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Development and Strength Properties of PP/PA6/RED Kaoline and PP/PA6/ Bentonite Blends

Dr.Najat J.Saleh*

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Abstract

In the present work a new type of composite material has been prepared from mixing of polypropylene and polyamide 6 at constant ratio (80/20)] and adding different weight percent (0, 5,10,15)% of both local bentonite and red kaoline fillers respectively by using single screw extruder .Some of mechanical properties such as tensile strength (Young modulus) tensile at fracture and elongation of filled and unfilled PP/PN6 blends were determined at different temperatures, and different weight percent of filler. Addition of filler increases the Young modulus and tensile strength at break. Bentonite filler gives better mechanical properties, than red kaoline fillers. Also empirical equations were obtained which could be utilizing to calculate one of the mechanical properties in term of temperatures and weight fraction of filler content. An equation was proposed to show the best fit with experimental data, relevant contour diagrams, for optimization of properties is also presented.

Keywords: polypropylene, bentonite, kaoline, blend, filler

تحضير ودراسة صفات اجهادات الشد لمخاليط من بولي بروبيلتي بولي اميد6 /لماولبن الاحمر وبولي بروبيلتي /بولي اميد6/بنتونايت

الخلاصة

في البحث الحالي تم تحضير مواد متراكبة جديدة التي هي عبارة عن مخلوط بـــوليمري ، يتكون من مزيج بولي بروبلين مع بولي أميد-6 بنسبة وزنية ثابتة (80/20) مع اضافة مختلــف النسب الوزنية(15,10.5.0) من مسحوقي البنتونايت والكاؤولين الأحمر المحليين علـــى التـــوالي وذلك باستخدام جهاز البثق المنفرد. وبعد ذلك جرت دراسة بعض الخصائص الميكانيكيـــة مثـــل اجهاد الشد عند الكسر (معامل يونك) والاستطالة ، ولجميع المتراكبـــات المحـــضرة وقورنـــت النتائج المستحصلة مع تلك التي تعود لمادة الأساس بمفردها وجرت الفحوصات بدرجات حرارية مختلفة وكسور وزنية مختلفة . من النتائج التي تم الحصول عليها لوحظ ازدياد كل من: معامـــل يونك وإجهاد الشد عند الكسر بزيادة نسبة الخلط ألوزني. من النتائج التي تم الحصول عليها تبين أن البنتونايت أعطى نتائج أفضل من الكاؤولين الأحمر .في البحث الحالي أيضاً تم ايجاد معادلات تجريبية يمكن استخدامها لا يجاد قيمة أحدى الصفات الميكانيكية بدلالة الحرارة والكسر الـــوزني للحشوة وضمن مدى قيد الدراسة.وتم افتراض المعادلات التي تظهر العلاقة المتطابقـــة للنتـــائج النظرية والعملية وتم رسم منحنى عدادي معتمدة على المعادلات المفترضـــة .

Introduction

Polymer blends are generally considered by mixing two or more polymers that are not bonded to each other. These blends are a well-established route to achieve a certain

* Chemical Engineering Department, University of Technology / Baghdad

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

amount of physical properties, without need to synthesize specialized polymer systems [1].By adjusting the composition of the polymer blend, it is possible to obtain a material possessing the desired mechanical and thermal properties.In most applications, polymers are normally modified by incorporation of fillers to modify properties so that acceptable engineering properties are obtained. The selection of filler used in polymer formulation is made, based on the property requirement of the end product Typically mineral fillers would be used to enhance strength characteristics significantly and reduced cost [2]. A wide range of particulate fillers is added to polymer compounds to improve the mechanical properties, reduced cost, and impart color to the polymer product [3] the term" reinforcement" refers to an improvement in end-use performance of the polymer compound associated with an increase in modulus and in the so-called ultimate properties including tensile strength, tear resistance and abrasion resistance. Reinforcing filler is a particulate material that is able to increase (a) the tensile strength, (b) the tear strength; and (c) the abrasion resistance of natural polymer [4].

