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Mechanical Properties of Polyvinyl-Acetate and Toluene Diisocyanate and Sulfonated Phenol-Formaldehyde Foam Composites

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Abstract
Blend of polyvinyl acetate (PVA) and Toluene diisocyanate (TDI) were mixed with different percentages by weight of sulfonated phenol-formaldehyde (SPF) foam of prepared sulfonated phenol-formaldehyde resin. The measured mechanical properties such as the tensile modulus (E_t) values are (107, 43.7, 84.7, 424 and 165) MPa, for samples (1, 6, 7, 8 and 9). Tensile strength (σ_M) before break are (0.923, 1.21, 5.56, 6.43 and 8.65) MPa, maximum force applied on the specimen number (9) is 355 N. Yield strength (σ_Y) values are (0.743, 0.897 and 8.65) MPa at samples(1, 6 and 9). The tensile strength at break (σ_B) are (0.697, 1.12, 5.38, 6.32 and 8.28) MPa for samples (1, 6, 7, 8 and 9). Rather than strain at tensile strength (ε_M) and strain at yield (ε_Y) and break (ε_B). These are studied and investigated.
Keywords: PVA; TDI; (SPF) foam; tensile modulus; force; stress; strain; elongation.

Introduction

Polyvinyl acetate (PVA) is a thermoplastic polymer with chemical formula -($C_4H_6O_2$)-$_n$. It is normally manufactured by free radical polymerization of vinyl acetate[1]. PVa is a synthetic resin polymer, which, due its non-polar nature, is insoluble in water, oil, fats or gasoline. On the other hand, it is soluble in alcohols, ketones and esters[About .com, (2013)]. Toluene diisocyanate (TDI) is an organic compound with the formula$CH_3C_6H_3(NCO)_2$. Two of the six possible isomers are commercially important 2, 4-TDI (CAS: 584-84-9) is produced in the pure state, but TDI is often marketed as 80/20 and 65/35 mixtures of the 2,4 and 2,6 isomers respectively. It is produced on a large scale, accounting for 34.1% of the global isoyanate marked in 2000, second only to MDI[WIKIMEDIA, (2013)]. Polymer are usually described as viscoelastic materials, that is emphasizes their intermediate position between viscous liquid and elastic solids. An ideal linear elastic solid obeys Hooke's law, i.e. stress is proportional to strain. An ideal viscous liquid obeys Newton's law, i.e. stress is proportional to the rate of change of strain[A. K. Bhowmick, (2014)]. Many of modern technologies require materials with unusual combinations of properties that can be conventional metal alloys, ceramic and polymeric materials. Materials property combinations and ranges have been extended by the development of composite materials[A. Grujic, et al (2010)]. Composite are engineering materials made from two or more constituents with significantly different physical or chemical properties which remain separate and distinct on macroscopic level with in the finished structure. One material (the matrix or binder) surrounds and binds together a cluster of fibers or fragments of much stronger material (the reinforcement). For the matrix many modern composites use thermosetting or thermoplastic polymers[S. Baghat (2013)]. Several methods have been proposed to prepare polymer composites, such as sol-gel reaction, interactive polymerization and polymerization via melt processing, depend upon the nature of nano-particles and types of polymeric matrix. The final properties of these composites depend upon various parameters like size of particles, method of preparation of composites and dispersion of particles into the polymeric matrix[R. Jotania, etal (2013)]. The dispersion of the particles differs with particle content and particle size that is determining the properties of the composites. For a certain size particle, the dispersion in composite changes with content[S. Zhang, et al (2011)]. The composite modulus is controlled to some extent by particle surface modification. This phenomenon is due to two factors: interfacial adhesion and matrix crystalline structure. The direct effect of the former is insignificant since modulus is a property at low deformation that is not sensitive to adhesion. The second factor is mainly responsible for the improvement of composite modulus because the crystalline of semi-crystalline polymers and hence the composite modulus is affected by the filler[S. Y. Fu, etal (2008)]. Other example is the study of the smart composites obtained by the combination of Fe_2O_3 nonoparticles with biocompatible response polymer. As smart ferrogels, by the encapsulation of Fe_2O_3 nonoparticles into chemically crosslinked polymers like poly(N-isopropylacril amide), pNIPAM[R. Turcu, et al (2009)]. Generally, reinforced polymers show an increase in modulus, hardness, tensile strength, abrasion and tear resistance as well, as resistance to fatigue and cracking. Frequently, however, only some of these properties are significantly improved by reinforcing filler[L. Bokobza, (2011)]. Many fiber-reinforced composites materials are widely used in manufacturing various parts in automotive and aero space industries. The major advantage of fiber reinforced composites is to offer a high strength and modulus that are either comparable to or better than many traditional metallic materials. Because of their low specific gravity, the

