

Study the Effect of kaolin on Secondary bonds, Porosity, Mechanical properties and Thermal Stability of Polyester Composites

دراسة تأثير الكاؤولين على الاواصر الثانوية, المسامية, الخواص الميكانيكية والثباتية الحرارية للمادة المركبة ذات اساس من البولستر

Abeer Adnan Abd

Polymer department, college of engineering materials, Babylon University, Iraq

Gmail:abeeradnanabd@gmail.com

Abstract:

Unsaturated polyester resin with fillers of kaolin samples were prepared by cast molding method for polyester with filler volume fractions (5%, 10%, 15% and 20%). The thermal conductivity constant, hardness, compression strength, porosity and density were studied. This experimental investigation is aimed at assessing the performance of polymeric insulators in high temperatures applications. Shore hardness tests were used to measure the hardness. Fourier transform infrared spectroscopy (FTIR) to study the bonds which enhanced the insulating properties of polyester material compounded with filler. Polymer composites Exhibits a new UV- visible absorption band at a wavelength range (200 -375) nm, which is attributed to interchain interaction. The thermal conductivity constant, hardness decrease with filler content increase. The experimental results showed that the (20% kaolin) sample has the minimum value of thermal conductivity. The porosity and density increase with filler content increase therefore the thermal isolation increase. On the other hand (5% kaolin) sample give the maximum value of compression strength. The glass transition temperature, melting point and degree of crystallization decrease by adding kaolin.

Key words: kaolin, polyester, thermal conductivity, filler, DSC, FTIR, secondary bonds.

الخلاصة:

تم تحضير نماذج البولستر مع مالىء الكاؤولين باستخدام طريقة الصب للبولستر وبكسر حجمي (5,10,15,20) % . تم دراسة التوصيل الحراري, الصلادة, مقاومة الانضغاط, المسامية والكثافة. الدراسة التجريبية سعت الى تحسين اداء العوازل البوليمرية في تطبيقات درجات الحرارة العالية. اختبار شور للصلادة استخدم لقياس الصلادة. التحليل الطيفي للأشعة تحت الحمراء (FTIR) لدراسة الاواصر التي تحسن خواص العزل للمادة المتراكبة من البولستر والكاؤولين. المادة البوليمرية المركبة تظهر امتصاص (UV) مرئي جديد بمدى طول موجي (375-200) nm والذي ساهم في التجاذب ما بين السلاسل. ثابت التوصيل الحراري, الصلادة تقل مع زيادة محتوى المالىء. النتائج التجريبية بينت ان النماذج الحاوية على 20% كاؤولين لها اقل قيمة من التوصيلية الحرارية. المسامية والكثافة تزداد مع زيادة كمية المالىء لذلك العزل الحراري يزداد. ومن جهة اخرى فان النموذج الحاوي 5% كاؤولين يعطي اعلى قيمة لمقاومة الانضغاط. درجة التحول للحالة الزجاجية, نقطة الانصهار ودرجة التبلور تقل باضافة الكاؤولين.

Introduction:

The progress of plastic technology led to use it in thermal insulator industry instead of steel, aluminum, wood & other installation materials [Tariék A. 2010] [1]. Plastic composites used as thermal isolation formed one of the important reasons to keep energy expenses and reduce required materials in heating and cooling [Asmaa 2010, 2011] [2,3]. The heat transfer through material achieved by impaction operation between molecules or atoms which formed the material, these phenomena is known as thermal conductivity [W.Bolten 1998] [4]. When direct touching of bodies transfer from hot side to cold side through material boundaries which isolated both sides [Charles A 2002] [5]. Chemical construction of molecules and atoms act as an

important rule to achieve heat transfer or isolating .In this study we used unsaturated polyester resin which can be classified as thermosetting plastic which is widely used in thermal and electrical insulator, boats, and in all life aspects such as high building, ships [Sachin Waigaonkar 2011, Ram Avatar 2012] [6,7].

London dispersion forces are electrostatic forces between molecules having an accidental or induced dipole .the existence of intermolecular forces in nonpolar materials, plus the small temperature dependence of intermolecular forces. All molecules have time-dependent dipole moments that average out to zero and which arise from different instantaneous configurations of the electrons and nuclei. these fluctuations lead to perturbations of the electronic clouds of neighboring atoms and give rise to attractive forces called dispersion forces.[Meha, 2015] [8].

The addition of kaolin to thermosetting and thermoplastic mixes gives good mechanical and physical properties, smoother surfaces, a more attractive finish, good dimensional stability, and high resistance to chemical attack therefore its used in many application like paper, electrical and thermal insulators and as a matrix material in many composite materials like brake disk because kaolin is ceramic which has lower thermal conductivity dielectric constant than polyester [Harper2001, D Chann and G W Stachowiak 2004] [9,10]. Also, the addition of kaolin lower the glass transition temperature which make the polymer more amorphous, amorphous polymer have lower thermal conductivity than crystalline.[AshaKrishnan.K 2012][11] .

Kaolin has high fusion point and it's the most refractory of most clays also imparts high strength [Dr. Zuhair Jabber Al-asade 2008]. Clays consist mainly of the mineral kaolinite, this being hydrated aluminum silicate ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$) with small amounts of other oxides like Aluminum oxide, Silicon dioxide, Iron oxide, Titanium dioxide, Calcium oxide, Magnesium oxide, Sodium oxide and Potassium oxide [Jorge C, 2003] [12].

Unsaturated Polyester interest comes from their low cost and easy processing. Due to their stable structure, good mechanical properties and good thermal stability. its contain the ester functional group in their main chain a synthetic polymer made of ethylene glycol and terephthalic acid as shown in figure (1)[Namessian, N.O.,2012] [13].

