Iranian Journal of Materials Science and Engineering, Vol. 21, Number 3, September 2024
RESEARCH PAPER

A Study on the Synergistic Effect of PEG and Triacetin Plasticizers on the Mechanical Properties of Acrylic resin

Ramin Dehghani, Seyed Mojtaba Zebarjad*

* *Mojtabazebarjad@shirazu.ac.ir*

Department of Materials Science and Engineering, Engineering Faculty, Shiraz University, Shiraz, Iran

Received: July 2023 Revised: June 2024 Accepted: August 2024
DOI: 10.22068/ijmse.3313

Abstract: *Acrylic resins are one of the most important thermoplastic resins used in various industries due to their significant properties. However, they are inherently brittle and the addition of plasticizers to them is very common. In this study, the role of both Polyethylene Glycol (PEG) and Triacetin on the mechanical properties of acrylic resin has been investigated. To do so, tensile test, bending, and wear tests have been performed. To achieve the optimal mixture of plasticizers, a tensile test has been carried out, and the best percentage of the mixture has been determined. Subsequently, bending and wear tests were conducted, which showed a significant increase in the bending strength of the acrylic resin after the addition of plasticizers. Furthermore, it was found that the abrasion mechanism of the resin was significantly altered compared to its pure state.*

Keywords: *Acrylic Resin, Plasticizer, Polyethylene Glycol (PEG), Triacetin, Mechanical Properties.*

1. INTRODUCTION

Thermoplastic resins are a type of polymer that can be melted and molded without undergoing any chemical change. In their molten state, they are paste-like and flowable, with no cross-links. Above their glass transition temperature (T_g), most thermoplastics are flexible. They typically contain crystalline regions that provide strength and rigidity, as well as amorphous regions that give elasticity. When heated above the melting point the crystalline areas are destroyed, and the viscosity is greatly reduced, allowing the material to be melted and molded repeatedly [1]. Due to these properties, thermoplastic polymers find applications in a broad range of industries. Among thermoplastic polymers, acrylic resins are one of the most important types that are used in a variety of industries, from construction materials to biomaterials. However, they are prone to cracking and brittleness over time. To address this issue, appropriate additives, such as plasticizers, are commonly used [2].

Plasticizers are essential components in the production of flexible plastics, which have a wide range of applications in the automotive industry, medical industry, and general uses. Nowadays the plasticizer industry has grown significantly with the increasing usage of plastics and accounts for about one-third of the world's additive consumption. The primary purpose of using plasticizers is to increase the flexibility of the polymer structure and to enable subsequent processes by reducing the glass transition temperature [3]. Typically, plasticizers are low molecular weight resins or liquids that form new bonds with the polymer, reducing the secondary bonds between the polymer-polymer chains, resulting in the polymer more easily deforming. The plasticizer acts as a lubricant to allow molecular chains to slide on each other and without it the molecular chains of polymers lock together, resulting in the brittleness and inflexibility of the polymer, leading to a rigid material [4]. It is worth noting that the plasticizer links with the amorphous part of the polymer, and the structure and dimensions of the crystalline part do not change [5]. It is expected that the addition of plasticizers will decrease the storage modulus, tensile strength, hardness, density, melt viscosity, glass transition temperature, and strength of the polymer. At the same time, the addition of plasticizers is expected to increase flexibility, elongation at break, toughness, and dielectric constant [6-11]. An ideal plasticizer should be highly compatible with the polymer, stable at high and low temperatures, and have lubrication properties in a wide temperature range. It should be resistant to solar ultraviolet waves, washing, and handling, cheap, and not harmful to health. Plasticizers can be divided into external and internal. In the case of external, the molecule of external plasticizer is not connected with polymer chains through primary bonds,

[DOI: 10.22068/ijmse.3313]

resulting in the possibility of separation from the polymer by evaporation, migration, or extraction. An internal plasticizer is inherently part of the polymer and remains part of it, but the problem with this type of plasticizer is the inability to maintain dimensional stability at high temperatures. Plasticizers are also divided into primary and secondary types. The primary plasticizer can be used alone or as the main component, while the secondary plasticizer must be mixed with a primary plasticizer to improve a specific property or reduce cost [7].

Polyethylene glycol (PEG) is an efficient plasticizer used for polymers due to its wide range of molecular weights, non-toxicity, miscibility, and biodegradability. PEG plasticizer can effectively increase the chain mobility of other polymers, improving their ductility and elasticity, and has a wide range of applications [8]. In 2017, Pal and Ghosh found that PEG caused stable thermal circulation [9]. Triacetin, also known as triacylglycerol (TAG), is an organic compound with the formula $C_3H_5(OCOCH_3)_3$ and is classified in the category of triglycerides [11]. Additionally, in 1993, Gutierrez-Rocca and McGinity found that the use of Triacetin resulted in a favorable change in glass transition temperature, elongation, and elastic modulus [10].

