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Assessing the Effect of Nylon 66 and Alumina on Mechanical and Thermal Properties of Epoxy-based Adhesives Through Taguchi Experimental Design Analysis

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ABSTRACT

The effect of alumina and tough nylon 66 on microparticles' presence the mechanical and thermal properties of epoxy adhesives is assessed here. In order to distribute the adhesive formulation components, in a uniform manner a mechanical stirrer is applied. The effect a combined percentage of nylon 66 at (20, 30, 40 pph) and alumina micro-particles 20 µ (50,60,70 pph) selected based on Taguchi experimental design method on the mechanical and thermal properties of the adhesives is assessed. The tensile test results reveal that the sample containing 20 pph nylon 66 and 70 pph alumina micro particles has the highest Young's modulus and tensile strength compared to other examples designed in Taguchi Table and Sample containing 30 pph nylon 66 and 50 pph alumina micro particles has the highest degree of toughness compared to other specimens. The results of TGA reveal that the sample with the highest mechanical properties has a degradation startup temperature and more residual coal than pure epoxy. All this is due to the presence of nylon 66 that contains active hydrogen which in turn can increase cross-linking and degree of networking high and ultimately a higher thermal stability than the epoxy matrix. The results obtained from the FT-IR test indicate that amide groups of nylon 66 are capable of interaction with epoxy rings. Prog. Color Colorants Coat. 11 (2018), 149-164© Institute for Color Science and Technology.

1. Introduction

Epoxy adhesives consist of chemical compounds applied in connecting many surfaces to each other. These adhesives are composed of an epoxy resin and curing agent. Epoxy resins have beneficial properties, including high strength against chemical agents, high corrosion resistance, environmental cure capability, low shrinkage during cure, high strength, electrical insulation and high adhesion strength [1]. The chemical and physical properties of epoxy resin and its derivatives gained epoxy adhesives great importance in industries like aerospace, construction, automotive, defense and marine. Epoxy resins in many applications need to develop a network structure by applying appropriate curing agent if achieving modulus and high tensile strength are sought [2]. This thermosetting

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structure becomes an undesirable property making materials relatively fragile. These materials have low resistance and begin to crack at the beginning of their growth [3]. Toughness affects the tensile strength, Young's modulus and thermal degradation temperature of the epoxy matrix and usually reduces these properties. It can be prevented from reducing these properties by adding fillers to the polymer matrix, the function of which is to establish a balance between the toughness and other mechanical properties, including tensile strength [4, 5]. The effect of silicon dioxide nanoparticles (SiO_2) and ATBN rubber on mechanical and thermal properties of epoxy base adhesives are assessed by Kinloch et al. Increase of SiO_2 composition percentage within 1 to 8% range mass improves the thermal properties, increases the glass transition temperature and the overlapping shear strength [6].

The failure toughness of nanocomposites containing epoxy, clay and alumina nanoparticles are assessed by Ghadami et al., where, an increase in the given nanoparticles in the composition by 5 and 3% by weight, respectively, improves the tensile properties, moreover as to alumina percentages above 3% by weight, due to the increased viscosity, the resin does not cure and the porosity increases during mixing. The fracture toughness and the critical energy release rate increase with an increase in alumina (up to percentage of 3% composition by weigh) and nanoclay [7].

The natural micro-particles of wool as a toughening agent in epoxy adhesives are applied in a study run by Barbosa et al., where these particles act like a crack inhibitor and by absorbing the shock(s), increase in energy. The range of composition percentage of wool is within 1 to 5% by weight and the wool surface modification with plasma improved adhesion between the two materials [8].

The effect of adding aluminum oxide and aluminum and copper on thermal stability and shear strength of the overlap is studied by Gosh et al., where the microscopic results reveal that at an optimal amount of microparticles, a good distribution of these particles is observed in the epoxy matrix. The composition percentage of microparticles at 10% by weight increase the thermal properties and shear strength of overlapping in a significant manner as compared with pure epoxy. Surfaces of failure are assessed through microscopic studies revealing that the failure mechanisms cause shear bonding, cavity growth, crack deviation, and a change in plastic shear shape [9].

The effect of adding alumina and silica fillers (20, 40, 60 phr) on the mechanical and thermal properties of epoxy adhesive (epoxy + hardening) in the application of single lap joint metal to composite is assessed by Jouyandeh et al. The lap shear test of the samples reveals that the shear strength of the samples containing 60 phr alumina and silica increased by 12% and 20%, respectively, in comparison with non-filler epoxy adhesives. The modulus of the samples improved by 797% and 472%, better than that of pure epoxy adhesive. The TGA results of the selected samples (samples with the best response in the tensile test) indicate that the thermal properties of these samples forego changes compared to pure epoxy specimen [10]. The effect of nano-sic particles as to a result of overlapping shear tests and TGA and DSC tests on the mechanical and thermal properties of epoxy/nano-sic composites, are assessed by Zhou et al., where the results indicate that the nano-particle surface modification with silane in an 8 percent volumetric composition of this modified nanoparticle increases up to 80% overlapping the shear strength. The results obtained from TGA and DSC tests indicate that the amount and size of nanoparticles do not affect the epoxy/sic composites destruction pattern and adding these nanoparticles could partially increase epoxy thermal stability [11].

The effect of benzimidazole presence on silica-filled epoxy matrix on the curing reaction, glass transition temperature and epoxy matrix toughness through TGA, DSC and Tensile tests are assessed by Natarjan et al., where, the PBI presence not only accelerates the curing reaction rate, but also increases the glass transition temperature up to 220 °C as a result of 10% by weight of PBI increase and the epoxy matrix toughness was significantly increased, confirmed by SEM images [12].

The resol-type of phenolic resins is applied by Sturiale et al. to enhance adhesive bond strength in epoxy-amine systems, where the adhesive mixtures are prepared within 0 to 30% by weight of the resol range: 10 to 20% in the interfacial fracture toughness and adhesive bond strength increased and Young's modulus decreased at 30%; the results of the FT-IR analysis indicate that epoxy reacts with phenolic resin [13].

The triple mixture of benzoxazine, epoxy and phenolic are tested by Rimdusit et al. and the results indicate that the novalac type phenolic resin acts as a initiator, while the creation flexibility and low viscosity relate to the epoxy component where benzoxazine has an incremental contribution in thermal curing ability, the mechanical properties, and the Crosslink Modified Density; the amount of mass reduction of this triple mixture is 5% at 370 °C [14].