Clays represent the largest volume filler used in polymer [5]. Clay minerals are widely used with polymer because of their cost effectiveness in terms of providing beneficial reinforcing and processing properties at a modest cost. The main clay mineral of importance is kaolin and the derivative produced by chemical treatment and heating (calcinations).Clay is classified as hard clay if it reinforces rubber and also imparts high modulus, tensile strength, and resistance to abrasion . Red kaolin clay is like Kaolin clay but is very rich in iron and has been widely applied as strong drawing clay used in mechanical preparations, as it is highly absorbent and draws oils and toxins from the skin Because of its drying capabilities it is effective in treating poison oak and ivy, and for application to rashes. It is also used as a colorant in soap making or to add speckles to soap [6].

Bentonite is a soft clay substance composed essentially of clay minerals of the smectite (montmorillonite) group and is formed from in-situ chemical weathering of volcanic materials such as tuft of glass, volcanic ash, other igneous rocks, or from rocks of sedimentary origin. .The color of Bentonite range from white to light olive green ,cream yellow, earthy red ,brown and When wet it is highly plastic and slippery. In addition, Bentonite ranges from white to light olive green ,cream , yellow, earthy red, brown and sometimes sky blue when fresh but yellowing rapidly with exposuretoair. When wet it is highly plastic and slippery. In addition, Bentonite is used to control the melt rheology of thermoplastics and to reinforce polyamides[7,8] Several authors studied the effect of addition of filler on composite properties like Sumiata, studied the effect of ultra fine particles on the elastic properties of PP composite. Young modulus of composites filled with relatively small particles increased with increasing filler content, whereas those of the composites filled with large filler decreased with increasing filler content and size [9] Vollenberg, and Heikens, studied the mechanical properties of chalk-filled PP. In this research, the effects of a variation of the particle size of the filler, the filler content and the interfacial adhesion on the properties were examined [10].Kojima studied the mechanical properties of Nylon 6 clay hybrid, he showed that there is an increase in the stress at break; this has been explained by the presence of ionic interaction of Nylon grafted to the silicate layer [11].

Hasegawa studied the preparation and the mechanical properties of polypropylene clay hybrid using a Maleic Anhydride- modified Polypropylene Oligomer [12], Yang studied the preparation and properties of a hybrid of Organo- soluble polyamide and montmorillonite with various chemical surface modification methods. He showed that at low filler tensile strength and elongation at break increased clay content up to 5wt%. At higher filler loading both properties experienced sharp drop towards values lower than those of the matrix alone. This decrease was explained by aggregation of montmorillonite at higher loading, which causes the composites to be much more brittle [13].Rattana studied the reinforcement of natural rubber latex by nano size montmorillonite clay. X-ray diffraction results indicated that clay platelets dispersed in the rubber matrix on the nanoscale level with some macromolecules intercalated into the clay gallery. The observed considerable improvement in mechanical properties, coupled with a theoretical model of composite modulus suggest a dispersed structure of clay in the composite, while not all clay particles are exfoliated [14] Abed-Alhakem studied the effect of Iraqi raw ceramic (Kaolin and Boxide) on epoxy resin, he showed that tensile properties (elongation at break, Young modulus, and stress at break,)of composites filled with relatively small particles all increased with increasing filler content, with decreasing filler size, and increasing filler content[15].Hashmi studied rheological and mechanical properties of polymer composite (red mud filled PP/PC and PP/Nylon-6 blend systems), he showed that addition of red mud (RM) particles to PP/ Nylon-6 blend increases the discontinuity and restricts the growth of crystal, and therefore crystalline peak intensity reduced in the field blend composites. A new type of cheaper blend is developed by melt mixing technique and incorporation of red mud modifies the PP/ Nylon-6 structure by interlocking the chains on the surface and composite. An increase in red mud content raises the tensile strength of the PP/ PC blend [16]. In this work PP/PA6/BN and PP/PA6/RK were prepared and tensile strength,(Young modulus) tensile at break as well as elongation of filled and unfilled PP/pA6 were studied empirical correlation were also developed.

Experiment

Materials

Commercial polypropylene was used; it was supplied by Sabic Saudi Arabia. The melt flow index and the density of the material were 11gm/10min and 0.908 (gm/cm^3) respectively.