To the best of our knowledge simultaneous role of both PEG and Triacetin on the mechanical properties of acrylic resin has not been under attention by the investigators and to fill the literature gap in this issue, two aforementioned plasticizers were chosen.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

Industrial-grade acrylic resin was bought from Subranco Co., Iran, and two industrial-grade plasticizers, PEG 400 and Triacetin were purchased from Seplochem Company, Iran. To mix these particles, pure acetone was needed as a solvent and was purchased from Dr. Mojalali Chemical Industries, Iran. To fabricate the samples, silicone rubber and its hardener, both supplied by Dr. OZ Industries, Iran, were used to make silicon molds.

2.2. Sample Preparation

The general approach for sample preparation was the same, but different molds were used for different tests to comply with their accordance standards. The specimens were divided into two groups (A and B). Groups A and B consist of specimens with a total plasticizer percentage of 20% and 30% respectively. Table 1 shows produced samples with different percentages of acrylic resin, PEG, and Triacetin along with the sample names and codes.

To produce the samples, 20 grams of acrylic resin was weighed. Then, 6 grams of acetone (30% of the acrylic resin's weight) was weighed and added to the resin. In the next step, both plasticizers were weighed and solved into acetone as a solvent (30% of each plasticizer weight) and then added to the acrylic resin. The weighted resin and plasticizers were then mixed. The mixed resin was heated on a magnetic stirrer at 70°C for 5 hours.

Table 1. Produced samples with different percentages of acrylic resin, PEG, and Triacetin along with the sample codes

Sample Code	Sample Name	Acrylic Resin (%)	PEG relative to resin's weight (%)	Triacetin relative to resin's weight (%)
Pure	100AC (Pure)	100	0	0
Group A				
Acrylic 1	AC20PEG0TAC	80	20	0
Acrylic 2	AC.15PEG.5TAC	80	15	5
Acrylic 3	AC.10PEG.10TAC	80	10	10
Acrylic 4	AC.5PEG.15TAC	80	5	15
Acrylic 5	AC.0PEG.20TAC	80	0	20
Group B				
Acrylic 6	AC.25PEG.5TAC	70	25	5
Acrylic 7	AC.20PEG.10TAC	70	20	10
Acrylic 8	AC.15PEG.15TAC	70	15	15
Acrylic 9	AC.10PEG.20TAC	70	10	20
Acrylic 10	AC.5PEG.25TAC	70	5	25

[DOI: 10.22068/ijmse.3313]

During this time, acetone was removed from the solution in the process of mixing, as its boiling point was 56°C. After the solution was fully dispersed, the samples were molded using a silicon mold and cured in an oven at 150°C for 20 hours. However, these samples were found to have porosities and bubbles. To remove these bubbles, the samples were placed in a vacuum oven at 150°C for about 30 minutes. Finally, the samples were polished with sandpapers with grit of 80, 100, and 200, respectively, to remove any corners and ridges.

2.3. Evaluations

2.3.1. Tensile Test

The tensile test played a crucial role in this research, serving as a filter to determine the optimized samples to avoid excessive testing. The ASTM D3039 standard [12] was followed for this test, and specimens were required to have dimensions of 25 × 250 × 2.5 mm. The test was carried out at a cross head of speed 0.1 mm/min at room temperature using a universal tensile machine equipped with a load cell of 100N. Figure 1 shows the silicon mold and the produced sample for the tensile test.

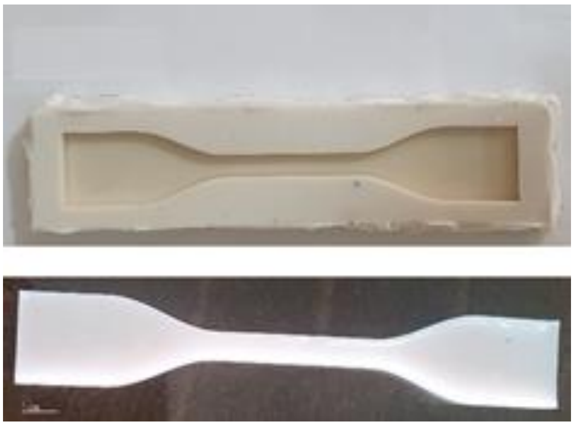

Fig. 1. The mold and the produced tensile sample.

2.3.2. Wear test

The Pin on Disk wear test is a destructive test used to measure the wear properties of materials. In this test, a pin moves in a circular path with a certain radius while applying a constant force on the sample. In the current research, the relevant ASTM G99 standard [13] was followed. The sample was a sheet with dimensions of 13 × 50 mm. The diameter of the rotation path of the pin and the distance of the wear test were 6 mm and 100 mm respectively. As the pin moved, the force applied (800 grams) on the sample and surface underwent wear. Depending on the friction coefficient between the pin and samples the rate of removal of materials and the wear mechanism can be different. After performing the test, to clarify the wear mechanism, the surface of worn samples was evaluated using electron microscopy. To avoid charge building up, the surface of the samples was coated before taking the micrographs.

