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## Mechanical Characteristics of Tire/Clay Modified Epoxy Used in Fabrication of Medical Prostheses and Artificial Human Parts

<sup>1</sup>Mohammad R. Aabadiaan, <sup>2</sup>Fakhroddin Alimoradi, <sup>3</sup>Ahmad Fakhkhar,  
<sup>1</sup>Azam Beigi Kheradmand, <sup>4</sup>Ameneh Langari and <sup>5</sup>Mohsen Gh. Kharaji

<sup>1</sup>Engineering Group, Shahrekord Branch, Islamic Azad University, Shahrekord, Iran

<sup>2</sup>Civil Engineering Group, Chaloos Branch, Islamic Azad University, Chaloos, Iran

<sup>3</sup>Mechanical Department, Kashan Branch, Islamic Azad University, Naein, Iran

<sup>4</sup>North Khorasan University of Medical Sciences, Bojnurd, Iran

<sup>5</sup>Sharekord University of Medical Sciences, Shahrekord, Iran

**Abstract:** Epoxy is used in many dental and medical applications such as manufacturing prostheses. This polymer is not toxic and is a good candidate for easily forming of artificial hand, leg, etc. In recent years, the recycled waste tire has been concerned as inexpensive modifier for improving the toughness characteristics of many thermoset resins such as epoxy. Herein, the influence of addition of nanoclay on mechanical characteristics of waste tire-modified epoxy was investigated. Mechanical properties i.e. compressive and flexural characteristics, fracture toughness and impact strength of the samples were investigated. The fracture surfaces of the specimens were examined using scanning electron microscope (SEM). Moreover the glass transition temperature ( $T_g$ ) of the samples were measured. Results reveal that nanoclay can improve the mechanical characteristics of waste tire-modified epoxies.

**Key words:** Epoxy resin • Recycled waste tire • Nanoclay • Mechanical characteristics

### INTRODUCTION

Recently, polymer materials are increasingly used in medical applications [1, 2]. Since the finished surface of polymers are non-toxic, these materials can be used in fabrication of medical devices and prostheses. Each polymer has its own benefits and limitations for medical application. Among them, epoxy resins are widely used due to their appropriate characteristics; This polymer is not toxic and is a good candidate for easily forming of artificial hand, leg, etc. In figure (1) some medical applications of the epoxy in making prostheses and dental applications are demonstrated.

In order to modify the characteristics of epoxy polymer modifying agents such as tire and clay are used. Waste tire has been applied to modify the toughness characteristics of many thermoset resins such as epoxy [3-5]. Sipahi-Saglam *et al.* [3] utilized ASTM standard tests to evaluate the mechanical characteristics of epoxy

toughened by regrind tire particles. A decrease in tensile properties and impact resistance of epoxy was observed. On the other hand, slight increases in fracture toughness values were observed in all samples. A fractographic examination of epoxy resin modified with scrap tire particles has been conducted by Kaynak *et al.* [4]. They used different surface treatment techniques to improve the epoxy/tire particles interface. In another work, Kaynak *et al.* investigated the use of different silane coupling agents to improve the interface between the epoxy resin and recycled rubber particles [5]. They observed that some of the coupling agents can improve the epoxy/rubber particles interface leading to increases in strength while slight decreases in toughness of the samples.

Addition of second modifier to waste rubber-modified polymer produces a ternary system, which may promote the simultaneous improvement of two or more mechanical characteristics [6-10]. The performance of the hybrid

**Corresponding Author:** Ameneh Langari, North Khorasan, University of Medical Sciences, Bojnurd, Iran.

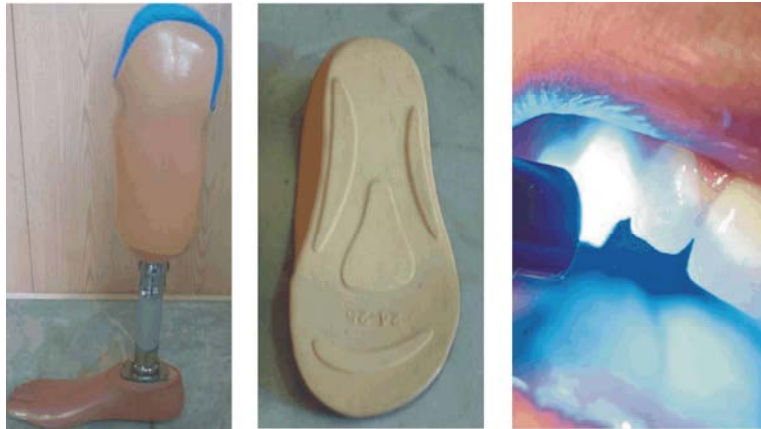


Fig. 1: Use of epoxy in medical applications: (a) prostheses (b) Medical shoes (c) Dental material