strength-weight ratio and modulus-weight ratios, these metallic materials. In addition, fatigue strength – weight ratio as well as fatigue damage tolerance of many composites laminates is excellent[K. N. Kumar, et al., (20130]. In this investigation the effect of (wt%) SPF foam on the PVa and TDI blend and to find out the mechanical properties of the composite for different percentages by weight of sulfonated phenol-formaldehyde resin (SPF) foam.

Experiment

Preparation of sulfonated phenol-formaldehyde (SPF) resin:

42.5 moles of phenol was put in clean tri-neck round 500 ml. in capacity, replace it in Isomental heater sort LabHeat BAECO, Germany. Close the side necks by stop-fit thermometer and the other side by a condenser which is connected to water pump in ice path, while a stirrer sort Heidolph, Germany is inserting in the middle neck. The system was operated and the phenol was heated to appropriate temperature to dissolve any solid bodies. The system was stopped and slowly 4 moles of sulfuric acid 97% in concentration was added, Thomas Baker India, from one side neck by using pipettes and the round was closed again as above, the system was operated while the stirrer adjusted to appropriate speed and the temperature is raised, which is maintained between 100-120 ^{o}C for two hours. The system was stopped and let the temperature cooled slowly, and then the round was emplaced in ice path and 12 moles of Formaldehyde Thomas Baker, India. was added by using pipettes a fizzing and bubbling is occurred, the temperature is raised stir by hand using glass rod and let the temperature cooled to 35 ^{o}C then below 22 ^{o}C. continuous stirring was done until a viscose solid mass is obtained, left the product over night, the pH was examined by using indicator paper which is colored red low PH. NaOH solution was prepared in a spread flask and drops was added until over saturation is reached high pH, a few drops of H_2SO4 was added for equilibrium until pH=7. The solution was removed into a container, this is SPF foam and the precipitate SPF resin was put in a glass plate to be dried at room temperature which is collected in plastic container. This is used for other applications[T. S. Bachari, (2014)].

Samples preparation

Percentages by weight 3:1 of polyvinyl acetate- Toluene diisosyanate (PVa-TDI) were blended and (1wt%, 2wt%, 3wt%, 4wt% and 5wt%) SPF foam was added to the blend and was mixed into flask. The mixture was poured on a specimen with appropriate dimensions (112, 18.7, 2) mm. in length, width and thickness, the neck dimensions are (5 and 40) mm. in width and length. These were cut into polyethylene sheet as shown in Figure (1). After 5 hours the samples were pressed by thump carefully to avoid distend in the samples, and the system was left over night to let the samples to be dried. Although this is not prevented changes that occur in samples dimensions through solidify. The samples were taken out from the specimen and then undergoing tension test. Samples number is according to the Tensile strength testing machines. Table 1 shows the samples preparations, and calculations of change in length of strain at tensile strength and the final length, change in length and final length at break.