2.3.3. Bending test

The bending test was conducted to evaluate the flexural strength of the samples, following the ASTM D7264 standard [14]. The samples with dimensions of 100 × 13 × 4 mm were produced and the distance between the two supports (span length) was kept at 7 cm.

3. RESULTS AND DISCUSSION

3.1. Tensile Properties

This research aimed to identify a specimen with the least reduction in tensile strength and the greatest enhancement in flexibility, simultaneously. As predicted, the addition of plasticizers to the acrylic resin led to a significant reduction in tensile strength. However, the flexibility and elongation at break were markedly increased. Figures 2-a and 2-b show the role of both plasticizers on the tensile strength and ductility of acrylic resin. Based on the trends observed in the tensile strength data, it might be interpreted that in group A, a decrease in PEG concentration and an increase in triacetin concentration lead to a slight increase in tensile strength. However, Acrylic 4, which contains 15% triacetin and 5% PEG, shows a sharp increase in tensile strength. This may be due to the synergistic effect of plasticizers on each other, which results in the best effect on the resin and the least reduction in tensile strength. Indeed, the reason for this effect can be attributed to the fact that the synergistic effect of plasticizers is the combination of a primary plasticizer with a secondary one. The primary plasticizer provides the main plasticizing effect by reducing the glass transition temperature (T_g) of the polymer, while the secondary plasticizer enhances the effect by improving the compatibility between the polymer and the primary plasticizer. This can lead to a greater reduction in T_g and increased flexibility of the polymer. In group B, despite the increase in plasticizer concentration in the resin, the tensile

[DOI: 10.22068/ijmse.3313]

strength remains within the range of the samples containing a total of 20% plasticizer. Acrylic 5 and Acrylic 10 show the highest tensile strength after Acrylic 4. Sample Acrylic 10, containing 25% triacetin and 5% PEG, ranks second after Acrylic 4. Meanwhile, Acrylic 6, which has the opposite percentage of plasticizers compared to Acrylic 10 (5% triacetin and 15% PEG), shows the lowest tensile strength by a significant margin. In general, the data shows that PEG has a much greater effect than Triacetin on reducing the tensile strength of the resin. However, in some cases, the simultaneous effect of these two plasticizers on each other results in a very low reduction in tensile strength, keeping it higher than the other samples. In acrylic 4, the least reduction in tensile strength can be attributed to the proper dispersion of plasticizer molecules and the suitability of the polymer matrix to include the soft phase. As seen in Figure 2-b, Acrylic 4 exhibits the highest flexibility among all the samples. The soft phase, which does not bear stress, is well surrounded by the hard phase (acrylic matrix) and bears less stress. Another reason for the reduction in strength by plasticizers is that the small molecules of the plasticizer have a greater ability to penetrate the large polymer molecules and weaken the polymer-polymer bonds [15]. The reason for the improvement in the flexibility of the resin after adding a plasticizer is the reduction of the bonds between the polymer chains. Softeners between the chains act like a lubricant, allowing the chains to slide over each other. Without the presence of plasticizers, the chains will lock together, leading to the brittleness of the resin [4, 6].

Figures 3, 4, 5 and 6 show the roles of plasticizers on samples with 5% triacetin (TAC), 10% TAC, 15% TAC, and 20% TAC, respectively.

Looking at in more detail on the data, one may conclude that Acrylic 4 (containing 15% by weight of triacetin and 5% by weight of PEG) with the least changes in tensile strength and the highest increase in elongation compared to the pure sample can be the most suitable and optimal sample. After selecting the optimal sample, the remaining tests were conducted only on this sample, and the pure sample was used as a control.