The epoxy/phenolic alloy are assessed by Tyberg et al. and it is found that by adding phenolic in adhesive mixture, the glass transition temperature decreases and toughness increases; the reason for increasing the toughness and reducing the glass transition temperature is to reduce the density of the grid; the mechanical properties and flammability increase with the increase in the amount of novalac in the system at 3 to 1 phenol to epoxy ratio [15].

The aluminum oxide, titanium dioxide and clay micro filler presence in a percentage composition of 10 to 30% by weight and aluminum oxide, titanium dioxide and clay nanoparticles within the 2.5 to 10% by weight range on mechanical properties of epoxy is assessed by Ozsoy et al., where the results indicate that the tensile strength, shear strength and elongation at the rupture point reduce by an increase in composition percentage of the micro filler and nanofillers, and the flexural and tensile modulus increased; as to micro-fillers, an increase in composition percentage causes weakens in interfacial adhesion between the matrix and filler and as to of nanoparticles, an increase in composition percentage cause accumulation and degrades the properties [16].

The effect of silica microparticles presence on mechanical and thermal properties of epoxy within 0 to 70% by weight range is assessed by Sang Jo et al., where at this range, the tensile strength and yang's modulus increase from 8 to 10 and 51 to 55 percent, respectively, compared to pure epoxy, while toughness decreases by 34 % compared to pure epoxy; the thermal stability modifications where smaller particles are more effective in lowering the thermal expansion coefficient are confirmed based on the composition percentage of silica [17].

Wernik et al. assessed the mechanical properties of epoxy-based adhesives reinforced with nano-tubes carbon, where PVP is applied as a surface-active agent contributive in stabilizing the distribution of carbon nanotubes in the epoxy substrate. Mechanical tests are run on adhesive specimens containing epoxy /carbon nanotube and epoxy/carbon nanotube and PVP (both with same values); the results of the dog bone test reveal that both stiffness and tensile strength increase in both systems; in the tensile adhesive puck test, for system containing pvp, a 90% increase in tensile bond strength and for the system containing only nanotube carbon, a 54% increase is observed in property compared to pure epoxy. In double lap shear test, a relatively small increase of about 25% is observed in shear bond strength in the system PVP-containing, but the system containing only nanotube carbon did not change significantly in this property. In all these tests, it is observed that the increase in the properties of systems containing PVP is greater than that of the systems containing only carbon nanotubes. This improvement in properties is observed within 1 to 1.5% by weight range of carbon nanotubes [18].

In 2017, Erkem et al. assessed the carbon nanotube and boron nitride nano plates' presence on epoxy base adhesives' shear strength and thermal stability. This adhesive was tested to determine the shear adhesion of the overlap in relation to aluminum surfaces. Mixing these nanoparticles with epoxy increase both the thermal degradation temperature and glass transition temperature to some extent. It is found that MWCNT and BNNP have a synergistic effect on shear strength. The energy required for bond failure and this synergistic effect will cause a change in branching and growth of the cracks that would increase fracture toughness [19].

In this study, the effect of compositions prepared with different percentages of nylon 66 and alumina fillers on the mechanical and thermal properties of DGEBA through Taguchi experimental design method epoxy adhesive are assessed. The tensile and shear single lap test is run to determine the mechanical properties and shear strength of the overlap, where TGA is applied in evaluating the thermal stability.

2. Experimental

2.1. Materials

Materials used in this research are detailed in Table1.

Table 1: Specifications of materials applied in this study.

Materials	Company Name	specification or Business Code	Role
Epoxy resin	Dow	Epon-828	Basic component
Nylon66	Arel	NLT25	Toughener
Aluminum powder	Toma Isfahan	20 µ	Filler
Formic acid	Merck	64-18-6	Solvent of nylon6.6
Triethylene tetramine	Dow	Epoxy hardener 828	Hardener
Xylene	Merck	1330-20-7	Adhesive solvent

2.2. Devices and Methods

2.2.1. Producing epoxy adhesive containing alumina filler and nylon 66

Here, the Taguchi method is adopted as a method of designing appropriate and applied test. The subject substances here consist of nylon 66 and alumina fillers. Choosing alumina filler instead of silica filler is based on the results obtained in [10], where Alumina is evaluated at three levels of 20, 40 and 60 per 100 parts of epoxy according to the results obtained and it is found that level 60 is the best level in addition to its ability to yield appropriate viscosity and increasing the thermal resistance (at relatively low levels). The design factors for testing the first phase are tabulated in Table 2.

At this stage, first, it is necessary to dissolve 5g nylon 66 into 10 milliliters of formic acid in a container put in a water bath of 100 °C to allow the nylon 66 to dissolve for 3 hours. In this test, component 1 including epoxy resin, xylene and alumina filler is dispersed into the reaction vessel, followed by mixing through a mechanical stirrer. The stirring speed fixed at 422 rpm, for 4 minutes after which the dissolved nylon 66 is added to the content of the reaction vessel. Component 2 (hardener) is added 8 minutes after the nylon 66 is added to the reaction vessel. The mixing continues for 5 minutes. The method of applying adhesive to surfaces, as described [10], with the only difference that here, curing is subject to ambient temperature. The reason for this is the inability of nylon 66 to cure at high temperatures. It is notable that here, in addition to preparing single lap test samples, a dog bone specimen is made from each adhesive for tensile testing. This test is run in three replicates for each adhesive specimen.

Table 2: Designing factors and levels testing by Taguchi method in the first stage.

Test number	Nylon66 (pph)	Alumina filler (pph)
1	20	50
2	20	60
3	20	70
4	30	50
5	30	60
6	30	70
7	40	50
8	40	60
9	40	70

2.2.2. Surface preparation

To obtain the highest joint strength, surfaces are prepared in two steps: the surfaces are rinsed and degreased in a solvent like thinner, for 15 minutes, placed in water at 100 °C for a few moments and transferred to the heat sink for drying. The areas of the surface where the adhesive is to be laid are roughened by sandpaper: for the composite, grade 1800, (very soft) and for the stainless steel, grade 180, (very rough).