Kaolin surface contain silica group (SiO_2) as shown in figure (2) which dehydration with water to produced saline functional group)(-SiOH).its acidic in nature and behave as carbocyclic acidic group (-SiO-H+) by reaction with amines and alcohol[Samon,2010] [14].

The electrical and mechanical properties of composites are significantly dependent on the filler's aspect ratio, interaction between fillers, polymer matrix and also the surface area. The usage of fillers in polymer needs to carefully study because fillers have its own aspect ratio. For example, a very high aspect ratio does not always improve the electrical and mechanical properties but maybe decrease it. [Salman Amin 2011, Mohd, 2008] [15, 16].

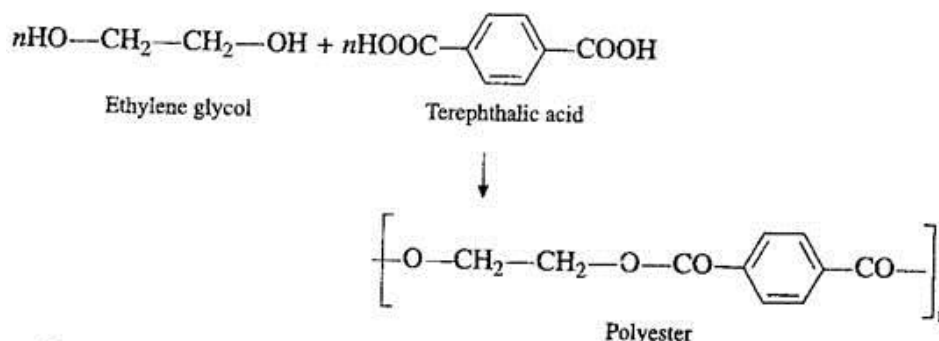


Figure (1) polyester formation reaction

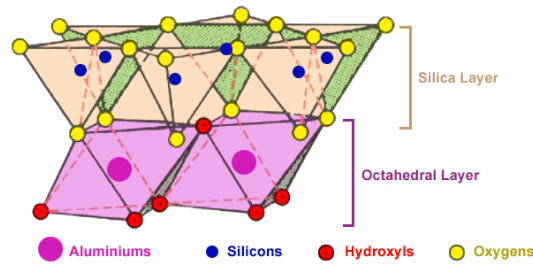


Figure (2) represent the structure of kaolin layer

The aim of the work

Enhance thermal, electrical and mechanical properties and provide smooth surfaces, dimensional stability and resistance to chemical attack, and to reduce shrinkage and cracking infra-red absorption characteristics to use it in thermal insulator in the manufacture of automotive parts based on engineering thermoplastics

Experimental work

Unsaturated polyester used as a matrix material (sudia arbia origin) The samples were prepared with filler volume fractions (5%, 10%, 15% and 20%) by using cylindrical plastic mold with dimensions (3 cm) height and (1.7 cm) diameter. Unsaturated polyester condensed by methyl ethyl ketone peroxides (MEKP) and cobalt actuate for solidification. Table (1) represents the components of the samples molded by Weight the components. The average particles size range of kaolin powder is (0.5-50) μm determined by using LBZA device to determine the required size [D50:2.23μm] as shown in figure (3) then Mixing the components well by using intensive mixer, Mold the mixture; keep it in the mold for 24 hrs, the molds kept in the oven for 24 hour in order to complete currying process.

The shore hardness D test was used to measure the samples hardness. The compression device was used to measure the compression strength. Thermal conductivity device was used to measure the thermal conductivity constant. Thermal conductivity measurement done by uses equation (1) thermal conductivity get by take the change in temperature ΔT between cold temperature (Tc) and heat temperature (Th) at Q= 10 W, V=40volt, I= 0.4 am.

$$K = \frac{QL}{\Delta T A} \quad (1)$$

K: Thermal conductivity coefficient

Q: the quantity of heat

L: the thickness of the samples

ΔT= Th – Tc

The Apparent porosity:

The specimen was dried in an oven at 110⁰C to a constant weight with an accuracy of 0.1 g. The dried specimen was immersed in distilled water such that the specimen does not touch the bottom or sides of the container. It was boiled for two hours while still immersed in water and afterwards it was cooled to room temperature and its weight noted. The specimen was removed from water and excess water was wiped off from its surface by lightly blotting with a wet towel and weighed in air (W).

Apparent Porosity (p) measured by using:

$$P = \frac{V1}{V2} * 100-$$

V1=actual volume of open pores of the specimen (Wa/Da)

V2=external volume of the specimen (Ws/Ds)

Wa=weight of the specimen in air (g)

Ws=weight of soaked specimen (g)

FTIR device was used to measure the Fourier transform infrared spectroscopy. DSC device was used to measure TG Spectrum peak pick device to measure UV absorbent wave.

Table (1) the component of the samples

Sample number	Polyester%	Kaolin%
1	100	0
2	95	5
3	90	10
4	85	15
5	80	20

Result and dissections:

Thermal conductivity:

The thermal conductivity decrease with kaolin ratio increase due to that Kaolin has lower thermal constant than polyester according to the rule of mixture of composite material. [J.P.Holman][17] Plastic essentially isolated materials because of its chemical structure. Adding filler to polyester the crystalline reign decrease and filler particles diffuse through polymer chains and make secondary bonds which increase the vacancies between chains and these vacancies decrees the heat conductivity, also heat transmit through polymer occur due to found crystalline spot or groups added to transfer the heat as in case of electrons in electrical conduction therefore the thermal conductivity decrease with filler content increase because the filler particles increase the amorphous portion as shown in figure (4)

Porosity:

The porosity increase with filler content increase as shown in figure (5) that's due to that kaolin has (0.5-50) μm in average particle size which increase the distance between the molecules chains and reduce crosslinks. Kaolin make Vander walls bonds with polyester and reduce crosslinks therefore the heat conductivity decrease because the porosity increase, the spaces increase the air (the best in insulator ($K=0.026\text{W/m}^\circ\text{C}$)) that's due to kaolin is hydrophilic contain aluminum silicate surface. Polymer convert the organophilic one, which can be carried out by ion exchange reactions with cationic surfactant.