Commercial polyamide-6 was used; it was supplied by Exxon-mobil Saudi Arabia. The melt flow index and the density of the material were 2.0gm/10min and 1.14(gm/cm^3) respectively. Iraqi red kaolin clay (RK) has particle size of 45 μm and density (2.64) gm/cm^3 , and has high melting point (1755)°C. Its chemical composition is shown in table [1] Iraqi Bentonite clay (BN) has particle size of 45 μm and density (2.55) gm/cm^3 .Its chemical composition is shown in table [2].

Procedure

Extruation procedure

PP (PA6), (RK), and (BN) samples were kept in an air circulating oven at 70 °C. for 4 hr to dry the materials. Weighted amounts of materials were mechanically mixed. The mixture was then fed into 25 mm single screw extruder machine (Betol BM 1820 extruder) . The barrel as well as die temperatures were monitored and controlled by a thermostat and was adjusted to yield uniform output. The temperatures are measured at different Zone across the extruder table (3) shows the temperature profiles of the extruder. PP and PA6 (80/20) were mixed with various compositions of filler (0, 5, 10, 15) %. This mixture was then extruded in 25 mm single screw extruder machine(Betol BM 1820 extruder) The extrudates produced in the form of about 2mm diameter mono-filaments were cooled in water, mono-filaments were uniform and cut in 3-4 mm in length.

Molding Procedure

The CININATI hydraulic press was used with maximum load (15000 kg) and working area (0.4*0.3) m, for compression molding. The mold used for pressing the composite material has dimensions of (30*30*4) mm. It is made of steel. The sheet was prepared by hot pressing at 200°C for PP/PA6/RK and PP/PA6/BN blends. A pressure of 20 Mpa was applied for 5min to allow the composite to melt and spread out between plates. Pressure was then increased to 100 Mpa for further 5min, the pressure was released and the mold sheet was quenched in water at room temperature.

Mechanical Properties

Tensile properties were obtained using an Instron Tensile Tester machine (model 1445) on Dumbbell-shaped die –cut samples according to ASTM(D 638) [18].The prepared samples were tested at different temperatures (25,50,75 and 100) ^{0}C.

Results and Discussion

It is clearly seen from figures (1, 2), that the modulus of elasticity of PP/PA6 increases with increasing weight percent of filler, this may be attributed to the fact that Young's modulus of composite depends on the Young modulus of the filler, polymer and the weight fraction of the particles [18] .These results agree well with results obtained by Sumiata who had found that the Young's modulus of composites filled with small particles increases with increasing filler content [9]. Also the effect of temperature on the modulus of elasticity of polymeric composite is clearly seen in these figures, the modulus of elasticity decreases with increasing temperature and this may be attributed to that, the modulus of elasticity, does depend on temperature [18]. In addition the decrease of modulus of elasticity was due to the decrease of binding forces between the molecules of the matrix and thus they become plastic and lead to a large deformation which is caused by the decrease of modulus of elasticity [19, 20]. These results agree well with results obtained by Mohammed [21]. It was found from figure (3) that the modulus of elasticity of PP/PA6/BN composite were higher than of PP/PA6/RK composite and this may be due to a good adhesion between the matrix and BN filler. A good improvement of modulus of elasticity of PP/PA6 through the addition of particulate mineral clay on modulus of elasticity and due to the small particle size [18] had been found in this study It is clearly seen that from figures (4-5) an increase in the stress at break is obvious in filled polymers. It is also obvious that even with the addition of such a low content of BN (5, 10 and 15)wf%, the tensile strength at fracture increases considerably. The effect of temperature on the tensile strength at fracture of polymeric composite was also seen, the tensile strength at break decreases with increasing temperature and this may be due to the decrease of binding forces between the molecules of the matrix and thus they become plastic and lead to a large deformation which lead to decrease of tensile strength at fracture [18], but when the temperature decreases the tensile strength increases. This happens due to the tensile force between the molecules which leads to decrease in the movement of the molecules and the material becomes solid and at a low deformation which leads to increase the tensile strength [20-21] .These results agree well with results obtained by Abdl-hakem, he found that the effect of temperature on the dispersed filler on tensile strength of composites filled with small particles increases with increasing filler content [15].

It is found that the tensile strength at fracture of PP/PA6/BN composite is higher than that of PP/PA6/RK composite and this is attributed to high strength that bentonite filler possesses figure [6].