2.2.3. Overlapping shear strength test (ASTM-D5868)

Lap shear test was performed according to ASTMD-5868 as illustrated in Figure 1. This test method essentially describes the characteristics of a single lap shear test in measuring the specifications of adhesives in bonding metals plastics reinforced with fiber. This test method is a branch of ASTM D1002 test method (single lap adhesive bonding of metals) [20]. The Santam 150 tensile test machine is applied in running this test. The metal thickness and composite are 1.5 and 2.5 mm, respectively, the specimen length in the clamp of tensile test machine is 25.4 mm and the loading speed is 13 mm / min.

2.2.4. The tensile properties of plastics (ISO 527-1,2,3) test

According to the test standard of ISO 527-1, 2, 3, dog bone mold with the specimen dimensions which are shown in the Figure 2 was used. This test consists of three separate and complementary sections, where the structural and mechanical characteristics of the dog bone plastics specimen are described [21].

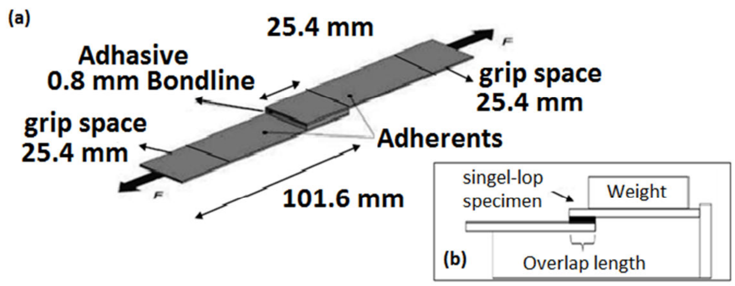

Figure 1: (a) Specifications and (b) method of bonding, (ASTM-D5868).

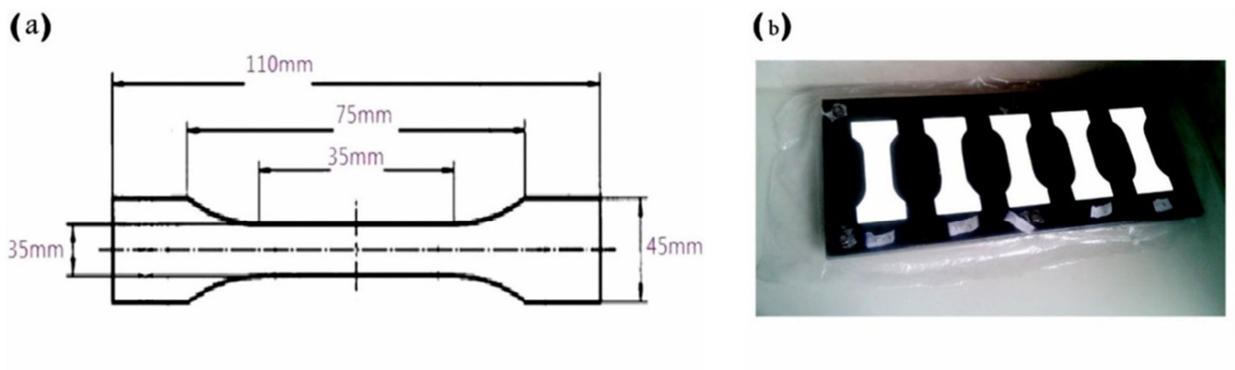

Figure 2: Specifications of (a) dog bone adhesive specimen mold and (b) the made samples.

2.2.5. TGA test

The thermal degradation and stability are assessed by a thermal gravimetric analysis device Model Q 5000 TA TGA. The samples are heated up to 800 °C subject to nitrogen gas at 10 °C / min rate. The samples weigh about 10 mg, which are cut into small plates. After placing the plates on aluminum plates, they are heated up to 800 °C. The initial degradation temperatures, the maximum weight loss rate and the carbon (coal) residue volume non-volatile fraction is determined after 800 °C. All tests here are run in Isfahan University of Technology.

2.2.6. FT-IR spectroscopy

The FT-IR test is run through JAPCO 6300 spectrophotometer (JASCO company, Japan) in order to determine the agent groups produced by epoxy interaction with the adhesive formulation components.

3. Results and discussion

3.1. Assessing the effect of nylon 66 composition percentage on tensile properties of epoxy adhesives

The results of the tensile test run on the dog bone samples are tabulated in Table 3, where, as observed nine tests are run on four outputs.

As expressed in the first section (overlapping shear strength) of this table, the highest tensile strength is for sample number 3 and the lowest is for sample number 8. Sample number 3 is contains pph 20 nylon 66 and pph 70 alumina fillers. Nylon 66 has three levels of 20, 30 and 40 pph and alumina at three levels of 50.60 and 70 pph. So, given these levels, it is clear that the lowest level of nylon 66 has the highest tensile strength for the formulated adhesive. It is always necessary for the adhesive to have high adhesion (high bond strength and non-elasticity) for high strength, and for high toughness, this adhesion should be at a low rate [22]. However, it is well known that an increase in nylon 66 content in the system containing epoxy resin increases the strength, which in turn together with the high modulus decreases toughness from one point to the next. Consequently, to yield a high strength, high modulus and appropriate toughness, adding nylon 66 at a proper ratio to the system containing epoxy resin is the only solution [23]. Here, on the one hand, because the nylon 66 breaks down the epoxy rings through its active hydrogens and form a bond and on the other, there is a strong competitor like TETA (TETA also as a hardener uses from its active hydrogen to bond and breaks down epoxy rings). Therefore, the excessive increase in nylon 66 content cause the amount of unreacted nylon 66 in excess. Increasing these extra masses disrupts adhesion performance and decreases the adhesive strength. So according to the results obtained in this section, in this formulation, the nylon 66 is suitable for low-level applications. This reaction is schematically illustrated in Figure 3.

Table 3: Results of the dog bone specimen's tensile test.