Hardness:

The hardness decrees with filler content increase as shown in figure (6) Because kaolin has (0.5-50) μm in average particle size which increase the distance between the molecules chains, reduce crosslinks and act as plasticizer or polymer modifier.

Density:

The fillers (kaolin) have higher density than polyester therefore the mass of the samples increase and the density increase with filler content increase as Shawn in fig. (5). It has flat hexagonal kaolin plates of aluminum silicate get high aspect ratio and high contact surface area as Shawn in figure(7).

Compression strength:

The compression strength of the samples decreased when filler ratio increase as shown in figure (8) implying a filler ability to occupy space and reduce crosslink content through polymerization and act as a cheap diluent of the more plastic product also offer some functional benefit that contributes to the process ability or utility of the plastic product. It has high surface area and high aspect ratio, the kaolin has good physical attraction with polyester therefore its diluent material enhance the movement of polymer chains and reduce the compression resistance.

DSC:

The amorphous structure increase by adding kaolin because the porosity increase for the same reason discussed .the glass transition temperature decrease by adding 20% of kaolin from (71.76-51.22)^oC and the crystalline degree decrease from (121.19-131.20) ^oC and melting point decrease from (286.89- 196.3) ^oC as shown in **figure (9)**

UV-spectra:

The UV- spectra of polyester compared with that of polyester – kaolin at 5% wt as shown in figure (10). It is shown that the adding of the filler to the polymer lead to increase the intensity of peak. Critical analysis of UV-Vis spectra of polyester - kaolin composites shows that the highest shift in absorption in all the wave length of the curve which indicate good physical attraction between polyester chains and kaolin.

The shift in the absorption edge from UV to visible region could be attributed to an increase in conjugation length , there are shifting in (1,2,3,4) absorptions and there are new visible absorptions (5,6,7). In the present case the optical band gap energy can be correlated with the number of carbon atoms per conjugation length for a linear structure polymer. The absorption of light energy by polymeric materials in UV and visible regions involves transition of electrons in n to * π orbital from ground state to higher energy states. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200-700). These transitions need an unsaturated group in the molecule to provide the π electron 6 . Similar trend has been done by using carbon black filler with unsaturated polyester. Carbon black filler make physical attraction between polyester chains [Al-Mosawi Ali, 2014] [18].

The result may be interpreted with inter chain interaction in the outside of polymer coils. While polymer coils approach each other, inter chain interaction in the outside of different polymer coils may induce the slight increase of absorbance. The local concentration of kaolin groups may increase linearly with polymer concentration. It is assumed that the micro viscosity increase slowly.

FTIR analysis:

Figure (12) represent transparence versus wave number for the samples. FTIR showed that there is physical interaction between polyester and kaolin by the appearance of the bonds with wave number (3751.55, 3699, 3697, 3649 and 2953, 2933.7, 2881.65, 2933.7, 2954.9) which was found in kaolin as shown in figure (13).

There is intermolecular H- bonding by single bridge with wave number (3500-3550) cm^{-1} represented by hydroxyl group. Aromatic group represented with wave number (3000-2950) cm^{-1} , O-C-O group of acid with wave number (1450-1500) cm^{-1} and ester group (C=O) with wave number (1600). The intensity of the ester group bonds and other bonds decreased in the samples which contain kaolin and decreased with filler content increase therefore the bonds be stronger and the insulation properties enhanced and the mechanical properties because the appearance of Vander walls bonds between filler and polymer matrix.