Figures (7) and (8) show the relation between the elongation at fracture and the weight percent before and after reinforcement with filler for both BN and RK at different temperatures respectively. From these figures, it is clearly seen that the effect of weight percent on the elongation at fracture of polymeric composite is that the elongation of polymeric composites decreases when the weight percent of filler increases because the elongation of polymeric composite depends on the elongation of filler and polymer and weight fraction of the particles [22]. This may be due to the fact that elongation of BN or RK being lower than the elongation of polymer. The elongation at fracture decreases with increasing filler content. These results agree well with results obtained by Al-Neamee[23], she found that a considerable loss in ultimate elongation, which exhibited brittle fracture, generally rigid fillers cause a dramatic decrease in elongation at break.

The elongation at fracture increases with increasing temperature and this is due to that elongation of polymer material are effect by temperature and this in term depends on glass transition temperature [24,25].These results agree well with results obtained.by Abid Alzahra, She found that the elongation of polymer and polymeric composite increases with temperature [26].

The value of spectral responsivity is low compared to those common silicon base transparent conductive oxides heterojunctions. E.g. SnO2/Si ,In2O3 ,ZnO/Si ,and CdO/Si may be due to

1-high resistivity of Ag_2O contributing to high series resistance.

2-large lattice mismatch between Ag_2O and Si which produce traps charges at recombination centers.

The Analysis of Empirical Correlation

The experimental results of this work are used to develop empirical correlation. The statistical program was used on high – speed personal computer (Pentium 4). The method of developing the present model is by introducing equations of different forms in the computer program. The calculated values of the dependent variables are compared with the actual values and the procedure is repeated until excellent agreement is obtained.The dependent and independent variables were used as input data in such a way that the developed models could be used for the composite material to find the change in mechanical properties, the independent variables, which affect the mechanical properties of the PP/PA6/RK and PP/PA6/BN blends composite, are weight percent of filler content and the temperature.

Equations (1) and (2) as shown in table (4) represent the developed models for the modulus of elasticity , tensile strength at fracture, with weight percent of filler on PP/PA6/BN blend composite content and temperature respectively. A three-dimensional plot of mechanical properties (the modulus of elasticity, tensile strength at fracture) vs. (T) and (W) using Eqs. (1)and (2), were made for the data which are shown in figure (10) for PP/PA6/BN and figure (13) for PP/PA6/ RK, these figures approximate the behavior of the system with reasonable accuracy for the values of (W)and (T)in this studied range. The square term in the equation plots indicates a curvature in the surface obtained in three – dimensions. Also the results can be presented in terms of contour plots as shown in figures (11) for PP/PA6/BN) and figure (14) for PP/PA6/RK. The practical use of such contour plots is that, given the value of the property (which needs not be any experimental data points itself), the temperature and weight percent of filler content needed to attain that value of properties can be directly obtained from the plots. That is the procedure optimizes the value of the variables needed to get any desired value of the properties.

Conclusions

The additions of mineral clays Red kaolinite (45µm) and Bentonite (45µm) was found to improve the modulus of elasticity, the modulus of elasticity increases with increasing in temperature for PP/PA6 blends before and after reinforcement with both types of clays (BN and RK). Tensile strength increased with reinforcement with these mineral clays(BN and RK) . The increase in weight fraction of fillers leads to increase in tensile strength while it deceases with temperature increases.

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Table (1) chemical composition of Red kaolinite clay [17].

SiO_2 %	AL_2O_3 %	Fe_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	P_2O_5 %	SO_3 %	CL%	L.O.I. %
56.77	15.67	5.12	4.48	3.42	1.11	0.60	0.65	0.59	0. 57	11.02

Table (2) chemical composition of Bentonite clay [17]

SiO_2 %	AL_2O_3%	Fe_2O_3%	TiO_2%	CaO%	MgO%	Na_2O %	K_2O_3%	L.O.I %
52.4	31.31	2.94	1.43	0.462	0.33	0.28	0.23	10.61

Table (3) PP-PA6 blends composition and temperature profiles of single screw extruder.