Test number	Tensile strength (MPa)	Young's Modulus (0.25-0.75) (MPa)	Strain (%)	Toughness (KJ/m^3)
1	1.064±0.01	23.6±0.03	4.36±0.03	25.8±0.09
2	1.268±0.007	24.4±0.02	5±0.045	36.1±0.4
3	1.671±0.03	32.5±0.07	6.9±0.085	74.9±0.8
4	0.64±0.06	1.8±0.03	67±0.23	333±0.06
5	0.52±0.009	2.1±0.03	75±0.84	299±0.9
6	0.74±0.03	4.5±0.05	48.3±0.235	261±1
7	0.27±0.02	3.2±0.09	26.6±0.285	52±0.3
8	0.09±0.004	0.2±0.01	126±0.65	106±2
9	0.19±0.005	1.1±0.02	82.3±0.3	115±1

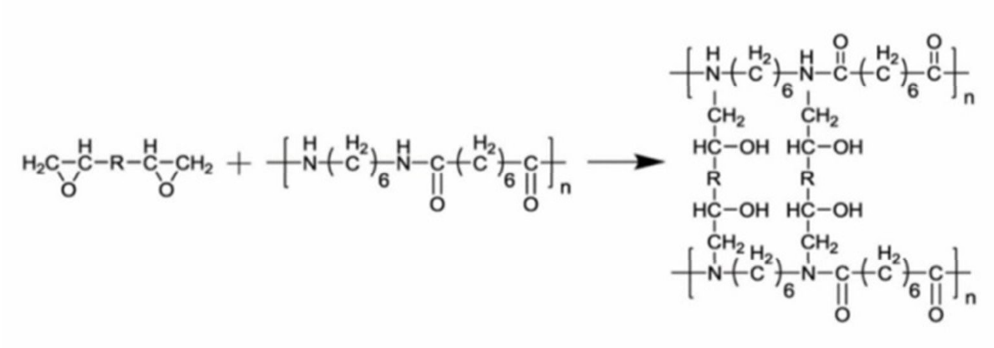

Figure 3: Nylon 66 reaction in the presence of epoxy rings [22].

Here, similar too findings in [10], it is proved that an increase in alumina increases the adhesive strength. Increasing the level of alumina and proper distribution of its concentration in the adhesive system of the epoxy resin increases strength [24]. This means that, along with the increase in level (for alumina), the proper distribution in the adhesive mixture is one of the factors enhancing the tensile strength. Here, by adding solvents, in this study, formic acid and proper mixing, the dispersion and distribution of alumina concentration is improved.

In the opposite case this is shown in sample No. 8. In this sample, nylon 66 is at its highest level, which results its performance is visible in the table above. As observed, as to the second property (modulus 0.25-0.75), Table 3, the highest modulus is of the sample 3 and the lowest is of sample 8. The strength reduction process begins from Test No. 4, where the nylon 66 enters its second level. The increased strength observed in specimens 6 and 9 (samples where alumina content is above its level) indicates the effect of increasing alumina levels on the final properties. As expected, nylon 66 presence will increase the amount of toughness. This increase at level 2 reaches its highest (specimens 4, 5 and 6), while at level 3 it undergoes a drastic decline. By considering the results on modulus' values and toughness, Table 3, an excessive increase in the modulus (together with high strength) reduces the toughness level (the surface below the graph), while, a drastic decrease in the modulus' level reduces the area under the curve.

3.2. Assessing the effect of nylon 66 composition percentage on overlapping shear strength of epoxy adhesives

The results of the single lap tensile test for bonding the metal to the composite are tabulated in Table 4.

Table 4: Results of the overlapping shear tensile strength test.

Test number	Tensile strength (MPa)	Young's Modulus (0.25-0.75) (MPa)	Strain (%)	Toughness (KJ/m^3)
1	6.1±0.0071	196±0.098	0.56±0.04	3.3±0.016
2	6.7±0.008	167±0.38	5.13±0.035	207±0.28
3	8.5±0.009	351±0.4	4.36±0.05	198.2±0.71
4	5.2±0.02	204±0.04	2.96±0.025	89.2±0.13
5	4.4±0.012	245±0.25	1.91±0.095	44±0.04
6	5.6±0.016	163±0.14	4.76±0.02	150±0.86
7	1.2±0.005	171±0.65	5.96±0.025	25.2±0.34
8	1.6±0.04	153±0.77	5.2±0.01	46.2±0.019
9	1.9±0.0069	193±0.17	1.14±0.015	11.5±0.043

The highest and lowest strengths are of samples number 3 and 8, respectively. In fact, this is the same result as the result in Table 3 where, sample 3 has the highest strength and sample 8 the lowest. In fact, this alignment of results indicates that the inner strength of the adhesive (observed in the dog bone shaped specimens) if able to soak the surfaces and it wet the surfaces well, it has outer strength (the strength observed in the bonding specimens), [25]. Presence of nylon 66 with low level in the proper solvent in the adhesive system of epoxy resin improves surface wetting [5]. Here, by creating a proper and homogeneous viscosity in the adhesive, the adhesive performance improves and the adhesive activity increases in bonding to the surfaces through penetration (adhesion through penetration occurs with more power provided that particle size in the adhesive mixture is small and homogenous with a good fluidity) and mechanical interactions (adhesive slippage and movement towards tiny cavities subject to surface preparation step). The result of this wetting is observed in the failure type section. It is notable that polymer molecules must be able to move for the proper penetration of polymer chains [25]. Nylon 66 in a mixture of epoxy resin can have sufficient mobility. Of course, issue is subject to the distribution [23]. In the results section of the modulus and toughness, it is observed that if the modulus is increase to a greater extent (with respect to the strength point), it would reduce the surface below the curved and reduces toughness. As observed, sample number 3 has a high modulus and strength but lacks the highest toughness. A decrease in the modulus in sample 8, decreases the level below the curve significantly and reaches its lowest value. In this sample, the amount of energy that the adhesive can absorb up to the breaking point lowers. The reason for this disorder is the performance of nylon 66 and the high accumulation of unreacted molecules in the system.

3.3. The main effects chart

The main effects chart is plotted in Figure 4. The responses applied in plotting this graph consist of only overlapping shear strengths. Because the objective is to achieve a high level of strength, Taguchi design is defined based on the principle of the bigger the better.

As observed in this graph, there exists a direct relation between strength and alumina volume, in this case both increase. These increments are from level 1 to 2 with a slope higher than that of the level 2 to 3. The drop-in gradient from level 2 to 3 is due to both the gradual increase in viscosity and the filling of the role of unreacted nylon 66. The changes in and the performance of nylon 66 in the 2nd level is appropriate and incremental, well suited in consuming active hydrogens in its capacity, while from the 2nd level to 3rd, unreacted molecules of this composition are accumulated next to one another and cause a loss of properties (overlapping shear strength) in the system.