Tension test

Tensile strength testing machine sort Zwic Roell serial no. 197735/2011, Germany, has been used for the samples tension test. Tensile test was carried out at crosshead absolute 413.943 [mm] and 423.571 [mm]. The results are as shown in Figure (1). The results were obtained, referred to tensile modulus (E_t), the tensile strength (σ_M), yield strength (σ_Y), tensile strength at break (σ_B), strain at tensile strength (ε_M), strain at yield (ε_Y) and break (ε_B).

The elongation (e) can be determined by using the formula:

$$e\% = \Delta L/L_o \times 1000 \quad (1)$$

Where Lo is the initial length of the sample in mm is equal to 55 mm, this was taken apart by the machine. ΔL the change in length after applied force in mm. is equal to $L-L_o$, L is the final length after applied force in mm. The maximum force applied is 355 Newton as shown in Figure (1).

The tensile strength (σ_M) can be calculated by the following equation[A. Grujic, et al., (2010)]:

$$\sigma_M = \frac{F_{max}}{b.d} \quad (2)$$

Where Fmax is the maximum force applied on the specimen in Newton. b: is the width of the specimen in [mm]. d: is the thickness of the specimen in [mm]. The elastic modulus E of the investigated composite material can be calculated by the equation:

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{\Delta F}{\Delta\varepsilon} \cdot \frac{1}{b.d} \quad (3)$$

Where the ratio $\Delta\sigma/\Delta\varepsilon$ is determined by linear regression method from linear portion of stress strain curves.

Table 1 Sample preparation and calculations of ΔL and L.

Sample No.	PVA Gm.	TDI gm.	Wt% SPF	Total weight gm.	ΔL mm. break	L mm. final at break
1	9	3	1	12.12	0.203	55.203
6	9	3	2	12.24	0.929	55.929
7	9	3	3	12.36	0.132	55.132
8	9	3	4	12.48	0.104	55.104
9	9	3	5	12.6	0.308	55.308