Blendes	Temperature °C Zone1	Zone2	Zone3	Zone4	Screw speed (RPM)
PP/PA 6	150	170	220	200	30
PP/PA 6/RK	155	190	250	220	30
PP/PA 6/BN	155	190	260	230	30

Table (4) Equations of the mechanical properties as a function of temperature and weight percent of filler content both for BN and RK

Eq. No	Equations	Correlation Coefficient BN	Correlation Coefficien RK
1	Eq. 1 : $E = a_0 + a_1 T + a_2 W + a_3 T W + a_4 T^2 + a_5 W^2$	0.998	0.994
2	Eq.2 : $\sigma = a_0 + a_1 T + a_2 W + a_3 T W + a_4 T^2 + a_5 W^2$	0.997	0.998

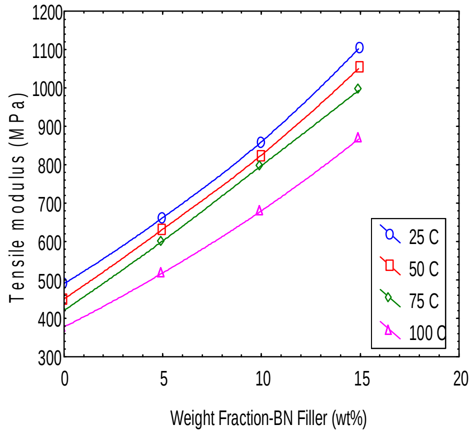

Figure (1) The relation between the tensile modulus of PP/PA6 with weight fraction of BN filler at different

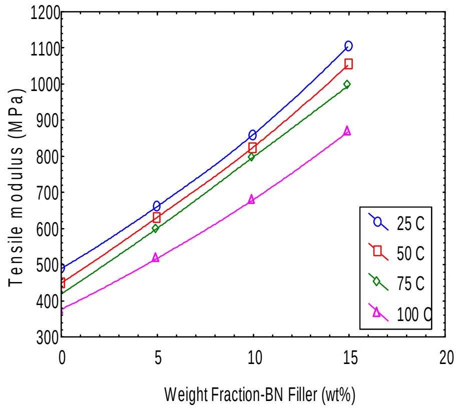

Figure (2) The relation between the tensile modulus of PP/PA6 with weight fraction of RK filler at different temperature (25,50,75,100) °C

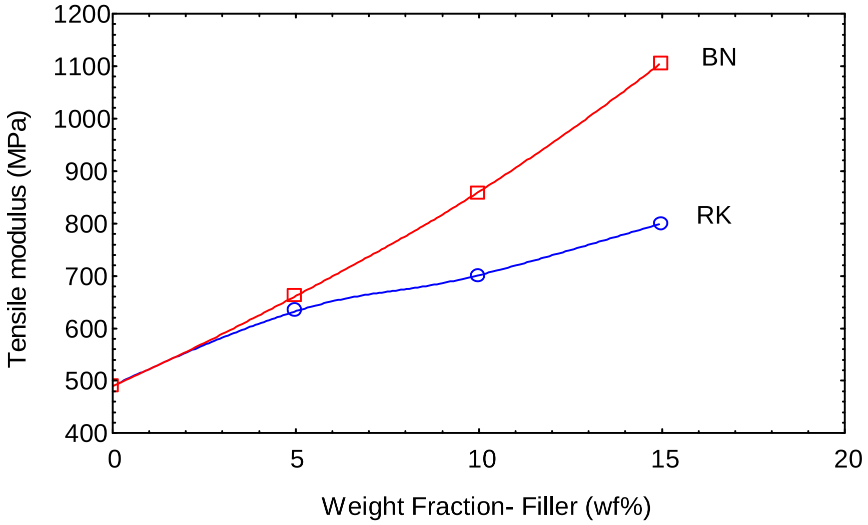

Figure (3) The relation between the tensile modulus of PP/PA6 with weight fraction of both RK and BN filler at temperature 25 °C