compound may be higher than that of a single tire particle modified resin. Hassan *et al.* [7] studied the influence of talc on physical properties of polyethylene/waste rubber composites. The synergistic effect of talc content and gamma irradiation on mechanical, thermal, electrical characteristics of the polyethylene/recycled rubber powder was investigated. In another work, Hassan *et al.* [8] examined the effect of carbon black on mechanical, thermal, chemical stability and micro-structural properties of polyamide/waste rubber compound. Navarro *et al.* [9] used recycled ground tire rubber to improve the thermal and rheological properties of recycled polyethylene-modified bitumen blends. They reported that much more enhanced mechanical characteristics can be achieved using a combination of both recycled polymers. Bagheri *et al.* [10] used a combination of CTBN and waste tire additives for increasing fracture toughness of epoxies. They reported synergistic toughening when 2.5 phr tire particle and 7.5 phr CTBN oligomer were incorporated. Similar trend was observed in study conducted by Boynton and Lee [11]. They investigated fracture behavior of elastomer-modified epoxy contained liquid reactive oligomer and waste tire particles. They reported that the fracture toughness of ternary epoxies was higher than that of those toughened with liquid rubber or recycled rubber alone.

The aim of this investigation is to evaluate the mechanical characteristics of hybrid ternary epoxy system containing nanoclay and grinded tire particles. Epoxy is used in many medical applications such as manufacturing prostheses. It is well-established that nanoclay can improve the mechanical characteristics of soft polymers [12, 13]. Therefore, the objective of present work is to improve mechanical characteristics of the waste rubber-modified resin by adding nano-particles.

## MATERIAL AND MATHODS

**Materials and Processing:** A DGEBA epoxy with an epoxy equivalent weight of 170 g/eq (Araldite LY564) from Hauntsman and the hardener (HY2962) from Vantico is used. Nanoclay was the organophilic montmorillonite with the CEC of 110–120 meq/100 g, NANOLIN DK4, from FCC. Recycled tire particles were the common grinded tire from Dena Co. with an approximate nominal particle size of 150  $\mu\text{m}$ . Through the paper, recycled tire is named Tire, for simplicity.

The stoichiometric ratio of the curing agent and resin were mixed and degassed at room temperature for about 20 min. The solution was then cast into a 5-mm-thick glass mould. The cast material was cured for 6 h at 90°C in a circulating air oven. The same curing schedule was employed for all modified epoxies as well. In formulations containing Tire particles, the epoxy/Tire blend has been mixed for 10 min before gelation. In the case of Nanoclay-modified formulations, Nanoclay was mixed with epoxy resin at 70°C for about 24 h under vacuum. Table 1 presents the formulations made in this study. In this study, the volume fraction of the waste tire and the nanoclay varied while maintaining a total volume fraction of modifiers at 10%.

Table 1: Formulations made in this study

Designation	Nanoclay		Tire Content	
	Content (phr)	(phr)	HY2962 (g)	LY564 (g)
E0	0	0	25	100
T10	0	10	25	100
N2.5/T7.5	2.5	7.5	25	100
N5/T5	5	5	25	100
N7.5/T2.5	7.5	2.5	25	100
N10	10	0	25	100

**Characterization and Observation Techniques:**

The glass transition temperatures ( $T_g$ ) of samples have been determined using a TA Instrument Q100 differential scanning calorimeter (DSC). Samples weighting about 7 mg have been scanned in the range of 60 to 130°C at a heating rate of 10°C/min in helium atmosphere. The reported data are the average of at least five tests.