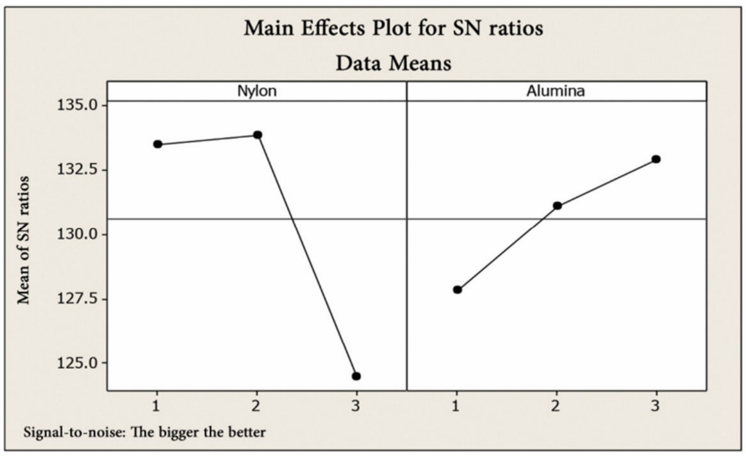

Figure 4: The chart of the main effects of adhesive sample as a result of in the overlapping shear tensile strength test.

3.4. Contour plot

The contour plot is designed to examine the details of the change in the performance of the adhesive system and the changes in overlapping shear strength by changing the levels of nylon 66 and alumina, Figure 5. As you can see clearly, the performance of both agents at the lowest level is weak and has the least strength. At the highest level of nylon 66, this weakness is also evident, so that other changes in alumina do not affect the system. The color changes indicate that the best performance of the adhesive system is at the highest level of alumina and from level 2 to less than that for nylon 66.

3.5. Analysis of variance

The results of variance analysis of overlapping shear strength test are tabulated in Table 5, where the most important features are not analyzed directly, while the changes are evaluated.

In the column of this table, the degree of freedom is given for each factor. Here, the degree of freedom for each factor is 2. The sum of squares is the amount of variation that each factor produces in relation to the average of all results. In fact, by this factor, one can find a simple insight into the effect of each factor on the final performance of the adhesive. Here it is found that nylon 66 is about 130 units higher than alumina, indicating that the changes made by the nylon 66 in the adhesive mixture are far higher than that of alumina. The average sum of squares is obtained by dividing the modified sum of squares of each factor by its corresponding degree of freedom among which the biggest average sum of squares indicates the high impact of that factor on the results. The F ratio in this table, and the average sum of squares, indicate the effect of each factor on the results. As expressed here, the highest amount of F is of nylon 66, thus, among these two components, nylon 66 variations have the greatest effect on maximizing strength process. The last column of this table specifies the P value for each factor, the smallest possible probability indicating the effect of a factor is not important. Here, if the confidence level is considered 90%, the importance of P value is less than 0.1, consequently, nylon 66 is a major factor in the system.

Table 5: Analysis of results of variance of overlapping shear strength test.

Source	Degrees of freedom	Sum of squares	Modified sum of squared	Average sum of squares	F	P
Nylon66	2	167.54	167.54	83.77	5.54	0.07
Alumina	2	39.74	39.74	19.87	1.31	0.364
The residual error	4	60.50	60.50	15.12	-	-
Total	8	267.78	-	-	-	-

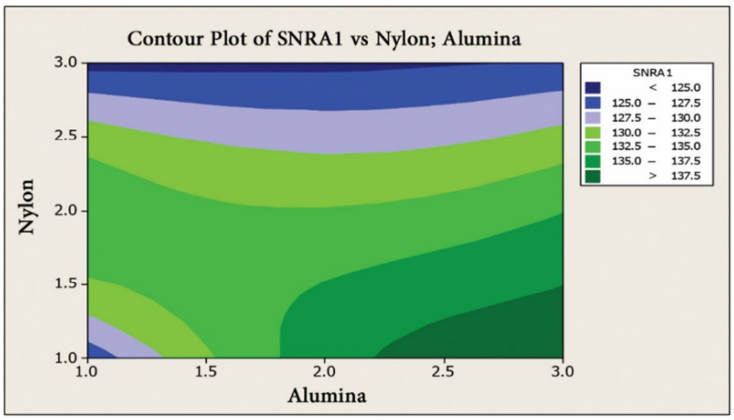

Figure 5: The manner of change in the final overlapping shear strength of the adhesive by changing the levels of the main factors.

3.6. Overall Evaluation Criteria method (OEC method)

Through this method the multi-output objectives obtained from an experiment or a process becomes united. The objective of this section is to reveal how to obtain a degree of strength where that the adhesive has a good stiffness and high toughness in the stress-strain curve. In order to have a balance between toughness and stiffness, the OEC method is adopted to transform the data of these two parameters into a data subject to one purpose, in a sense that it can be analyzed as one unit. It is expected that these parameters be at their highest levels. In the formulation design and OEC method, the obtained data are assessed for analysis, by following the bigger the better principle. By applying Qualitek 4 software, the results of these parameters become one response and then Taguchi analyzes run through Minitab software. The equation applied in converting all results into one is (Eq. 1).

$$OEC=[\left(\frac{y_m - y_-}{y_+ - y_-}\right)\times W_a]_{QC=B}+[\left(\frac{y_t - y_-}{y_+ - y_-}\right)\times W_b]_{QC=B} \quad (1)$$

In this equation there exist two relations, the first, for the modulus responses and the second, for the toughness responses, where y_m is the corresponding modulus' test response in every test run and y_t is the corresponding toughness response test in the same test run, y_- and y_+ are the worst and the best responses among all responses in every column, respectively, W_a and W_b are the percentages of weight, which are defined based on what is required from a given study as to every parameter, with respect to their importance order. In this equation, the percentages of weight are defined in terms of the equilibrium in the response and are selected with respect to the surface below the curve (as the toughness index), equal to 50% and the modulus (as the stiffness index), equal to 50%.