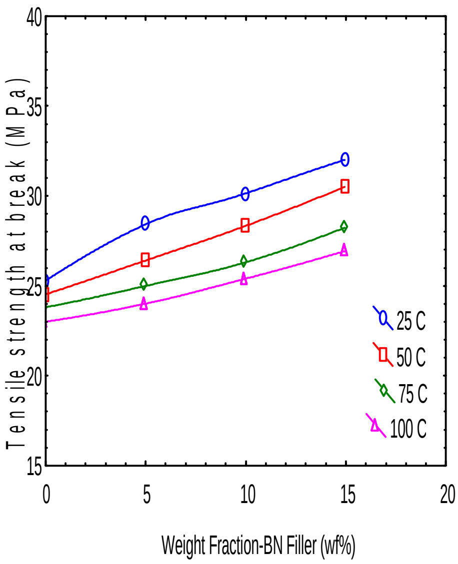

Figure (4)The relation between the tensile strength at break of PP/PA6 with weight fraction of BN filler at different temperature (25,50,75,100) °C

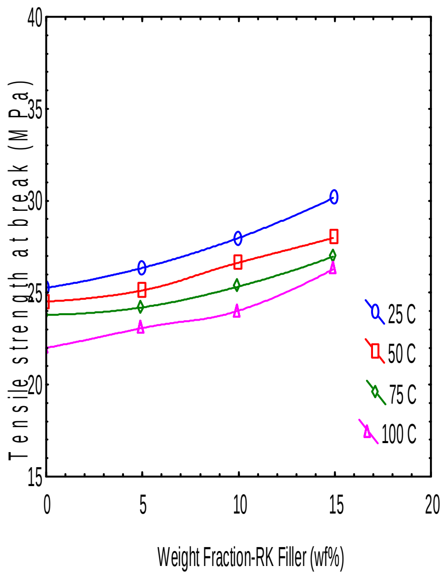

Figure (5) The relation between the tensile strength of PP/PA6 with weight fraction of RK filler at different temperature (25,50,75,100) °C

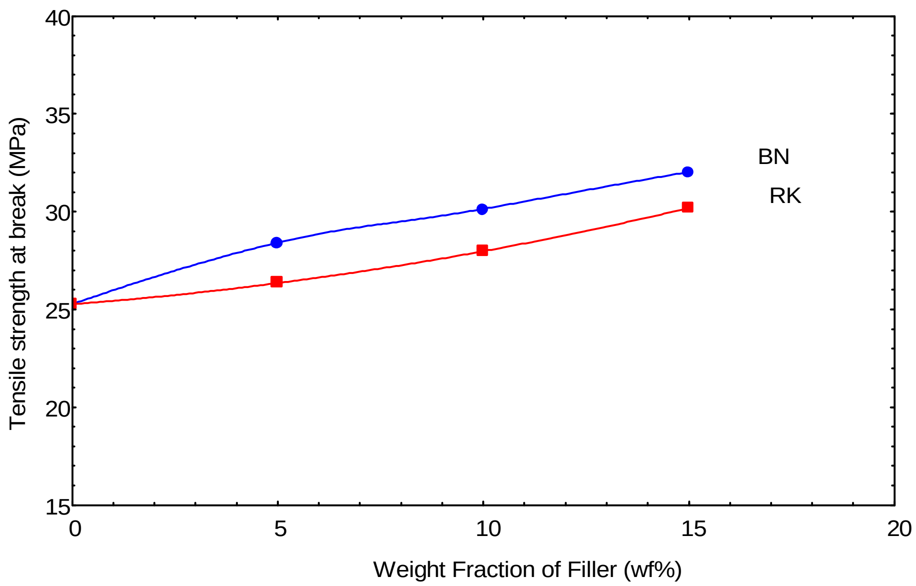

Figure (6) The effect of weight fractions of both BN and RK fillers in the tensile strength at break at 25°C

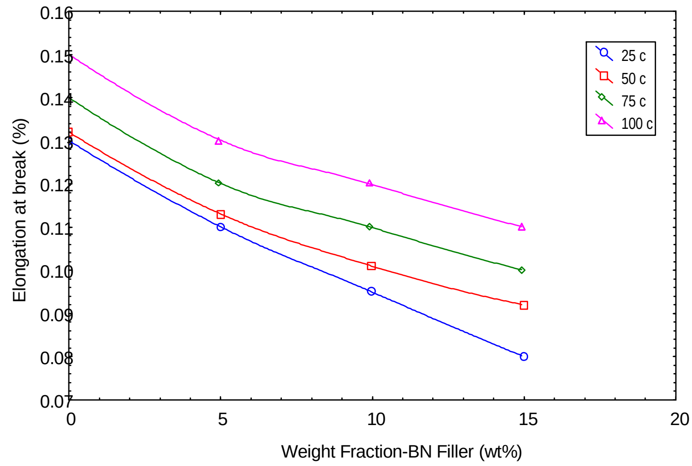

Figure (7) The relation between the Elongation at break (%) of PP/PA6 with weight fraction of BN filler at different temperature (25,50,75,100) °C

