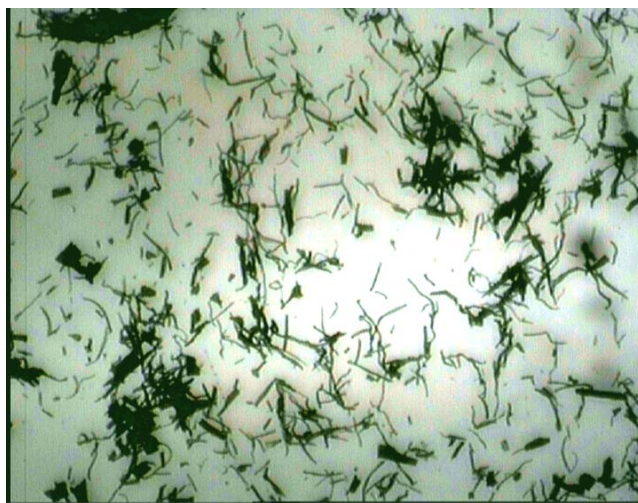


Figure (2): illustrated Zirconia fiber.

Results and Discussion:

Many tests are carried on to define the extent of the addition effect of the different percentages of zirconia fibers and boron carbide and their mixture on the properties of the unsaturated polyester, such of these tests are:

1) Hardness Test:

Brinell hardness was performed according to the ASTM D1415 with samples dimension (30Øx6) mm, by using universal testing machine (PHYWE). Figure (3) shows the effect of zirconia fibers, boron carbide, and their mixture on unsaturated polyester hardness, the results show that, hardness increased with increasing

reinforcement materials percent this due to diffusion of reinforcement particles between the polymer chains results in movement inhibition of these chains that increases its stability besides to hardness for this additives are high, and the results show the hardness with zirconia higher than polymer reinforced with boron carbide because the first materials used as fibers (see figure 2) and this configuration gives more stability to polymer chine and this will reflected on hardness ⁽¹¹⁾.

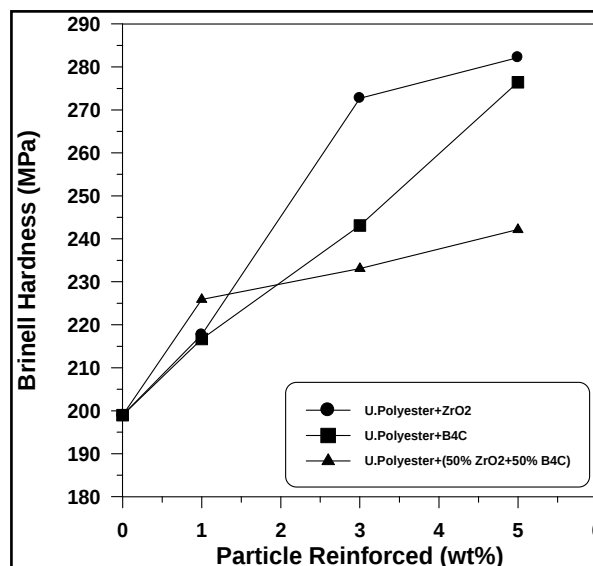


Figure (3) Effect of Particle contents on Hardness.

2) Bending Strength Test:

By using same universal testing machine and were performed according to the D790-86 with samples dimension (120x16x6) mm. The effects of reinforcement materials percent on bending of polymer shown in figure (4), from this curve can be observed that with low percent of additives the bending strength increasing this due to stability of polymer chins because the diffusion of reinforcement particles between the polymer chains ⁽¹¹⁾, while in high percent of additives the bending strength decreases this due to the particles extended the distances between the polymer molecules, i.e. breaking the intermolecular forces between these molecules and this lead to decreasing the cross –linking density ⁽¹²⁾.