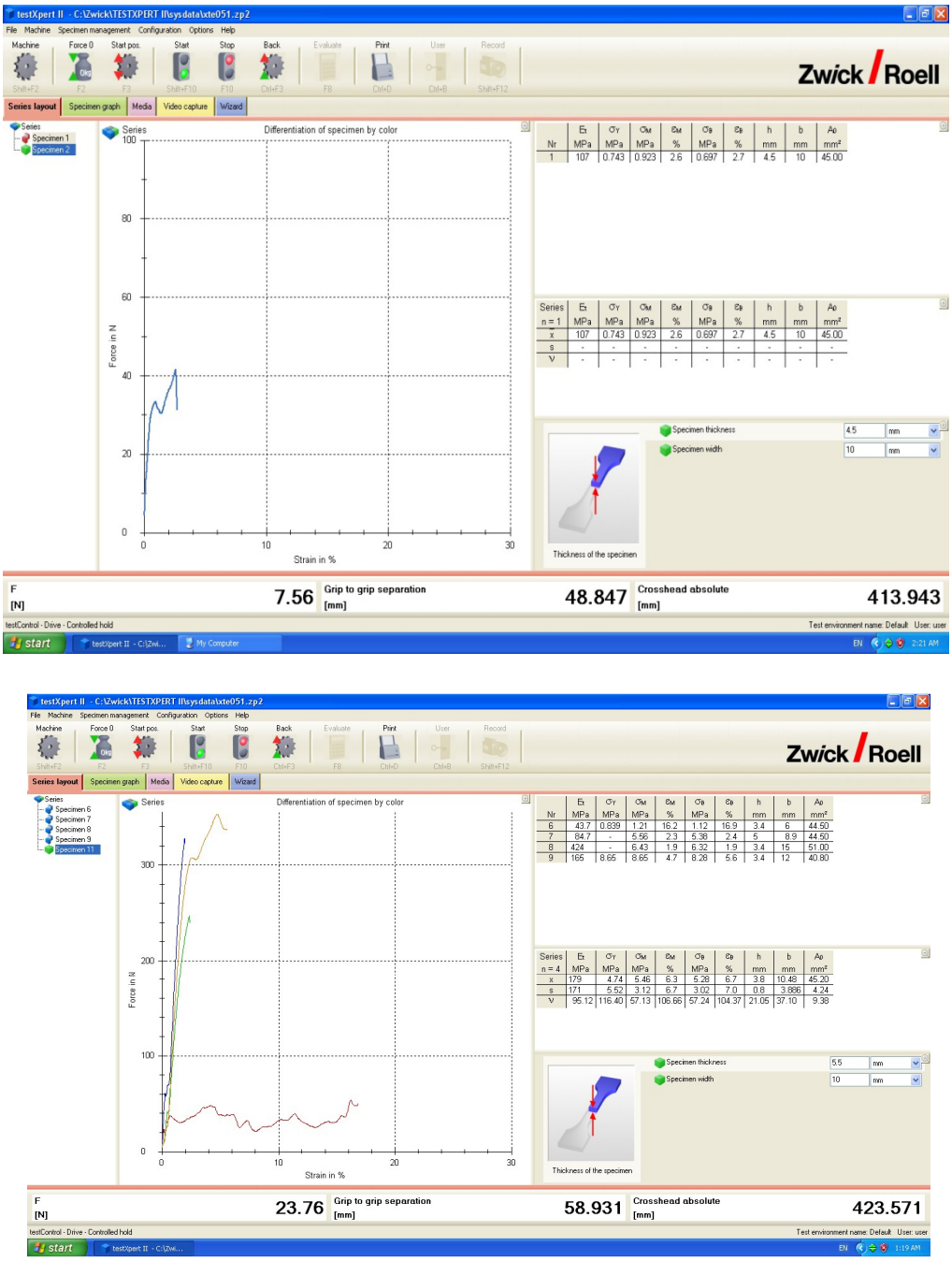

Fig.(1). Tension test of samples

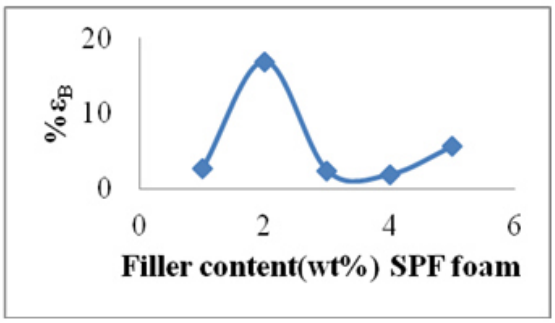

Fig. (2). The relation between ε_B% at break of Pva-TDI with wt%SPF foam

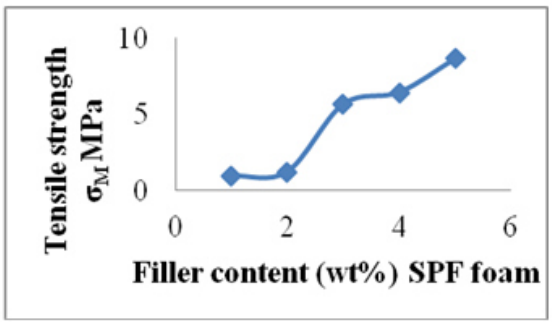

Fig.(3).The effect of filler content of SPF foam on tensile strength σ_M.

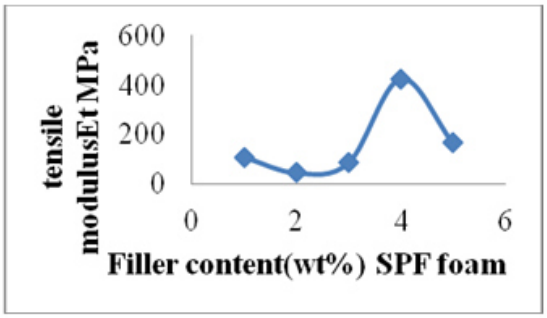

Fig.(4). The relation between tensile modulus of PVa-TDI with wt%SPF foam.