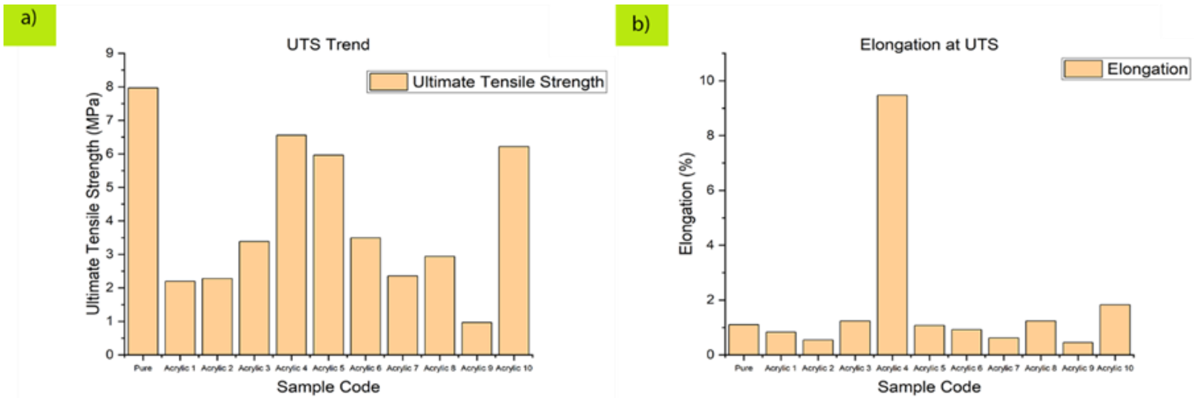

Fig. 2. Role of both plasticizers on the tensile properties of acrylic resin. a) Tensile strength b) Elongation.

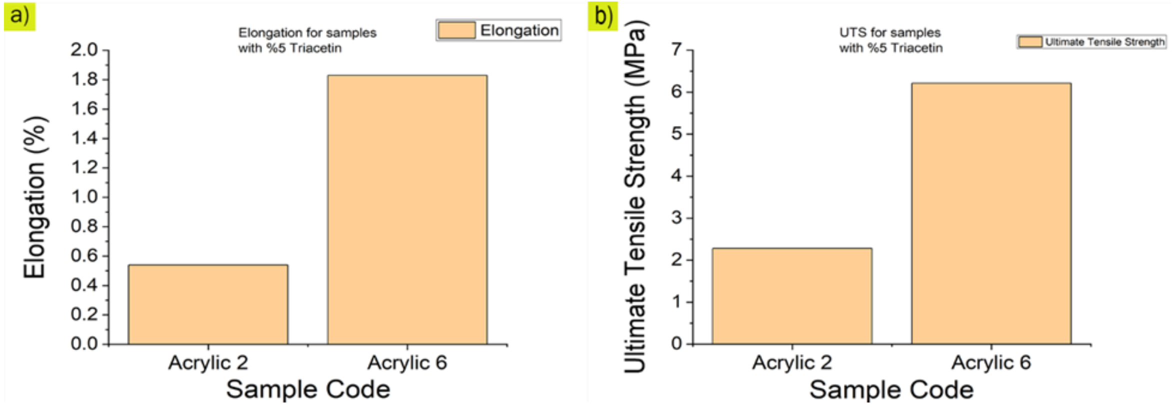

Fig. 3. Role of both plasticizers on the tensile properties of acrylic resin with 5% triacetin, a)Tensile strength, b) Elongation

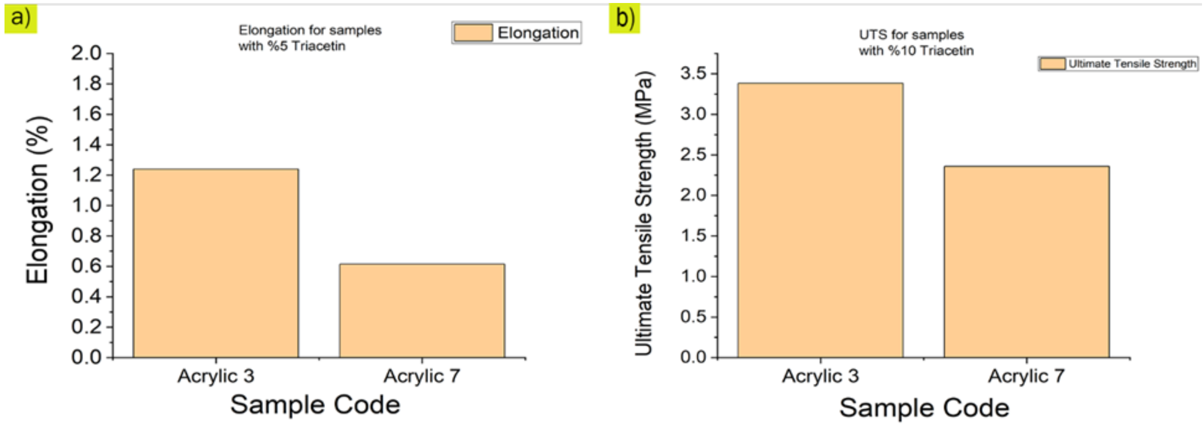

Fig. 4. Role of both plasticizers on the tensile properties of acrylic resin with 10% triacetin, a) Tensile strength b) Elongation