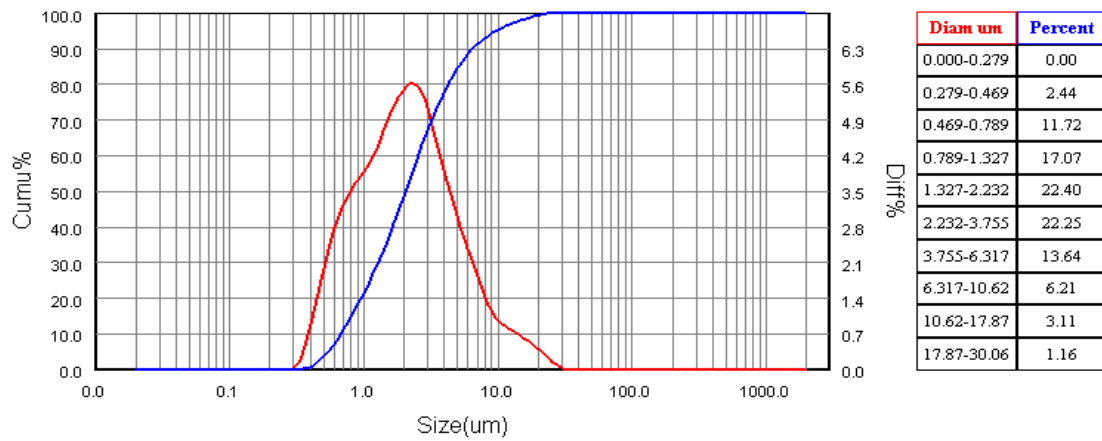


Figure (3) LBZA chart of particle size analysis of kaolin

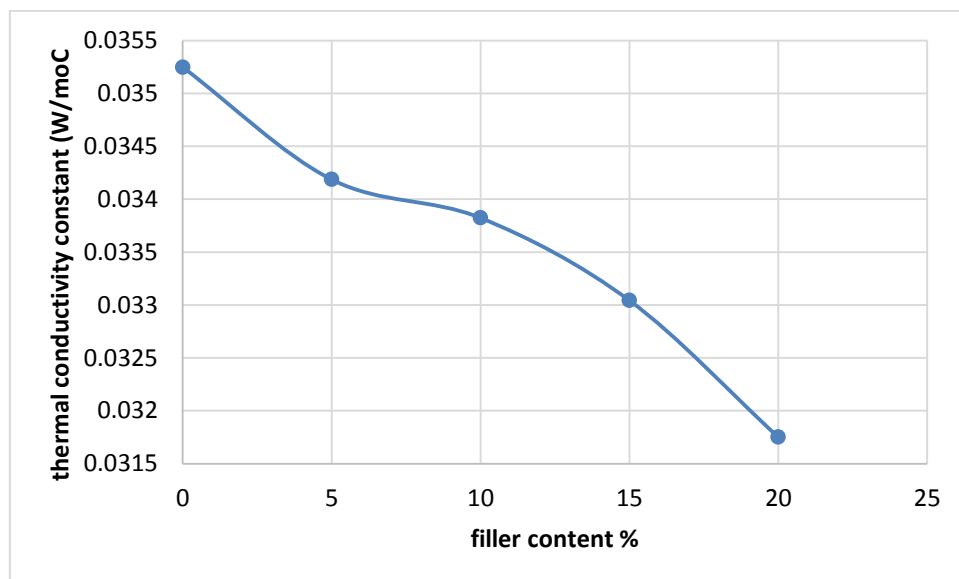


Fig. (4) Thermal conductivity verses filler content

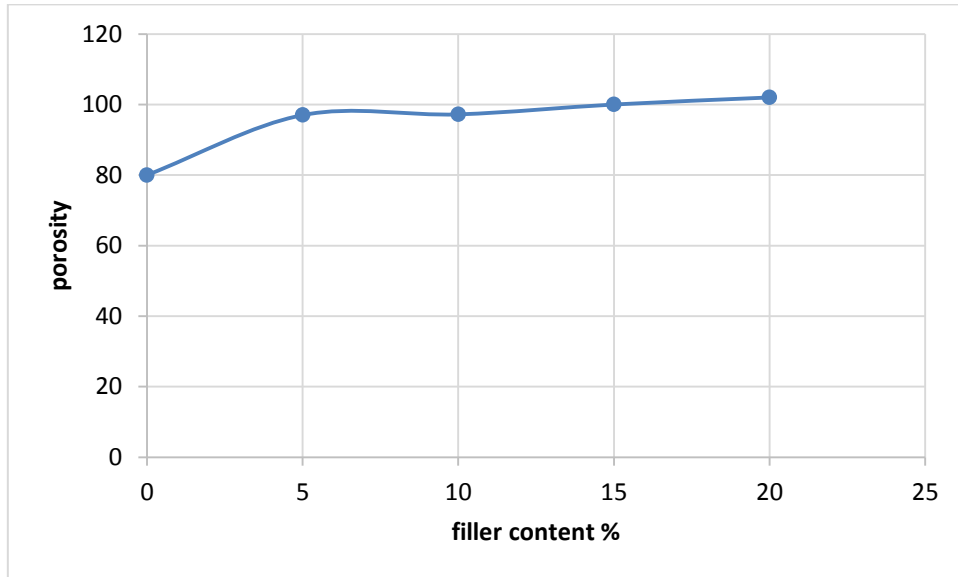


Fig. (5) Porosity verses filler content