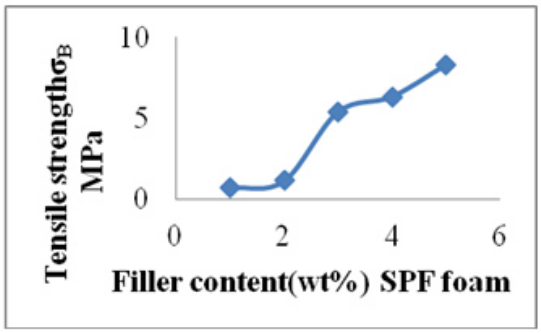

Fig.(5). The effect of filler content on the tensile strength at break σ_B.

Results and discussion

Table 1 shows the results of the change in length ΔL at ultimate condition and final length L for the percentages by weight (1wt%, 2wt%, 3wt%, 4wt5 and 5wt%) SPF foam of the percentages by weight of PVA:TDI blend. The calculated values for the change in lengths ΔL at strain at break (ε_B) (2.7, 16.9%, 2.4%, 1.95 and 5.6%), are (0.203, 0.929, 0.132, 0.104 and 0.308) mm. and the final lengths L are (55.203, 55.929, 55.132, 55.104 and 55.308) mm. although the variations in lengths depend on force applied and the percentages by weight of SPF foam, because of the random variations, there are decreased then increased in values obtained. In Figure (1), the tensile modulus (E_t) values are (107, 43.7, 84.7, 424 and 165) MPa. The tensile modulus of PVA-Polyol and SPF foam composites increases with wt% SPF foam but does not depend on particle size, therefore the composite is unaffected by particle size. Similarly the particle size does not affect the modulus of the composite. From above it is shown that the particulate composite modulus is insensitive to particle size. However, when the particle size is decreased to a critical size, such as 30 nm, and then will be obvious effect of the particle size on the modulus predicted theoretically. Moreover, nano-indentation modulus has been obtained on the composite coating reinforced with wt% SPF foam. To summarize, it seems there is a critical particle size above this particle size there is no effect on composite modulus. When the particle size is below this critical value the effect on composite modulus is more significant. The magnitude of this particle size cannot be predicted a prior for it depends on the particle matrix and particle matrix adhesion[S. Y. Fu, et al (2008)]. The tensile modulus for sample (4) 424 MPa, indicates that the residual deformation of the specimen is very small[A. M. Bragov, et al., (1994)]. And from Figure (1), the yield strength (σ_Y) is only for samples (1) 0.734 MPa, (6) 0.833 MPa. and (9) 8.65 MPa because the curve does not exceed to the second region the yield region for samples (7) and (8). While the curve for samples (7) and (8) show only the variation at first region, the linear region, at this region Hooke's law is applied. While the proportional limit is the greatest stress that the material is capable of sustaining without any deviation from proportionality of stress-strain curve (Hooke's law). This should not be confused the elastic limit, that is the maximum stress can be applied without any permanent strain remaining when the stress is released. Both of these values are extremely difficult to accurately determine because of the problem of finding the exact point where the curve ceases to be linear. For this reason, it's generally recommended that one use a yield strength measurement instead with small offset (0.01%)for test on critical materials[Pamphlet4, (2014)]. Proportional limit usually is not used in specifications because the deviation begins so gradually those controversies are sure to arise as the extent stress that the line begins to curve [ENGNEERS EDGE, (2014)]. The