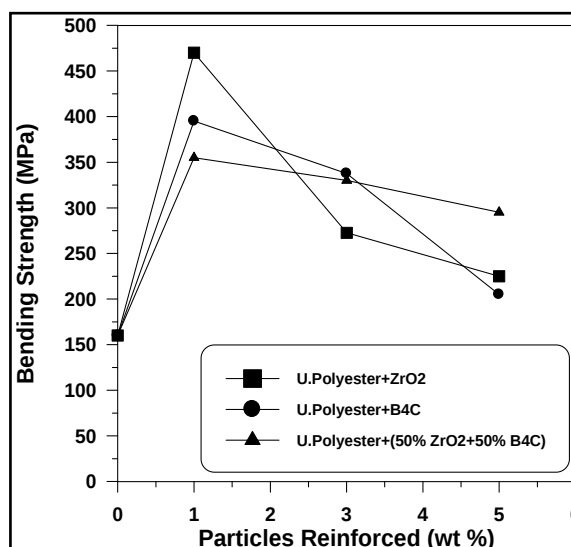


Figure (4) Effect of particle contents on bending strength.

3) Compression Strength Test:

Figure (5) shows the effect of zirconia fibers, boron carbide, and their mixture on compression strength of unsaturated polyester composite. The compression strength increasing with increases the additives percent this due to same above reasons and this additives work as filler which distances between the polymer molecules and the compact of composites was increasing and the compression also increased.

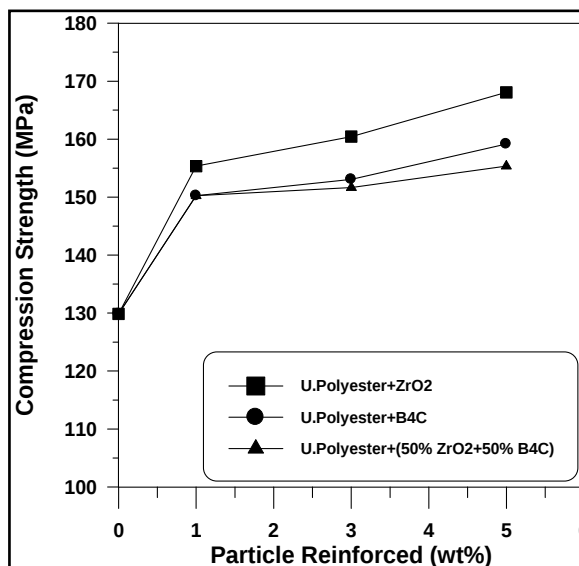


Figure (5) Effect of Particle contents on compression strength.

4) Thermal conductivity Test

It is noticed from Figure (6) that, the additive doesn't show effect on thermal conductivity of the polymer, this is due the reinforcement materials was used have low thermal conductivity.

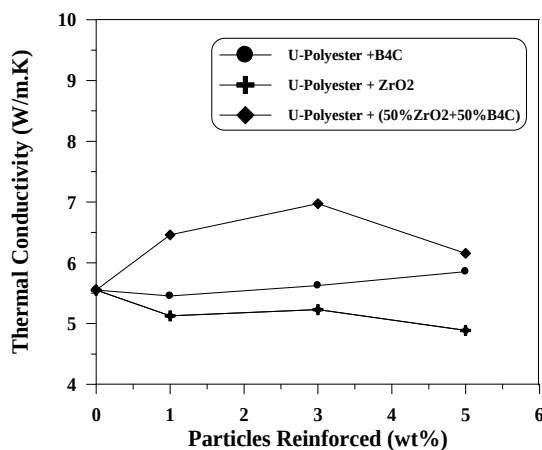


Figure (6) Effect of Particle contents on thermal conductivity.

5) Effect of Heat on Samples Weight Loss:

The polymers samples with and without additives are exposed to 120 °C. This temperature is considered to be as a good accelerating test due to the large difference with the ambient temperature that polymer exposed to it.

Figure (7) shows the effect of time exposure of heat on weight loss. The addition of B₄C shows the increasing in the weight loss of the polymers; this due to

additives particles extended the distance between the molecules and breaking the intermolecular forces between them. Figure (8) shows the same result when ZrO_2 was added to polymer.