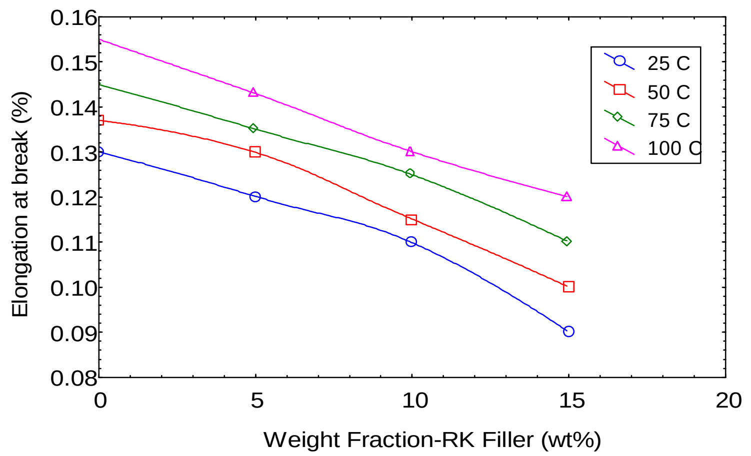

Figure (8) The relation between the Elongation at break (%) of PP/PA6 with weight fraction of RK filler at different temperature (25,50,75,100) °C

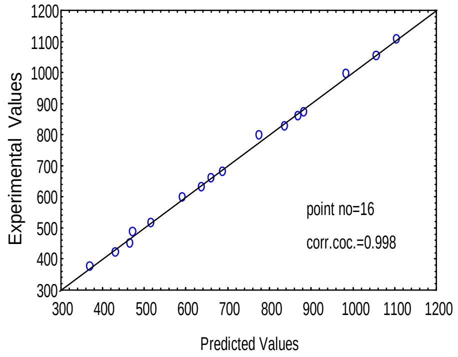

Figure (9) Experimental versus predicted values for Eq. (1)

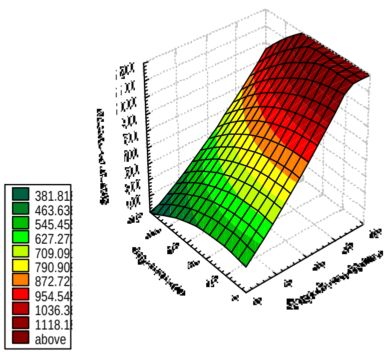

Figure (10) Three-dimensional representation of the Eq. (1) describing the variation of modulus of elasticity with weight percent of

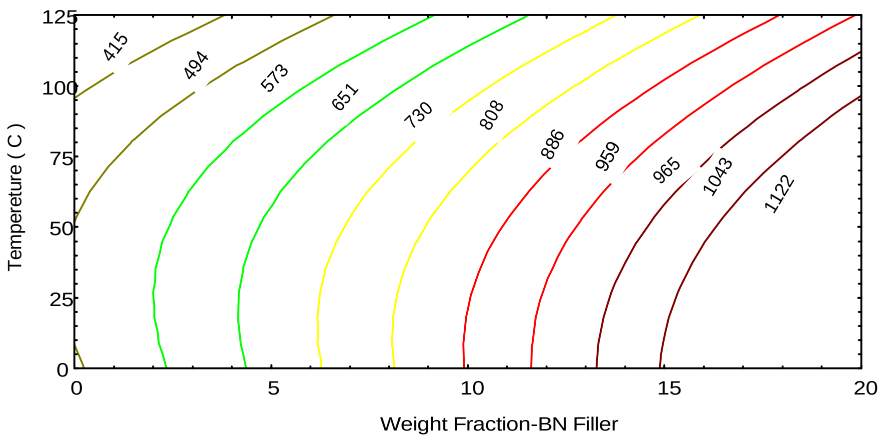

Figure (11)contour plot obtained from the Three-dimensional plot (Figure (10)).