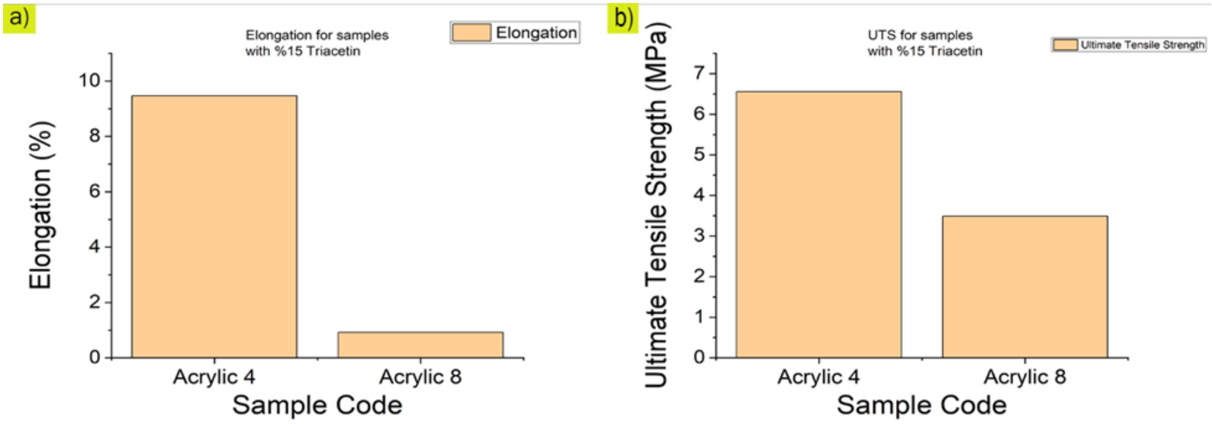

Fig. 5. Role of both plasticizers on the tensile properties of acrylic resin with 15% triacetin, a) Tensile strength, b) Elongation

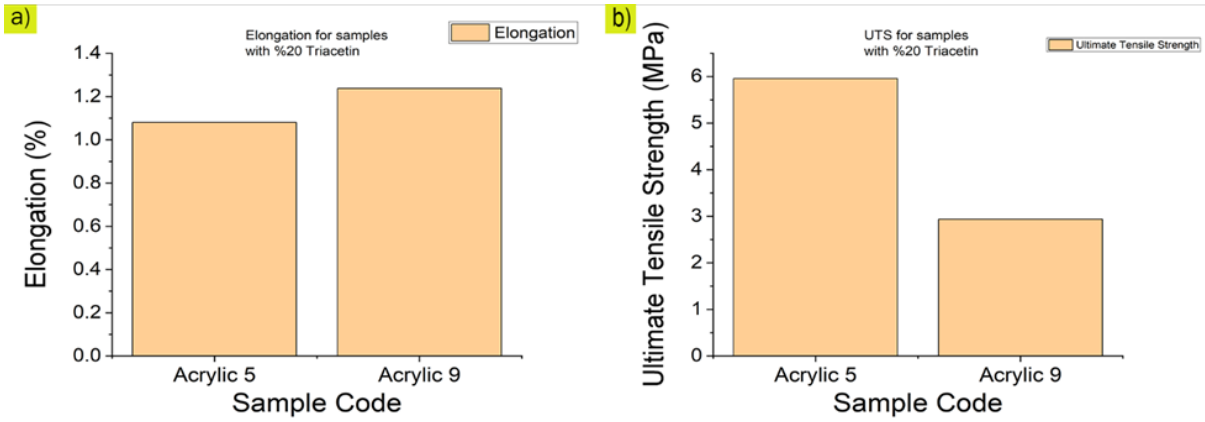

Fig. 6. Role of both plasticizers on the tensile properties of acrylic resin with 20% triacetin a) Tensile strength, b) Elongation

3.2. Wear Behavior

The wear test was conducted to measure the friction coefficient of the samples, which is an important parameter. Figure 7 compares the friction coefficient of the pure Acrylic and Acrylic 4. As seen, the addition of plasticizers to the resin causes a significant increase of about 80% in the friction coefficient. An increase in the friction coefficient increases contact between foreign objects and the surface of the resin, leading to an increase in the wear resistance of the resin. The friction coefficients measured in this research fall

[DOI: 10.22068/ijmse.3313]

within the range of friction coefficients observed for acrylic resins and are consistent with those reported in the literature [16]. A higher surface friction coefficient in the Acrylic 4 sample, means that the effective force and stress applied to the surface of the resin is higher, although the applied force is constant and similar to the pure sample. This happens because of the viscoelastic behavior of the resin. While the applied force is constant, some of this force is consumed for the deformation of the surface and results in a higher friction coefficient and effective force. This issue is presented in Figure 8, which displays the stress diagram in terms of the distance between two samples. The stress diagram in terms of distance is identical to the friction coefficient diagram in terms of distance. This indicates that the friction coefficient and stress in terms of distance have a direct and identical relationship. Therefore, the increase in the friction coefficient of the softened sample has resulted in an increase in stress on it.