3.7. Chart of the main effects of converted responses

The behavior of the main effects is displayed by changing the levels, Figure 6. By comparing Figures 4 and 6, no significant change is observed in the behavior of nylon 66, that is, the effect of nylon 66 on the system is high, while the alumina behavior changes. The level 1 to 2 gradient of alumina is greater than that of level 1 to 2 in Figure 4, while in Figure 6 the level 2 to 3 gradient decreases. The high gradient of alumina from level 1 to 2 is indicative of alumina consumption from existing spaces and the effect of the appropriate concentration distribution in this increase. More reduction in levels 2 to 3 of alumina (alumina as a factor of increasing strength and stiffness) in Figure 6 indicates the filling of epoxy functional groups and reduced space for the proper distribution of alumina which in turn, the increase in unreacted mass of nylon 66. By examining the same changes in the gradient of the curve and comparing them with the original effects curve (Figure 4), according to the objective function, it is reveal that it is necessary to make changes around the levels of Alumina to achieve a balanced state of toughness and stiffness, while holding the nylon 66 at its assigned level, consequently, based on these results, in future experiments, the nylon 66 should be around level 2 with a slight fluctuation. In achieving this objective, the fact that any increase in alumina increases the strength and stiffness should be of concern.

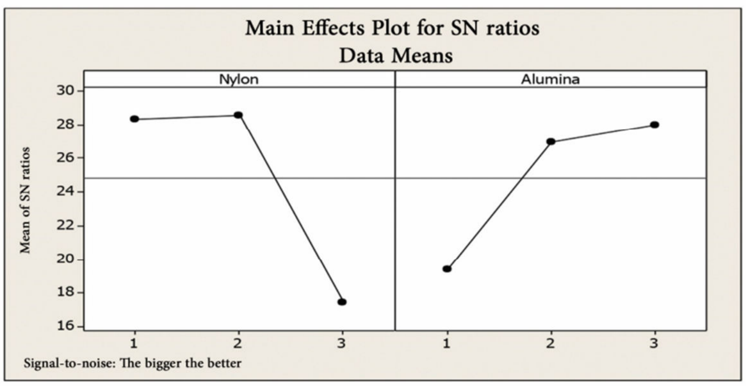

Figure 6: The main effects chart of the adhesive sample made in the tensile test.

3.8. Analysis of the variance of the transformed responses in the tensile test

The analysis of the variance of the result of the transformed response is observed in Table 6. Comparing this table with Table 5 reveals that changes made in nylon 66 properties which affect the system are still high, that is, the most important change in the adhesive system of epoxy resin is the reaction rate of active hydrogen with the epoxy rings, while the observed change here compared with Table 5 is an increase in the effect of alumina on the final response of the system. In Table 5, it is observed that the reported values for alumina are one-third of the nylon 66 values, while, these values are halved in Table 6, indicating that in order to establish a state of equilibrium within stiffness and toughness, this increase in sensitivity against changes in alumina levels in the system should be considered as the predicted and unpredicted interactions on the final response. However, considering the 90% confidence level (Considering slight error in responses), nylon 66 is still the most important factor affecting the system.

3.9. Contour plot of the transformed response

The contour plot in Figure 7 is to check the details of the changes made in adhesive system performance with a change in the levels of nylon 66 and alumina (when both the toughness and modulus responses with a weight percentage of each 50% are converted into one response). As observed, the performance of the system at level 1 of both factors and level 3 of only nylon 66 is weak. Here, similar to Figure 6, the positive trend of change from level 2 of nylon 66 has begun, with a fluctuation in 2 to 3 level of alumina, its highest level.

Table 6: Analysis of the variance of the result of the transformed responses in the tensile test.

Source	Degrees of freedom	Sum of squares	Modified sum of squared	Average sum of squares	F	P
Nylon66	2	244	244	121.98	4.20	0.104
Alumina	2	131	131	65.52	2.26	0.221
The residual error	4	116.1	116.1	29.01	-	-
Total	8	491.1	-	-	-	-

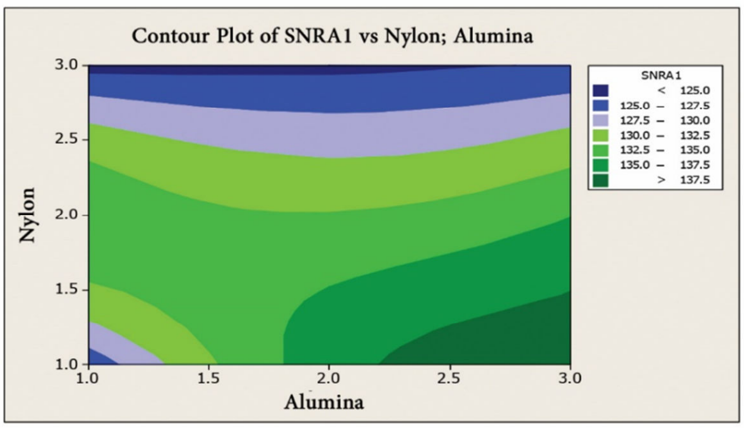

Figure 7: Details of how to change system performance and adhesive strength with transformed responses.

3.10. Assessing the failure mechanism in epoxy adhesives

The surfaces broken subject to test are shown in Figure 8, where the failure is of cohesive type (cohesive failure is the intermolecular bonding forces' breakdown in a given adhesive substance). This type of failure occurs in the bulk layer of the adhesive [5], is where the adhesive is able to establish good bonds with both the surfaces and wet both of them well. It can be deduced that weak adhesive is the one which cannot stick to the surfaces, although it is highly resistant against failure. Adhesive and surfaces should be compatible with together. This compatibility can be in adhesive, like wetting properties, or at surfaces how to prepare surfaces. To establish a good adhesion between the two surfaces, one or more of the principles of adhesion theories which examine: 1) adhesion between the two surfaces in terms of porosity and roughness (mechanical theory), 2) the compatibility and proper mobility of polymers (penetration theory), 3) contact angles and wettability (absorption theory) and 4) the difference between the electronegativity of the sticky material (electrostatic adhesion theory) must hold true [26]. As observed the desired surface is engaged with adhesive. Initial preparation of surfaces together with presence of nylon 66 in formic acid (enhancement of solvents) makes it possible to introduce toughness in the adhesive and reduce viscosity which would increase irregularity in the adhesive and eliminate the possibility of surfaces wetting. A sample subject to the single lap shear tensile test is shown in Figure 8a, where the adhesive is very stretch between the joints and is not easily detached from the joints, this function is due to the high adhesion of the adhesive. One of the reasons for this flexibility is the presence of nylon 66 as the toughening factor with a linear chain structure and together with all the features mentioned with high direct functionality in the system.