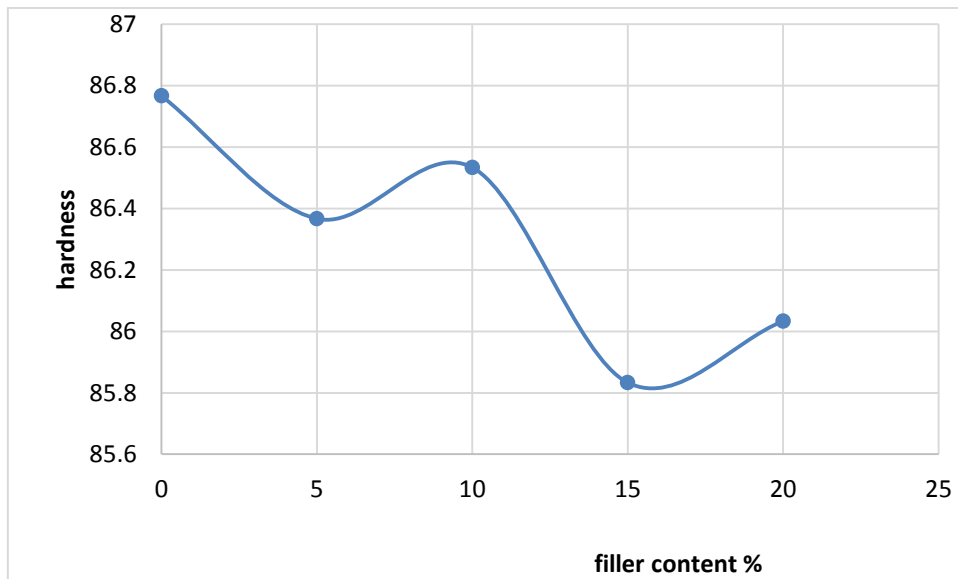


Figure (6) the hardness verses filler content

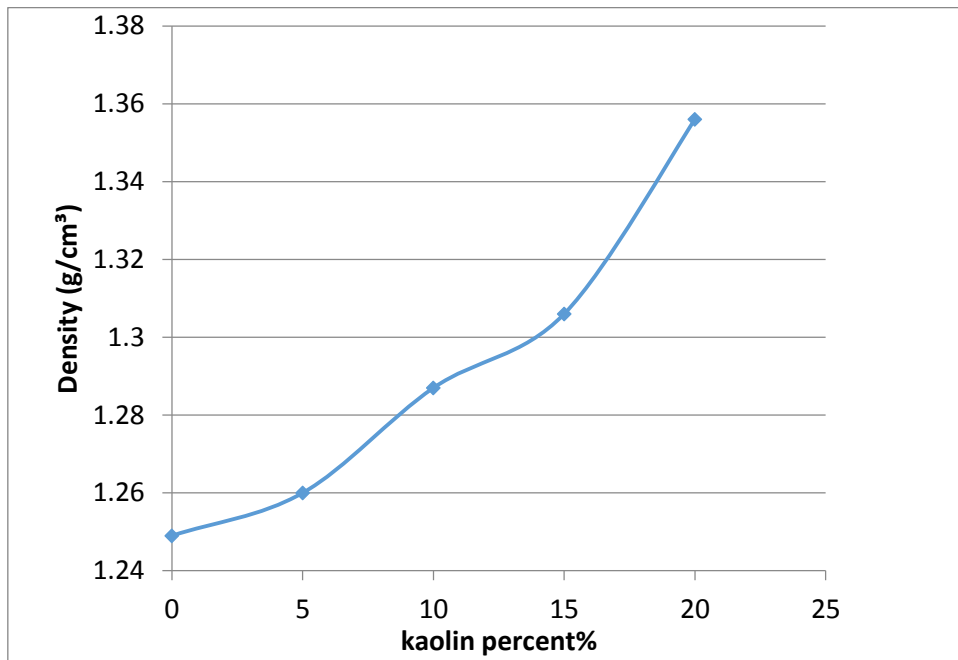


Figure (7) the density verses filler content

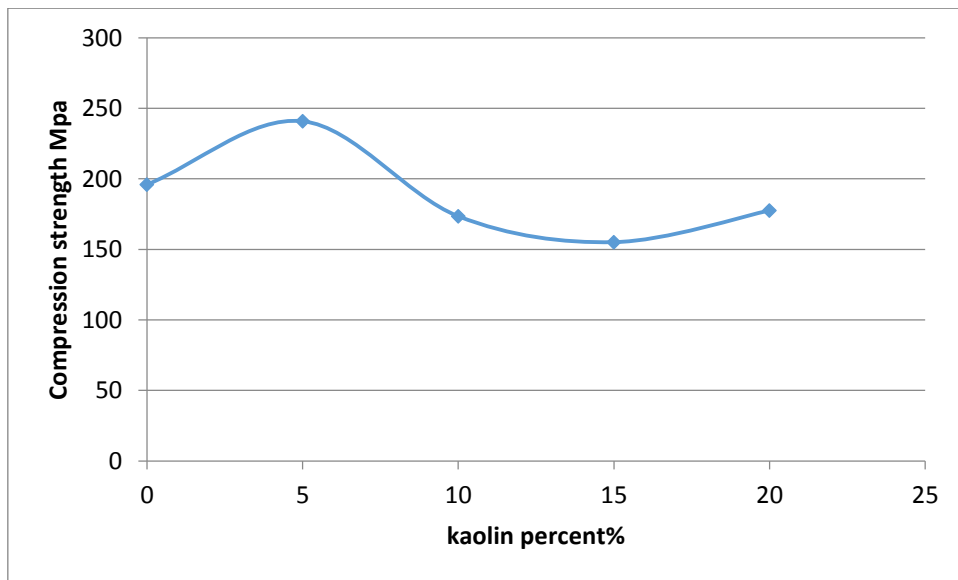


Figure (8) the density verses filler content

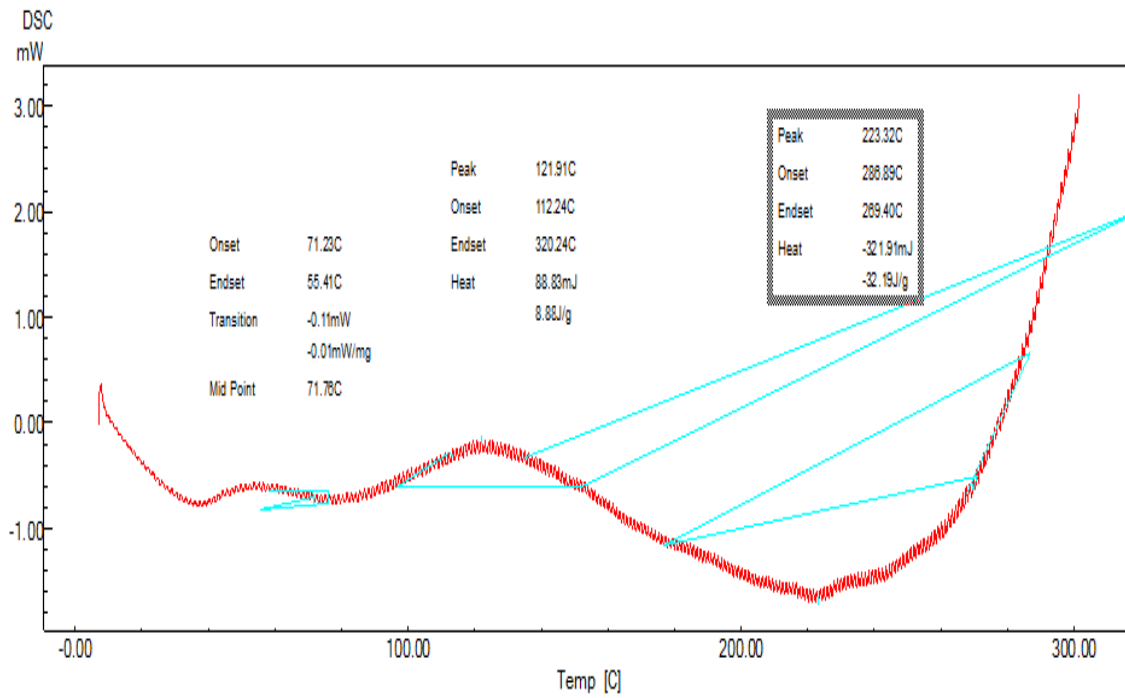