Compressive yield strength and Young’s modulus were determined according to ASTM D695 using specimens with dimensions of  $6 \times 6 \times 12 \text{ mm}^3$ . Flexural strength was determined according to ASTM D790 using tetragonal-shaped specimens of  $3.2 \times 12.7 \times 125 \text{ mm}^3$ . Izod impact test was conducted according to ASTM D256. Samples were prepared and machined to the standard dimensions of  $62 \times 12.7 \times 4.2 \text{ mm}^3$ . Plane strain fracture toughness,  $K_{IC}$ , was determined using single-edge-notch (SEN) specimens. The ASTM D5045 guideline was followed to measure  $K_{IC}$ . The following formula has been applied to calculate  $K_{IC}$ :

$$K_{IC} = \frac{3(a/w)^{1/2}[1.99 - (a/w)(1 - a/w)]}{2(1 + 2a/w)(1 - a/w)^{3/2}} \frac{Ps}{tw^{3/2}} \quad (1)$$

where  $P$  is the maximum load at the instant of crack initiation,  $t$  is the thickness of the specimen,  $s$  is the span width,  $w$  is the width of the specimen and  $a$  is the initial crack length.

Fracture surfaces of the specimens were examined using scanning electro microscope (SEM) at an accelerating voltage of 20 kV. Samples have been coated with a thin layer of gold before examination.

**RESULTS AND DISCUSSION**

**Compressive and Flexural Characteristics:** Figures 2 and 3 show the compressive strength and modulus of samples, respectively. Furthermore, Table 2 presents the flexural strength of modified samples. As seen, the compressive strength and modulus of Tire-modified epoxy sample (T10) is less than the unmodified epoxy (E0). This is due to the fact that the strength and modulus of rubber is much lower than that of the epoxy matrix [14]. Moreover, rubber particles act as stress concentrators and decrease the yield strength of epoxy [14]. Similar reduction is observed in flexural strength of samples where Tire particles induce a deteriorating effect on flexural strength of epoxy. On the other hands, addition of

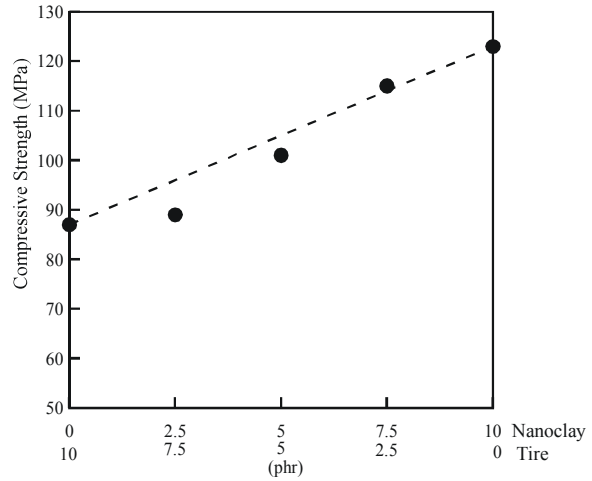


Fig. 2: Compressive strength of samples

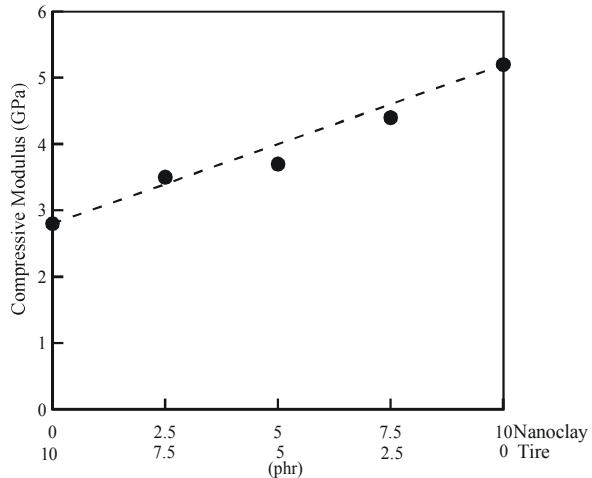


Fig. 3: Compressive modulus of samples

Table 2: Flexural strength of samples

Designation	Flexural Strength <sub>(MPa)</sub>
E0	129
T10	91
N2.5/T7.5	97
N5/T5	102
N7.5/T2.5	126
N10	141

nanoclay improves the compressive and flexural properties of the blend. As seen in Table 2, the strength and modulus gradually increases with increasing nanoclay content. This is attributed to the strengthening effect of rigid nanoclay layers which increase the load-bearing capability of the soft polymeric epoxy matrix [13].