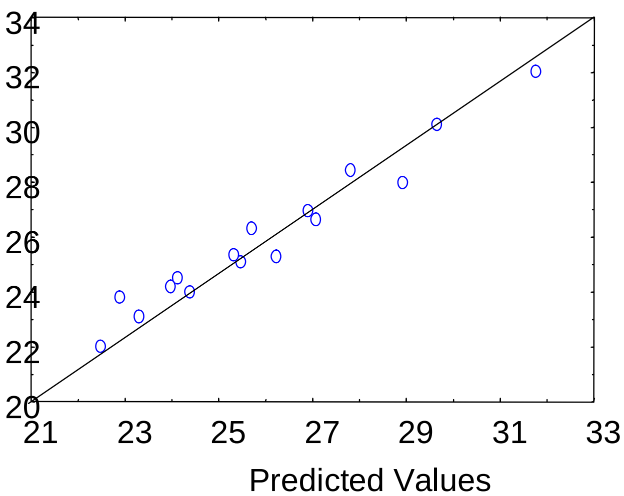

Figure (12) Experimental versus predicted values for Eq. (2)

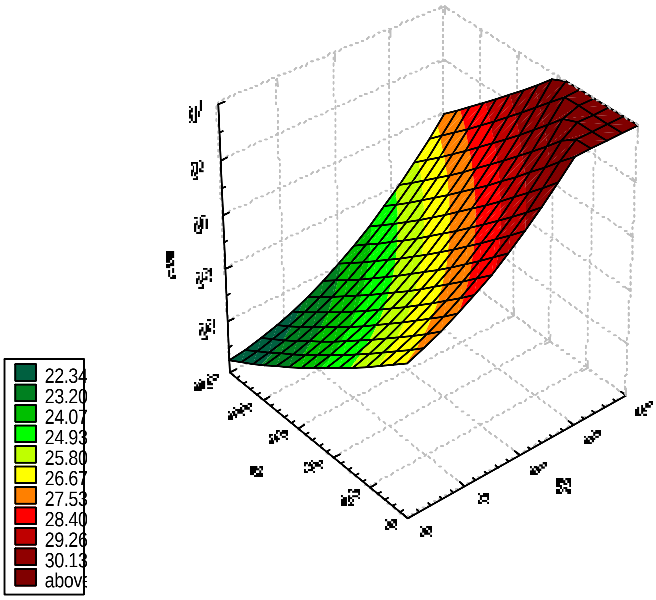

Figure (13) Three-dimensional representation of the Eq. (2) describing the variation of, tensile strength at break with weight percent of filler content RK and the temperature for PP/PA6/RK.

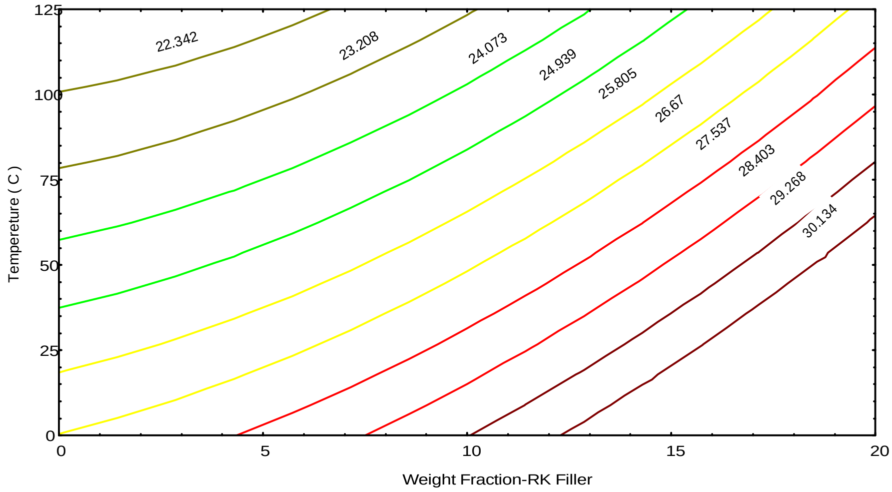

Figure (14)contour plot obtained from the three-dimensional plot (Figure (13).