Fig. (9) DSC of polyester versus filler content

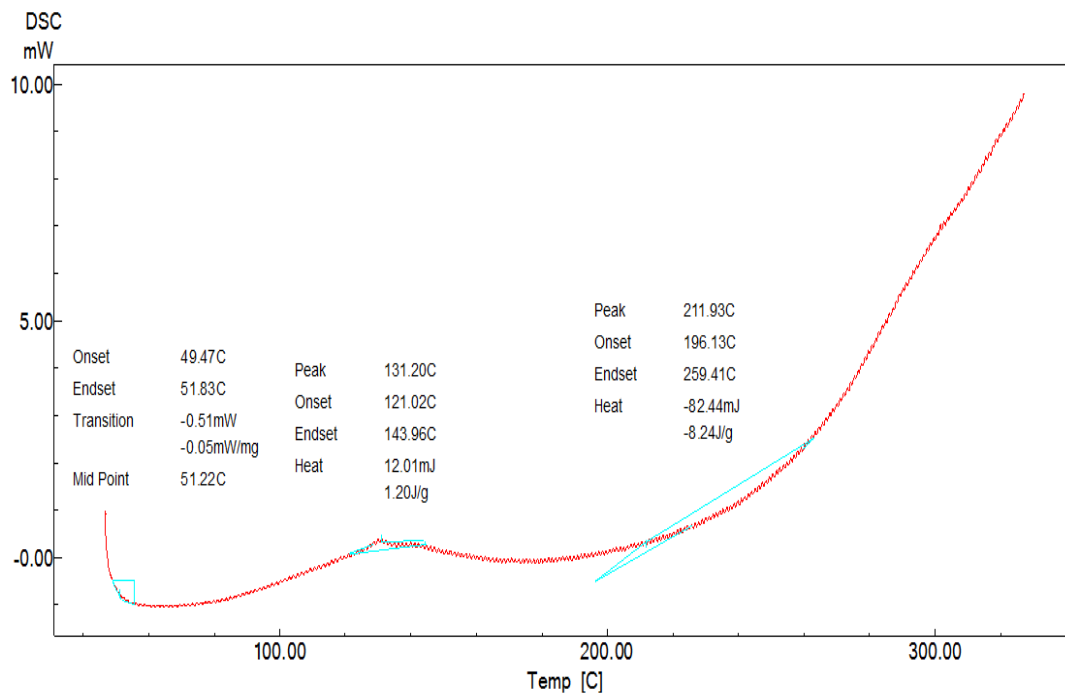


Figure (10) DSC of polyester with 20% kaolin versus filler content

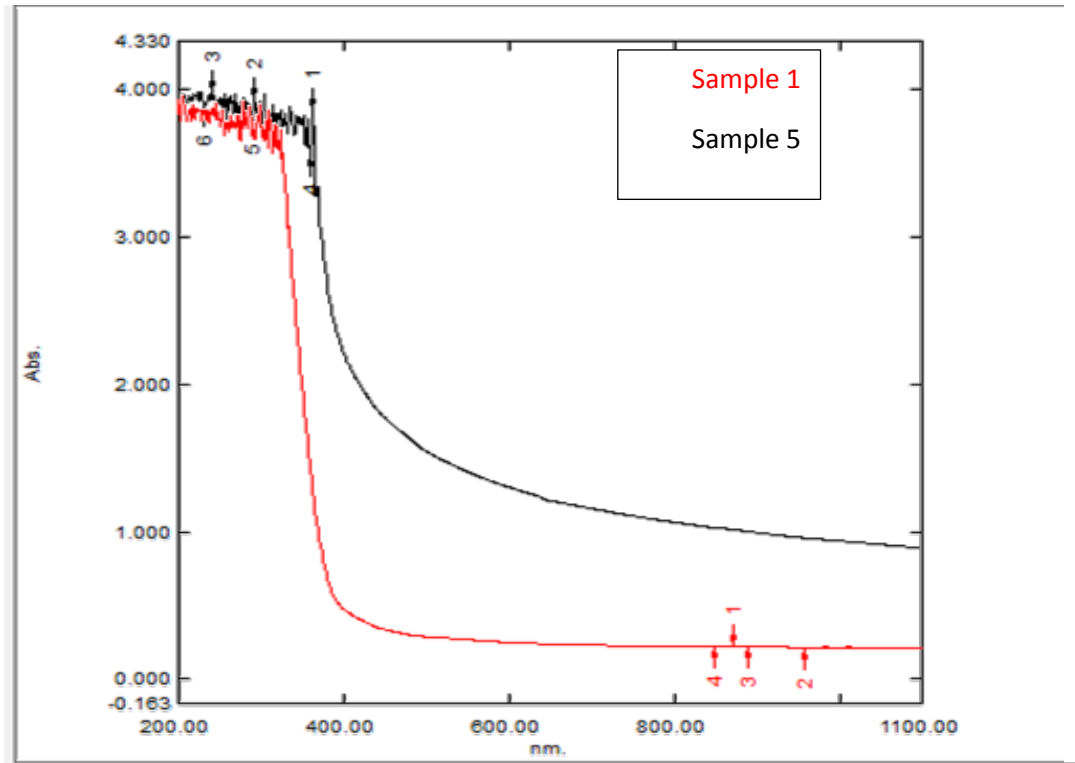


Figure (11) UV spectrum absorption verses wave number for sample 1 (polyester) and sample5