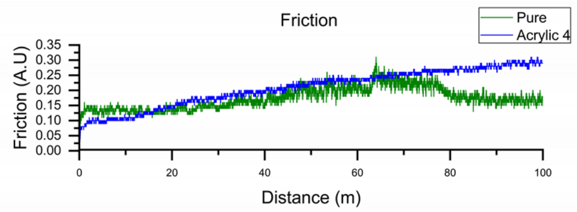

Fig. 7. Comparison of coefficient of friction of pure Acrylic and Acrylic 4

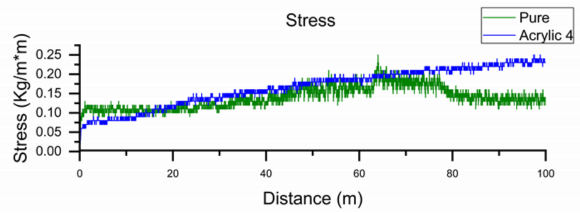

Fig. 8. Comparison of wear stress of pure Acrylic and Acrylic 4

Another parameter evaluated in the wear test is the weight loss of the samples after the test. Table 2 displays the initial weight, final weight, and weight loss percentage of the samples. Another parameter evaluated in the wear test is the weight loss of the samples after the test. Table 2 displays the initial weight, final weight, and weight loss percentage of the samples.

It was expected that the softened sample, due to the significant increase in the friction coefficient and higher engagement of the pin with the sample, would experience a higher percentage of mass loss compared to the pure sample. However, as shown in the Table 2, the achieved results are not in the direction of the expectation. Please note that, the primary weight of samples is of minor importance, however, the parameter which has prime importance is the weight loss. This parameter clarifies to which extent, the mass is lost from the surface of the specimens, so, mass loss is not related to the primary weight. Thus, the difference between the primary weight of the specimens is due to different size of the chosen specimens for this test, which doesn't exert any effect on the final mass lost. The main reason for these unexpected results is the change in the wear mechanism in the softened sample. Figure 9 displays SEM micrographs taken from the worn surfaces of Acylic 4.

The excessive softness of the resin in the softened sample, along with the chains' ability to slide on each other, caused the wear mechanism of the resin to shift towards the scratch mechanism, resulting in a change to the fish scale mechanism. This mechanism reduces the wear of the sample, but it can lead to tearing and displacement of the sample surface [17]. Since the soft phase, cannot withstand the pressure of the pin, besides, the hard phase of the resin is not hard enough to fully surrounds the soft phases in this test, therefore when the pin hits the surface of the resin, it sinks into it and is drawn on the surface. This results in a severe shape change in the material, which simulates the scratch test. This is why the fish scale mechanism is observed in this test, where tears and cracks occur at almost equal intervals. As mentioned earlier although the friction coefficient is higher in the softened sample, the weight loss is less than that of the pure sample.

The main reason for this is that the stress applied to the softened sample has increased, due to the high softness of the sample, this stress is not sufficient to separate the material from the surface of the sample.

Table 2. The primary weight, final weight, and percentage of weight loss

Sample	Primary Weight (g)	Final Weight (g)	Weight Loss (%)
Pure	1.9596	1.9533	0.32
Acrylic 4	0.9841	0.9837	0.04

[DOI: 10.22068/ijmse.3313]