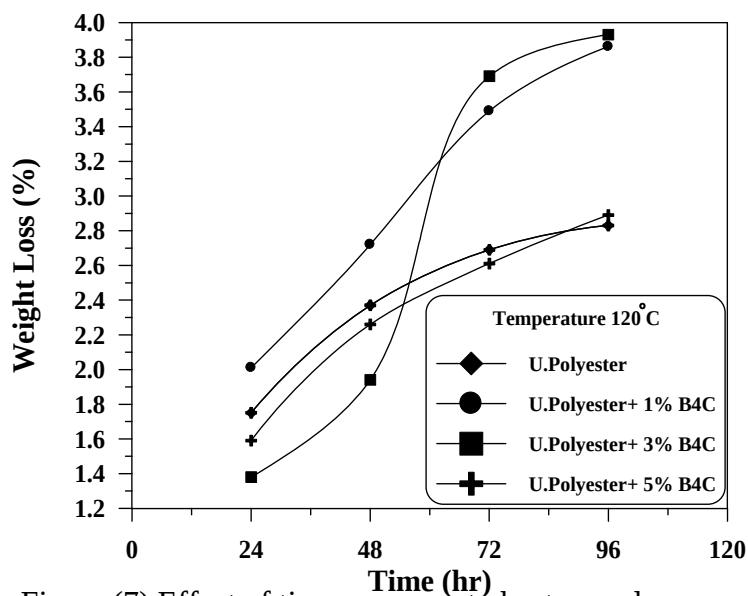


Figure (7) Effect of time exposure to heat on polymer weight loss.

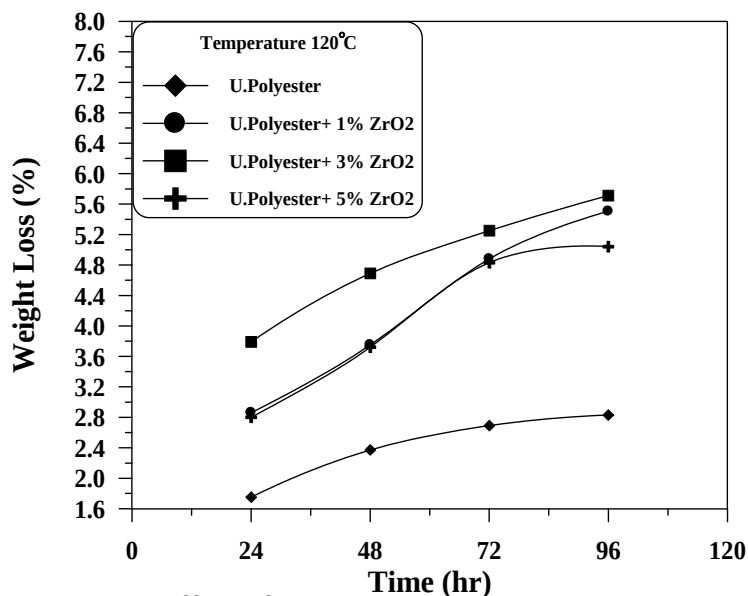


Figure (8) Effect of time exposure to heat on polymer weight loss.

Figure (9) shows that, in small percent of ($B4C + ZrO_2$) shows the increasing in the weight loss of the polymers, above these percent the weight loss depression which explained as, in the low percent additives decreasing the cross- links density between polymer molecules so the weight loss increases, while at high percent additives acts as protector to polymer molecules so the weight loss decreasing and this show clearly in figure (10).

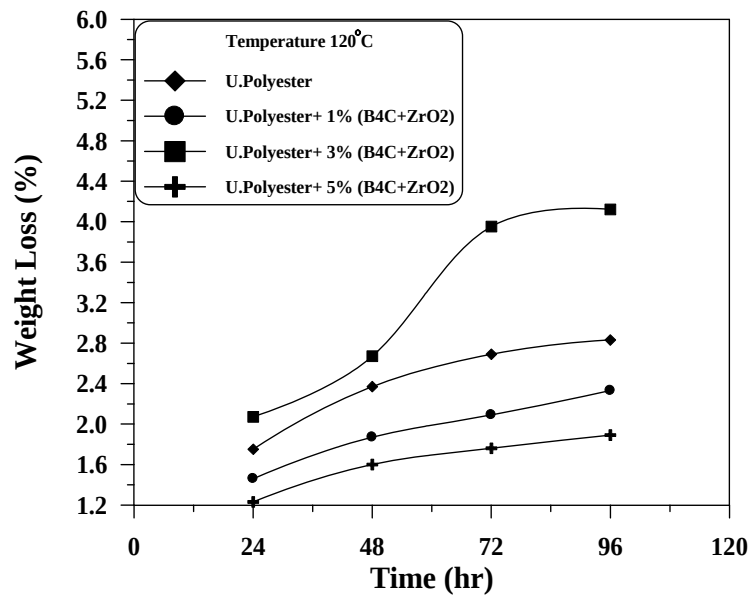


Figure (9) Effect of time exposure to heat on polymer weight loss.