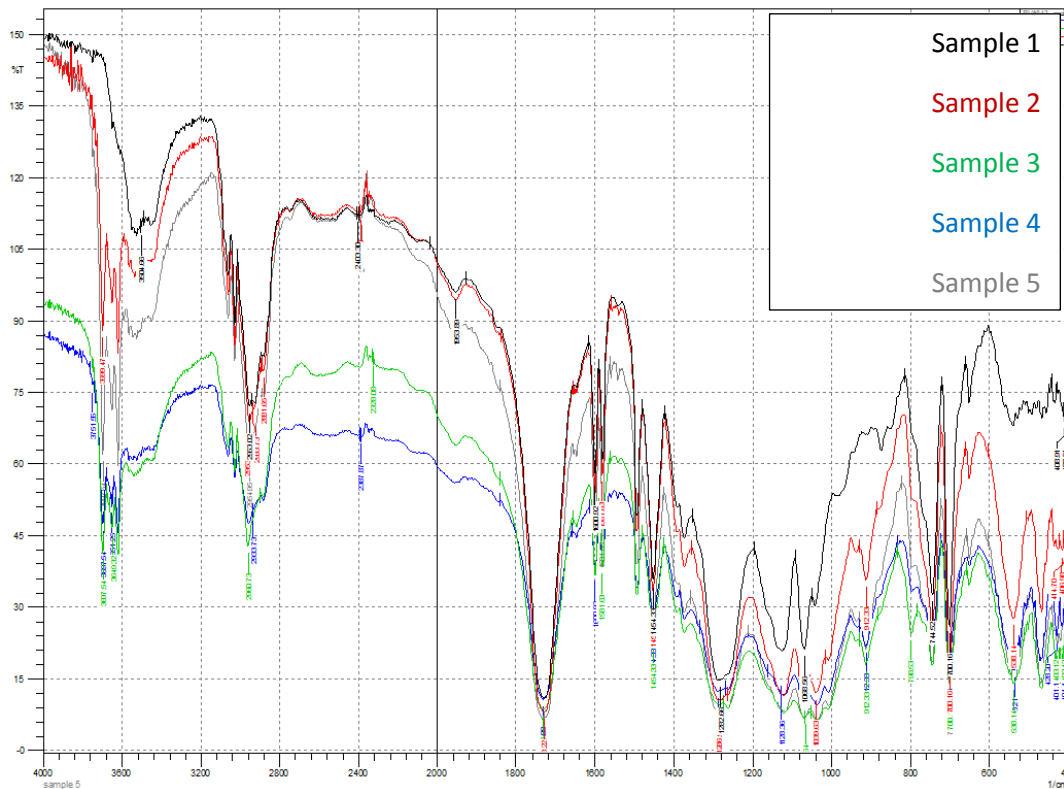


Figure (12) Intensity Verses Wave Number of the samples

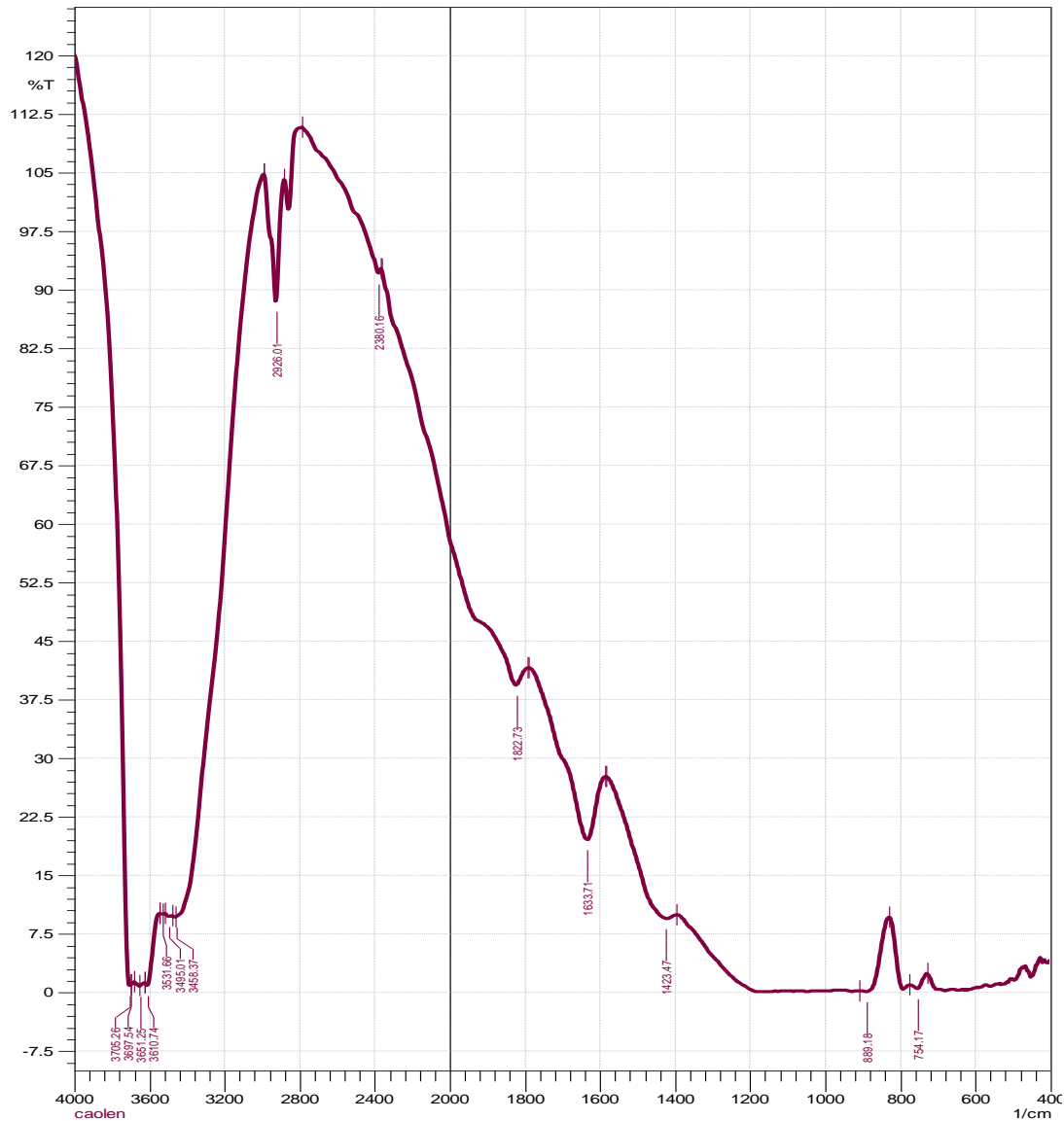


Figure (13) Intensity Verses Wave Number of kaolin

Conclusion:

From this study, it was found that the polyester containing 20%g of kaolin give better mechanical as well as thermal properties among the other kaolin loading because the physical interaction between molecules chain by Vander walls bonds between matrix molecules and filler as indicative in UV spectrum absorption.

The addition of kaolin led to enhance the thermal properties because the kaolin has hydrated aluminum silicate dispersed just inside the composite material and decreased the heat conductivity, enhance the manufacturing process by decreasing the glass transition temperature , degree of crystalline and melting point and ,leading to a lower formulation cost.

The compression strength has maximum value (240.8 MPa) at 5% of kaolin while the hardness has maximum value (86.36) at 10 % of kaolin. Density, porosity increased to the maximum value (1.35) g/cm³, (102) at (20%), and thermal conductivity constant decreased by adding kaolin (0.03175W/m^oC) to the minimum value

References:

1. Tariq A. Al- Anie, Khalil Th. Hassan, Asmiet R. Al-Hadithy "Preparation and Study Hardness and Thermal Conductivity (Tc) to Polyester Resin Composite with (Titanium Dioxide, Zinc Oxide, Acrylonitril, Wood Flour Coconut" Baghdad Science Journal, Vol.7(4)2010.
2. Asmaa Shawky, Harith Jafeer, Ekram AL-Ajaj, "The Effect of metals as Additives on Thermal conductivity of Epoxy Resin" Vol. 8, No.12, PP. 74 -79, Iraqi Journal of Physics, 2010.
3. هناء عرير سميح "تأثير التقوية بمسحوق اوكسيد الزنك على الخواص الميكانيكية لمادة متراكبة ذات ساس من البولي استر غير مشبع" 29,2 المجلد 29, العدد 10, مجلة الهندسة والتكنولوجيا 2011.
4. W. Bolton, "engineering materials technology" Butterworth Heinemann-Great Britain, 1998
5. Charles A. Happer "handbook of plastics, elastomers, composites" McGraw-Hill companies fourth edition, 2002.
6. Sachin Waigaonkar, BAJ, Amit Rajput, "Curing Studies of Unsaturated Polyester resin used in FRP products "Indian journal of engineering and material science, pp.31-39, 2011.
7. Ram Avatar Sharma, Dawid D'Melo, Subhendu Bhattacharya, Lokesh Chaudhari, and Sarojini Swain "Effect of Nano/micro Silica on Electrical Property of Unsaturated Polyester Resin Composites" Vol. 13, No. 1, pp. 31-34, February 25, Transactions on Electrical and Electronics materials, 2012.
8. Meha Jasim, "Effect of natural pigments on the polymer secondary bonds" thesis at Babylon University, polymer department, 2015.
9. Harper, "handbook of ceramics, glasses, and diamonds" McGraw-Hill companies, 2001.
10. D Chann and G W Stachowiak, "Review of Automotive Brake Friction Materials", Proc. Instn Mechanical Engineering, vol. 218 part D: Journal of Automobile Engineering, 2004.
11. Asha Krishnan, K. Tresa Sunitha George, K.E George, Polymer nanocomposites based on blends: Effect of vinyl silane modified kaolin clay on Polypropylene/ Polystyrene Nanocomposites "National Seminar on Polymer Science and Technology, June, 23, 2012.
12. Dr. Zuhair Jabber Al-asade Dr. Jasem Mohammed Al- Murshdy " An Investigation of Kaolin influences on Mechanical Properties of Unsaturated Polyester Composites" Journal of Kerbala University , Vol. 6 No.1 Scientific . March. 2008.
13. Jorge C. Miranda-Trevino, Cynthia A. Coles " Kaolinite properties, structure and influence of metal retention on pH" Applied Clay Science 23, 133– 139pp, 2003.
14. Namessan, N.O., J.N. Maduako² and S.A Iya., " Effect of polyester and filler on water absorption behaviour, density and porosity of kenaf fibre reinforced brake pads" International Journal of Basic & Applied Sciences, 33-44 pp, 2012.
15. Samon Masulubanye Mohomone " Preparation and characterization of polychloroprene modified clay nanocomposite" Master sciences (M.Sc.) Qwaqwa Campus, April, 2010.
16. Mohd Asyraf Reduan Azmi, "The Effect Calcium Carbonate and Calined clay micro filler Materials on the electrical characteristics of polyvinyl chloride for cable insulation" May 2008
17. Salman Amin, and Muhammad Amin "Thermoplastic Elastomeric (TPE) Materials and their Use in Outer door Electrical Insulation Thermoplastic elastomeric (TPE) materials and their use in outdoor electrical insulation "Rev. Adv. Mater. Sci., 29, pp 15-30, 2011.
18. J.P. Holman "heat transfer" mechanical engineering series, Graw-Hill international, EDMONS.
19. Al-Mosawi Ali I, Al-Maamori Mohammad and AL-Mayalee Khalidah, " Spectroscopic Studies of Polyester – Carbon Black Composites", Research Journal of Material Sciences , Vol. 1(2), 10-14, March, 2014.