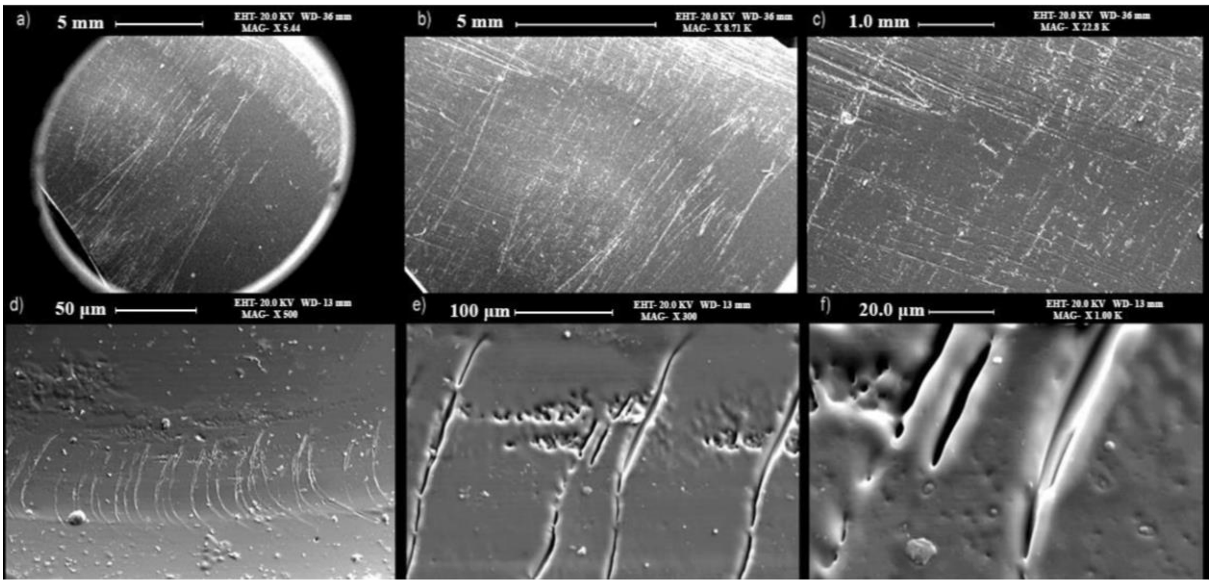

Fig. 9. SEM micrographs taken from the worn surface of Acrylic 4.

Instead, it leads to deform and tear the sample surface. In the pure sample, the stress applied to the sample is consumed in separating the material from the sample surface. This is also the reason for the reduced weight loss and the shift from the abrasive wear mechanism to the fish scale mechanism in the softened sample.

3.3. Bending Test

Figures 10-a and 10-b demonstrate the flexural behavior of pure Acrylic and Acrylic 4 during bending test. Comparing the graphs implies that the pure sample reaches the breaking point with a small change in length, indicating low flexibility. In contrast, the softened sample (Acrylic 4) shows a significant improvement in flexibility, as it does not fail. The reason of this behavior can be referred to the sliding of polymer chains on each other, which is facilitated by the presence of plasticizers. Figure 11 compares the flexibility of pure Acrylic and softened acrylic. In fact, not only does the softened sample remained unbroken but bent up to 90 degrees, demonstrating excellent flexibility unlike pure sample which is broken immediately.

The data obtained from the test device are presented as force. To convert these forces into stress at the moment of failure, equation 1 can be used. This relationship is specific to the three-point bending test [14].

$$\sigma = \frac{3PL}{4bh^2} \tag{1}$$

where σ is the stress in the area between the two supports, P is the applied force before failure, L is the distance between the two supports, b is the width of the sample, and h is the thickness of the sample.

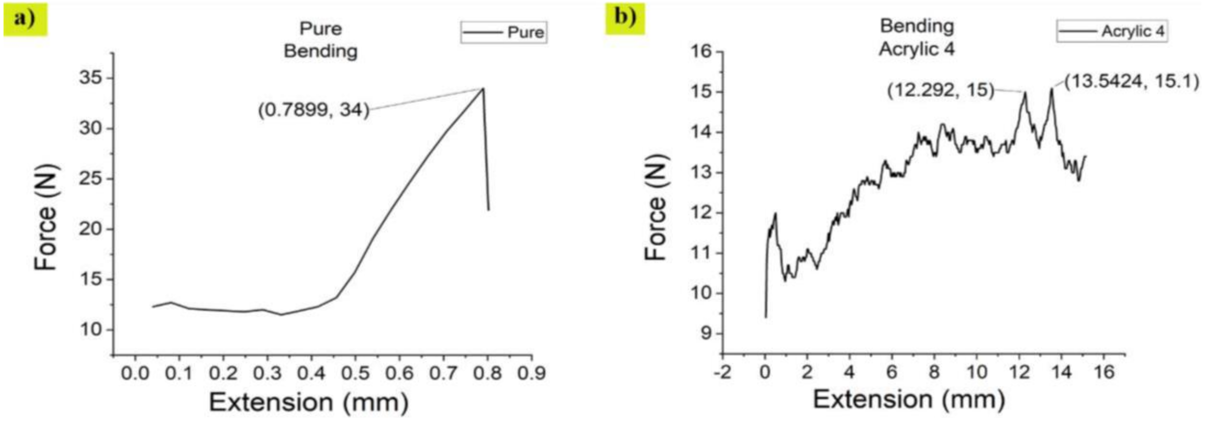

Fig. 10. Flexural behavior of a) Pure Acrylic b) Acrylic 4

[DOI: 10.22068/ijmse.3313]

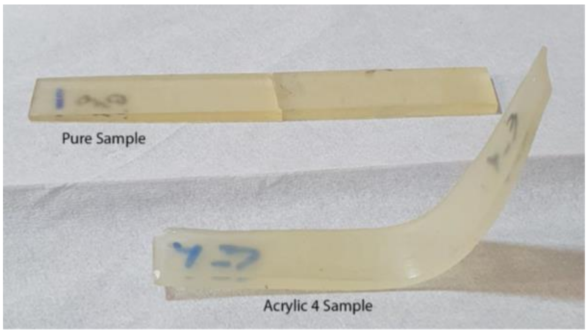

Fig. 11. Comparison of flexibility of pure Acrylic and softened acrylic

It is important to note that this relationship can only be used as flexural strength for pure samples in which failure has occurred. In the case of the softened sample that did not break, this value only represents the stress experienced by the sample up to 90 degrees of bending. Table 3 Compare the bending strength of Acrylic and Acrylic 4.