tensile strength (σ_M) are (0.923, 1.21, 5.56, 6.34 and 8.65) MPa. These values show as wt% SPF foam is increased; the tensile strength (σ_M) is increased. Ultimate strength prediction are less rigorous, in part due to the role played by filler-matrix adhesion[J. R. M. D' Almeida, et al., (1988)]. The measured values at the third region, the break region, of tensile strength at break (σ_B) are (0.697, 1.21, 5.38, 6.32 and 8.32) MPa. These are the same behavior as in (σ_M). The deformation at this region is irreversible, results from the displacement in the molecules in content of PVA-Polyol with (SPF) foam and end in cut of specimen. Polymer composite are intensively studied for the new properties these are given by the combination of the properties of both polymer matrix (SPF) foam and binds together a cluster or fragments of a much stronger material (the reinforcement) respectively[Y. P. Mamunya, et al (2002)]. Figure 2 shows the effect of weight percent of filler content on strain at break, there is no rule governed the behavior of the relation between the weight percent of filler content of SPF foam and ε_B %. Figure 3 shows the effect of filler content of SPF foam on the tensile strength as the filler increased the tensile strength (σ_M) increased. In Figure 4 the relation between the tensile modulus and wt% filler content of SPF foam, as the filler content increases the tensile modulus increased. Figure 5 shows the effect of filler content wt% SPF foam on the tensile strength at break σ_B as the percentage by weight of the filler increases (σ_B) is increased this is the same behavior as in Figure 3.[S. N. Mustafa (2012)].

Conclusion

1-Interaction between SPF and PVA/TDI was investigated, and can play an important role in determining the ultimate performance of the polymer composite.
2- Percentages by weight of PVA:TDI blend is chosen 3:1 from high to low molecular weight.
3-Percentages by weight (1wt%, 2wt%, 3wt%, 4wt% and 5wt%) SPF foam were mixed with PVA:TDI blend. The composites show different behavior such as (ε_M), (ε_B), (σ_Y) and (σ_M).
4- There are three distinct regions, the first region, the elastic region, the second region, the yield region and the third region, the break region.
5- There is no detection of yield strength (σ_Y) in sample (7) and (8) because the variation did not exceed to the second region, the yield region and limited in the first region, the elastic region that Hooke's law is applied.
6- Yield stress, measured at large deformations, is much more independent on interfacial adhesion with respect to the elastic limit, measured at small deformation.
7- The highlights that the incorporation of fillers into polymer matrix improves stiffness of the composites.
8- Uniform particle distribution and good adhesion between polymer matrixes and filler were obtained, these are crucial for superior mechanical properties.

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الخصائص الميكابيكية للبولي فينايل-اسيتيت والتلوين داي ايسوسيانيت مع رغوة الفينول-فورمالديهايد المسلفن المحضرة

ثامر سلمان بجاري
مركز أبحاث البوليمر- قسم علوم االمواد – جامعة االبصره

الملخص:
تم تحضيرمزيج البولي فينايل اسيتيت والتلوين داي ايسوسيانيت بنسبة وزنية ثابتة وخلط المزيج مع نسب وزنية مختلفة لرغوة الفينول الفورمالديهايد المسلفن المحضرة مع مادة راتنج الفينول- فورمالديهايد المسلفن. الخصائص الكهربائية المقاسة مثل معامل و 6.43 5.56, 0.923, 1.21,). قوى الشد قبل الأنهيار (9 و ,8 7, , 6 1, ميكاباسكال للنماذج (165) و 424 84.7, (107, 43.7,المرونة و 6,1 ميكاباسكال للنماذج (8.65) و 0.743, 0.897). قوى الشد عند منطقة الوهن (9 نيوتن عند النموذج (355) ميكاباسكال. أعلى قوة 8.65). فضلا عنالأنفعال في قوة الشد, 9 و 8 7, 1, 6,ميكاباسكال للنماذج () 8.28و6.32 5.38, 0.697, 1.12., قوى الشد في منطقة القطع (9) الأنفعال في منطقة الوهن ومنطقة القطع.

كلمات مرشدة: البولي فينايل-اسيتيت, تلوين داي ايسوسيانيت, رغوة الفينول فورمالديهايد, معامل المرونة, قوة, قوى الشد, الآستطالة.

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