3.11. Effect of increasing the nylon 66 on thermal stability of DGEBA epoxy adhesive

Following the tensile test and the analysis of the obtained results, the appropriate and inappropriate formulations in terms of mechanical properties of adhesives, are identified. In this test, sample formulation 3 is appropriate and sample 8 is inappropriate (best and worst). For this purpose, the TGA test is run to determine the properties of these two formulations. The results of this test are shown in Figures 9 and 10. The maximum degradation temperature (T_{max}) and the residual coal content, as a measure of thermal stability of the samples are tabulated in Table 7. The maximum degradation temperature in the DTG, Figure 10 is well defined as the minimum point of the curve.

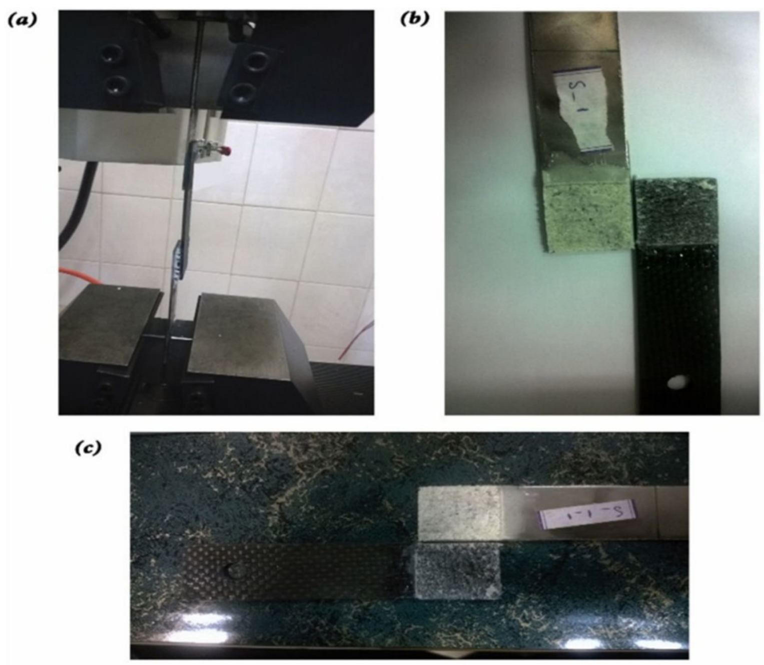

Figure 8: How to detach adhesive joints, (a): Adhesion of adhesive when tensile inside the machine, (b) and (c): Adhesive failure of cohesive type.

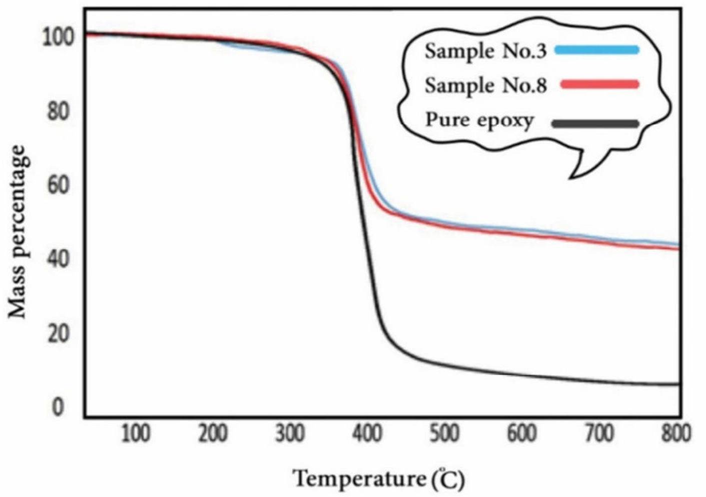

Figure 9: TGA curve for epoxy / nylon 66 adhesive alloy and pure epoxy.

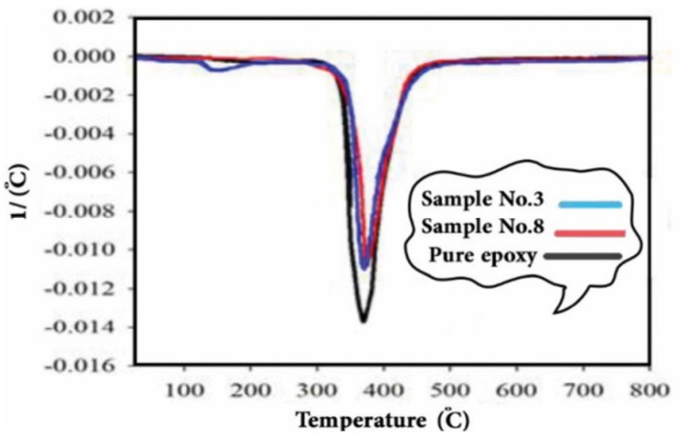

Figure 10: DTG curve for epoxy / nylon 66 adhesive alloy and pure epoxy.

As observed in Figure 9 (better resolution in Figure 10, before the highest point of the speed (the minimum point), at 177 ° C, a rapid increase is observed in the loss of instantaneous mass (sample No. 3). This phenomenon, at this point of the curve can be justified by evaporation and loss of small molecules. As observed, in the pure epoxy sample, and even in sample 8, there is no initial loss on the curve (increasing the speed of loss of instantaneous mass). In pure epoxy adhesive system, the filler is applied completely to the solvent causing an increase in the viscosity of the system, while in the epoxy / nylon 66 alloy system (especially sample 3), solvent nylon 66 (formic acid) is introduced as a new substance, causing the number of small molecules to increase and a significant decrease in mixture viscosity. This increase in the speed of loss of instantaneous mass is due to solvent evaporation [14, 26]. By comparing the sustainability in this study with that of [10] indices that the initial degradation temperature in the following two samples is significantly higher. The initial degradation temperature for adhesive containing alumina filler in [10] is 286 °C, while here the same is 327.5 °C on average. Presence of nylon 66 solution in formic acid justifies this increase in temperature. The nylon 66 containing active hydrogens causes an increase in the number of cross-links and the degree of networking (although it has less power to combine compared with theta). This increase at networking degree increases the initial degradation temperature. This justification can be confirmed by observing the maximum temperature in Table 7 for sample 3 and 8, where the latter, due to high nylon 66 content, has a higher maximum temperature.

3.12. FT-IR spectroscopy

After examining the results of tensile and TGA tests the FT-IR test is run to identify the functional groups involved in this formulation and the qualitative comparison of the adhesives in two samples. The spectra of numbers (a) and (b) in Figure 11 represent the results of the FT-IR test for sample 3 adhesive (as a high strength adhesive) and sample 8 (as a low strength adhesive).