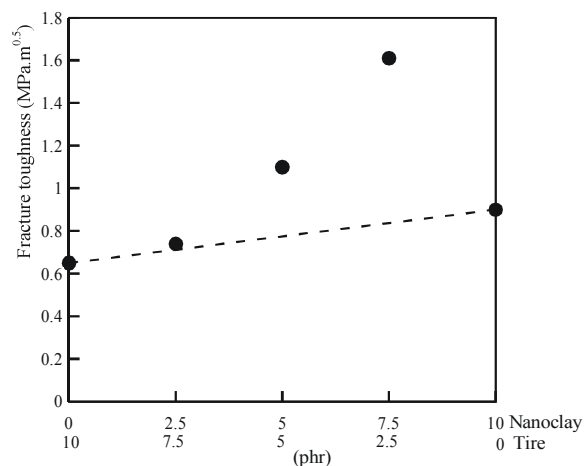


Fig. 4: Fracture toughness vs. blend composition. Synergistic toughening is evident in N7.5/T2.5 and N5/T5.

**Fracture Toughness:** The results of fracture toughness ( $K_{IC}$ ) measurements are illustrated in Figure 4 where the fracture toughness is shown vs. the modifiers composition. While the incorporation of 10 phr of Tire alone enhances  $K_{IC}$  by 20%, addition of 10 phr nanoclay improves the  $K_{IC}$  of resin more than 60%. As seen in Figure 4, N2.5/T7.5 almost follows the rule of mixtures (The dashed line in Figure 4 presents the rule of mixture). However, Figure 4 shows a significant increase in the  $K_{IC}$  value (200%) for the N7.5/T2.5 which is a positive deviation from the rule of mixtures. Interestingly, the fracture toughness value of this material is higher than that of N10. Therefore, synergistic toughening occurs when 7.5 phr nanoclay and 2.5 phr Tire are incorporated.

Similar trend is observed for N5/T5 sample. These results are similar to the finding of previous researchers who reported positive deviation from the rule of mixtures in rubber-toughened polymers when bimodal size particles were incorporated [10].

Figure 5 presents the SEM micrographs taken from the fracture surface of SEN specimens. T10 specimen has a smooth fracture surface (Figure 5(a)), due to the lack of inelastic deformation. Similarly, fracture surface of N10 shows limited surface roughness indicating lack of sever deformation in this material (Figure 5(b)). However, looking at fracture surface of N7.5/T2.5 (Figure 5(c)), stepwise surfaces are observed in the vicinity of Tire particles. It is as the result of interaction between crack tip and Tire particles. The large amount of roughness is observed which can be attributed to the significant inelastic deformation at the crack tip. This inelastic deformation results in energy dissipation at the crack tip and consequent high  $K_{IC}$  value of the N7.5/T2.5 ternary blend. This observation is parallel to the fracture toughness data seen in Figure 4 where N10 and T10 specimens have lower  $K_{IC}$  in comparison with N7.5/T2.5 sample.

**Impact Resistance:** The impact energy absorption (impact strength) of samples are reported in Table 3. Despite  $K_{IC}$  results, addition of nanoclay does not improve the impact strength of neat epoxy (E0 in Table 2). However, it slightly enhances the impact strength of waste tire-modified blend.