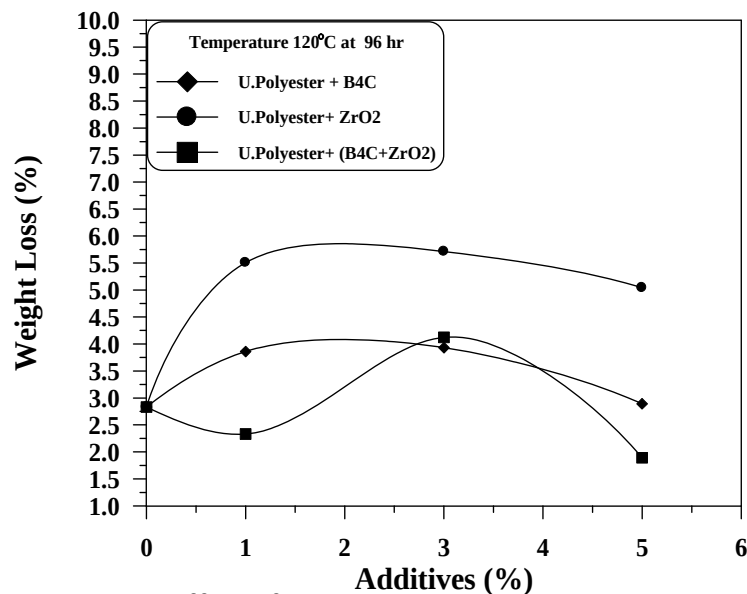


Figure (10) Effect of time additives percent on polymer weight loss.

Conclusions:

Addition of ZrO_2 , B_4C , and ZrO_2+B_4C to an unsaturated polyester resin in the 1-5% (this considered relatively low percent) shows that additives act as particulate and fibers reinforcement results in improvement in the mechanical properties of the unsaturated polyester via the resulting composite (Table 3).

Table (3) The variation of properties with addition of additives on unsaturated polyester.

Properties	Improvement Percent		
	ZrO_2	B_4C	ZrO_2+B_4C
Hardness 5% add.	41	38	21
Bending 1% add.	193	146	121
Compression 5% add.	29	22	19
Weight Loss 5% add.	-	-	33

References:

- 1-Michael F Ashby and David R H Jones, “ Engineering Materials 2”, Elsevier publisher, (2006).
- 2-Christos Chamis and Levon Minnetyan, " Impact Damage and Strain Rate Effects for Toughened Epoxy Composite Structures", NASA, New York, (2006).
- 3- H Z Zhang, R M Wang, L P You, J Yu, H Chen, D P Yu and Y Chen,” Boron carbide nanowires with uniform CN_x coatings”, New J. Phys. 9 13, Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, (2007).
- 4- Huang, Paul Chu,” Study the bioactive and dielectric properties of zirconia thin films”, Journal of Physics D: Applied Physics 40, City University of Hong Kong, China, (2007).
- 5- Burdick,R. B. ; Hoskyns,W. R.,” Research on the Thermal Properties of Zirconia”, Search DTIC's Public STINET for similiar documents, (2008).
- 6- Kah Chun Lau *and* Brett I Dunlap, J. Phys.: Condens. Matter 21 145402 (6pp), (2009).
- 7-Materials and AZojomo, "AZo Journal of Materials Online"...AZoM™.com Pty.Ltd Copyright ©, (2009).
- 8-Mathew philip and Bill Bolton, "Technology of Engineering Materials", Butter worth, Helnemann, oxford, 1st published, (2002).
- 9- Dr. Jan Gou., "Composite Materials, Mechanical Engineering" ME. S90, University of South Alabama, (2005).
- 10- I.J.MC Coil and N.J.Clark, "Forming, Shaping and Working of High-Performance Ceramics" first published by blackie and son LTD, (1988).
- 11-KaKani, "Material Science"^{1st} addition, now. Age International Publishers Ltd., (2004).
- 12-Marc Andre, Meyers and Krishan Kumar chawla, "Mechanical Behavior of Materials" Prentice Hall, New Jers