The widespread wavelength of 3595.63 cm^{-1} is of the tensile vibration of OH group and the hydroxyl network of the epoxy adhesive. The growth of this peak in sample 8 (Figure 11b) is due to the high level of nylon 66 in an interaction with epoxy rings, which leads to the formation of OH groups in this formulation and reveals itself widespread. The disappearance of the two existing peaks alongside the 2976 cm^{-1} peak also suggests an excessive accumulation of amide groups after the excessive increase in nylon 66 in relation to the adhesive mix that caused the disruption of spectrum detection. This figure confirms the analysis nylon 66 groups' accumulation at high levels. The observed vibrations in wave lengths 2976.59 and 2942.84 cm^{-1} correspond to the groups CH and CH_2. The tearing and destruction of these groups as to joining the amid groups of nylons 66 appear at wave length 1263 cm^{-1}. The presence of amide groups of nylon 66 in the adhesive mixture at wave length 2886.82 cm^{-1} can be detected in the short domain. Two tensile vibrations with lengths of 1671.62 and 11618.95 cm^{-1} relate to the tensile absorption of the aromatic ring.

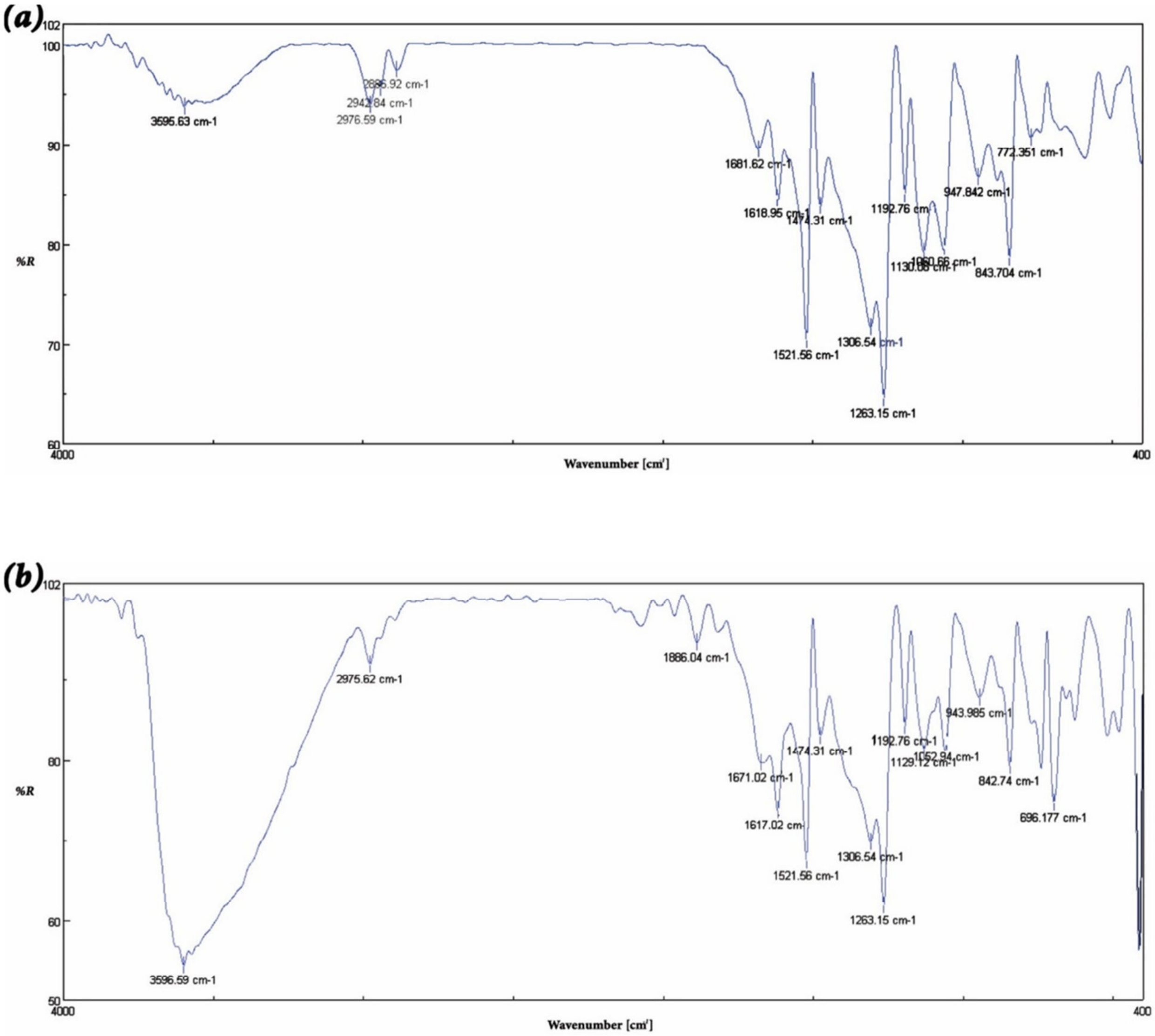

Figure 11: FT-IR Spectrum Epoxy / Nylon66 adhesive Samples (a) Sample No. 3 and (b) Sample No. 8.

The peaks at wave length 1521.56 cm^{-1} relate to carbon double bonds with elements like oxygen in the nylon 66 composition, which appears after a further increase in nylon 66 with a gentle slope. The vibrations obtained in wave lengths 1306.54 and 1414.31 cm^{-1} relate to carbon-carbon bonds of linear groups of nylon 66 present in the adhesive sample. The vibrations lower than 1190 cm^{-1} relate to carbon-nitrogen bonds, which after an increase in nylon 66 content, it's nitrogen joins the carbon groups on the epoxy opened rings. The peak containing wave length 843 cm^{-1} relates to the aluminum reinforced bending vibration with oxygen due to the presence of alumina [27, 28].

4. Conclusion

In this study, the effect of adding alumina and nylon 66 micro particles on the mechanical and thermal properties of epoxy adhesive is assessed. Adding nylon 66 to epoxy adhesive increase toughness and reduce strength. Addition of alumina at high levels increases the strength and reduces toughness. The results of TGA indicate that with the addition of alumina and nylon 66 to the epoxy adhesive, the temperature of primary thermal degradation increase up to 32 °C. This increase is higher in the presence of nylon 66.

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