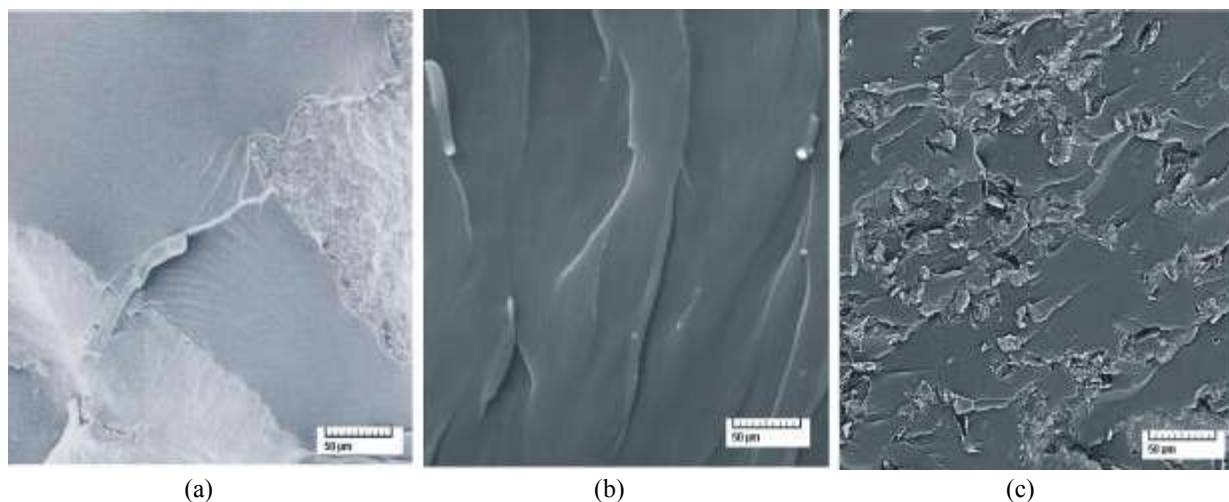


Fig. 5: SEM photos taken from damage surface of samples: (a) T10, (b) N10, (c) N7.5/T2.5

Table 3: Impact strength of samples

Designation	Impact Strength (kJ/m <sup>2</sup> )
E0	3.1
T10	1.4
N2.5/T7.5	1.7
N5/T5	1.9
N7.5/T2.5	2.3
N10	2.8

Table 4: Glass transition temperature of samples

Designation	T <sub>g</sub> (°C)
E0	108
T10	107
N2.5/T7.5	108
N5/T5	108
N7.5/T2.5	108
N10	107

Note that the mechanical behavior of polymers is rate-dependent in nature. Modified epoxies exhibit improved toughness from the development of a process zone around the crack tip [15]. Energy dissipates in the process zone via various toughening mechanisms. At relatively high deformation rates such as impact, dynamic instable fracture occurs and toughness of the resin decreases dramatically [15]. Therefore, modifiers might not be effective in ameliorating the impact strength of polymers.

**Glass Transition Temperature (T<sub>g</sub>) Evaluation:** To further investigate the behavior of hybrid epoxies, the variations of T<sub>g</sub> of the specimens were measured and listed in Table 4. As seen, introduction of modifiers does not lead to a sensible change in glass transition temperature. Note that the recycled tire particles are not enough small to induce a plasticizing effect and consequent T<sub>g</sub> reduction. Some researchers reported ameliorating or deteriorating effects of nanoclay on glass transition temperature of epoxy due to the altering the chain mobility of the matrix by clay nano-layers [12, 16]. In this study, however, the T<sub>g</sub> of epoxy remains almost constant by addition of nanoclay.

These findings reveal that the source of change in mechanical characteristics of the resin is not the plasticizing effect of rubber or the nanoclay-induced chain mobility of the matrix.

## CONCLUSIONS

Epoxy is used in many dental and medical applications such as manufacturing prostheses e.g. artificial hand, leg, etc. due to non-toxic and good

processing characteristics. In this work effect of addition of clay nano-particle on mechanical characteristics of waste tire-modified epoxy was examined via ASTM standard tests. It was found that nanoclay improve compressive strength and Young modulus of the waste tire-modified epoxy. Similar improvement were observed in flexural and impact strength of the ternary blends. Furthermore, experimental results revealed synergistic toughening in some hybrid formulations particularly when 7.5 phr nanoclay and 2.5 phr waste tire were incorporated.

Interestingly, the result of measuring glass transition temperature (T<sub>g</sub>) of the samples reveals that the improvement of mechanical characteristics were achieved without any reduction in thermal stability of the samples. The findings of this work emphasize that the ternary blend exhibits excellent performance in comparison with the waste tire-modified epoxy.

## ACKNOWLEDGEMENT

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