Table 3. Comparison of bending strength of Acrylic and Acrylic 4

Sample	**Flexural Strength (MPa)**	**Maximum Stress at 90° of bending (MPa)**
Pure Acrylic	7.05	-
Acrylic 4	-	3.14

4. CONCLUSION

The results of this research confirm the hypothesis that plasticizers significantly increase the flexibility of acrylic resin. Tensile tests show that the addition of plasticizers (15% triacetin and 5% PEG) results in a 13.06% decrease in tensile strength, but a 535% increase in elongation. The bending test results support the tensile test findings, showing that the plasticized sample can be bent to 90° with a stress of 3.14 MPa without any signs of failure, while the pure sample breaks easily. However, the wear test results show that adding plasticizers to the resin increases the friction coefficient, which is expected to cause an increase in weight loss. Surprisingly, the weight loss in the plasticized acrylic resin is lower than in the pure resin. This is due to the transformation of the wear mechanism to the Fish scale mechanism in the plasticized resin.

REFERENCES

[1]. Heger, F. J., Sharff, P. A., “Buildings: Plastics and Composites”, 2nd edition, Encyclopedia of Materials: Science and Technology, Simpson Gumpertz & Heger, Inc., Arlington, Massachusetts, USA, 2001, 833–841.

[2]. Aalto-Korte, K., Acrylic resins, Kanerva’s Occupational Dermatology, 2nd Edition, Berlin Heidelberg, Germany, 2012, 543–558.

[3]. Brazel, C. S., Rosen, S. L., Fundamental principles of polymeric materials, 3rd Edition, John Wiley and Sons, New Jersey, USA, 2012, 360-368.

[4]. Rahman, M., Brazel, C. S., ‘’The plasticizer market: An assessment of traditional plasticizers and research trends to meet new challenges’’, Prog. Polym. Sci., 2004, 29, 1223–1248,

[5]. Fedorko, P., Djurado, D., Trznadel, M., Dufour, B., Rannou, P., Travers, J. P., “Insulator-metal transition in polyaniline induced by plasticizers”, Synth. Met., 2003, 135, 327–328.

[6]. Matthews, G, PVC: production properties and uses, Institute of Metals, London, UK, 1996.

[7]. Godwin, A. D., Krauskopf, L. G., Handbook of Vinyl Formulating, 2nd Edition, John Wiley and Sons, New Jersey, USA, 2007, 173–238.

[8]. Li, D., Jiang, Y., Lv, S., Liu, X., Gu, J., Chen, Q., Zhang, Y., “Preparation of plasticized poly (lactic acid) and its influence on the properties of composite materials”, Plos One, 2018, 13, 3, 0193520-0193535.

[9]. Pal, P., Ghosh, A., “Charge carrier dynamics in PMMA-$LiClO_4$ based polymer electrolytes plasticized with different plasticizers” J. Appl. Phys., 2017, 122, 0151011-0151019.

[10]. Gutiérrez-Rocca, J. C., McGinity, J. W., “Influence of water soluble and insoluble plasticizers on the physical and mechanical properties of acrylic resin copolymers”, Int. J. Pharm., 1994, 103, 293–301.

[11]. Kong, P. S., Aroua, M. K., Daud, W. M. A. W., Lee, H. V., Cognet, P., Pérès, Y., “Catalytic role of solid acid catalysts in glycerol acetylation for the production of bio-additives: a review” RSC Adv., 2016, 6, 68885–68905.

[DOI: 10.22068/ijmse.3313]

[12]. “Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials.”, https://www.astm.org/d3039_d3039m-08.html.

[13]. “Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus.”, https://www.astm.org/g0099-17.html.

[14]. “Standard Test Method for Flexural Properties of Polymer Matrix Composite Materials.”, https://www.astm.org/d7264_d7264m-07.html.

[15]. Ullah, A., Wu, J., “Feather Fiber-Based Thermoplastics: Effects of Different Plasticizers on Material Properties” Macromol. Mater. Eng., 2013, 298, 153–162.

[16]. Chen, J., Cao, Y., Li, H., “Investigation of the friction and wear behaviors of polyoxymethylene/linear low-density polyethylene/ethylene-acrylic-acid blends” J. Wear, 2006, 260, 1342–1348.

[17]. Bellemare, S., Dao, M., Suresh, S., “The Frictional Sliding Response of Elasto-Plastic Materials in Contact With a Conical Indenter” Int. J. Solids Struct., 2007, 44, 1970–1989.

[DOI: 10.22068/ijmse.3313]