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ARTICLE

Effect of Water Absorption on Some Mechanical Properties of Unsaturated Polyester Resin/Natural Rubber Blends

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Abstract: Binary polymer blend (UPE/ NR) with a weight ratio of (95/5)% was prepared by mixing of unsaturated polyester resin (UPE) with natural rubber (NR). Standard dimensions of specimens were prepared from the polymer blend. Compression, bending and impact tests were carried out on the prepared specimens. This investigation was conducted before and after the immersion of the specimens into three types of water (distilled, tap and rain water) for different periods of time (1, 2… 5 weeks). The (stress-strain) curves were obtained from compression test; while the Young's modulus values (E) were obtained from three-point bending test. The impact strengths (I.S.) were found from the impact test before and after immersion into water. The results have exhibited that the mechanical behavior of the prepared blend is affected by the nature of water and immersion time. In general, the strain rates and the impact strength of the polymer blend have increased after immersion; while the Young's modulus has decreased at the same conditions.

Keywords: Polymer blend; Unsaturated polyester; Natural rubber; Compression; Bending; Impact strength.

Introduction

An advance in science and technology requires a variety of modified polymers with demanded performance properties at lower cost. However, it has become more difficult to find all the requested mechanical properties in the existing homopolymer; thus polymer blends or alloys and composite materials have been considered to be the more promising approach to the production of new materials and have been extensively studied [1].

The term polyester is analogous to the term steel in metals. Just as there are many types of steels with widely varying properties, so too there are a multitude of polyesters with a significant range of properties. Unsaturated polyesters are sold in a liquid form that requires catalyzation in order to cure [2].

Unsaturated polyesters are manufactured by condensation and polymerization of dicarboxylic acid (maleic acid) and dihydric alcohol (e.g., glycol) followed by curing with a cross-linking agent (styrene). They have good resistance to heat and most chemicals except strong acids and alkalies. They are affected by sunlight unless stabilized [3].

Natural rubber is an elastic material present in the latex of certain plants. More than 95 percent of this rubber is obtained from the latex of rubber trees. It is polymerized from isoprene. The polyhydro-carbon chain rubber consists of 2000-3000 monomer links. The polymerization occurs by a biochemical reaction in which a particular type of enzyme acts as a catalytic agent [3].

The important properties of cured resins which determine their service life are resistance to deformation and fracture under different time / temperature or sudden loading conditions.

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Among the curable resins, the unsaturated polyesters, particularly multi-component, polymaleate compounds, have the lowest stress-strain indices. This is probably due to deficiencies at the supermolecular level in their microheterogenous structure when cured. The defects distributed between the dense network globules or particles, serve as points of stress concentration. In the defective areas, weak regions are formed where the basic processes responsible for the deformation and fracture of cured polyester resins take place [4].

Blends and alloys are made by physical mixing of two or more polymers (also called homopolymers). At least 5% of another polymer is necessary to create a blend or an alloy, and a number of microstructures can result. If the homopolymers are miscible, a single-phase blend or alloy will result. If the component polymers are immiscible, a multi-phase alloy or blend results. The additive polymers can form spheres in the host matrix; they can form cylinders that are usually oriented in the direction of flow in processing; or they can form lamella (alternating layers, like plywood) [2].

The addition of elastomeric components improves some mechanical properties; particularly the fracture toughness of cured polyester resins. Several authors have shown that the improvement of the fracture toughness of thermosetting resins depends on three factors [5]:

(a) The miscibility of the rubber with the modified resin in the liquid phase.

(b) The particle size of the rubber.

(c) The selectivity and reactivity of the functional groups in the rubber.

Cao *et al*. [6] studied the mechanical properties of an epoxy resin toughened by polyester. The results showed that the impact strength and tensile strength of the modified epoxy resin were remarkably greater than those of the unmodified cured epoxy resin. And the mechanical properties depended greatly on the congregating state of the polyester added.

LaPlante and Sullivan [7] investigated the behavior of cured FM300 epoxy; a structural film adhesive, subjected to partial and full moisture saturation. In this investigation, three separate but interrelated test methods were used: stress relaxation, fracture toughness and dynamic mechanical testing. Fracture testing showed that the material toughness increased with increasing moisture concentration; plasticization effects were dominant.

In a previous publication [8], a preliminary work was carried out for preparing and evaluating the mechanical properties of polymer blend obtained from unsaturated polyester resin (UPE) compound with synthetic rubbers (Styrene Butadiene Rubber (SBR), Nitrile Butadiene Rubber (NBR) and Butadiene Rubber (BR)). In the present work, Natural Rubber (NR) was replaced as an addition material for the same resin (UPE) to study the mechanical behavior of the prepared polymer blend (UPE/ NR). The aim of this work is to study some mechanical properties of (UPE/NR) blend before and after immersion into (distilled, tap and rain) water for different periods of time.

Experimental part

Procedure of sample preparation

(UPE/ NR) polymer blend with a weight ratio of (95/5) % was prepared by mixing of unsaturated polyester resin (UPE) with natural rubber (NR). The (NR) was supplied by Babylon Tires Factory in Babylon, Iraq; while the (UPE) resin was supplied by Saudi Industrial Resins (SIR) Company, Saudi Arabia. The curing agent (hardener) was methylethylketone peroxide (MEKP); while the catalyst system was a solution of cobalt octoate in dibutyl phthalate as accelerator of reaction. After mixing the two liquid polymers (UPE with NR), the hardener was added to the mixture with 2% ratio; while the ratio of the accelerator was 0.5%.

This binary polymer blend was poured into a metal mould (Aluminum) with dimensions of (14x12x5) cm at room temperature; then after solidification, the resulting cast was put into an oven with a set temperature of 50^{o}C for (1 hour) to ensure that full curing was achieved. Post-curing treatment reduces weight loss significantly; while higher temperature and relative humidity increase the weight loss rate [12].

The compression and bending test specimens were prepared from the casted sheet according to ASTM-D695 and ASTM-D790 standards respectively; while the impact test specimens were prepared according to (ISO-179) standard.

In addition to the points mentioned above, it is vital to mention the following:

a) An addition more than 5% of NR reduces the stiffness of resin and makes it behave as a ductile material, therefore the addition ratio of (5%) was selected.

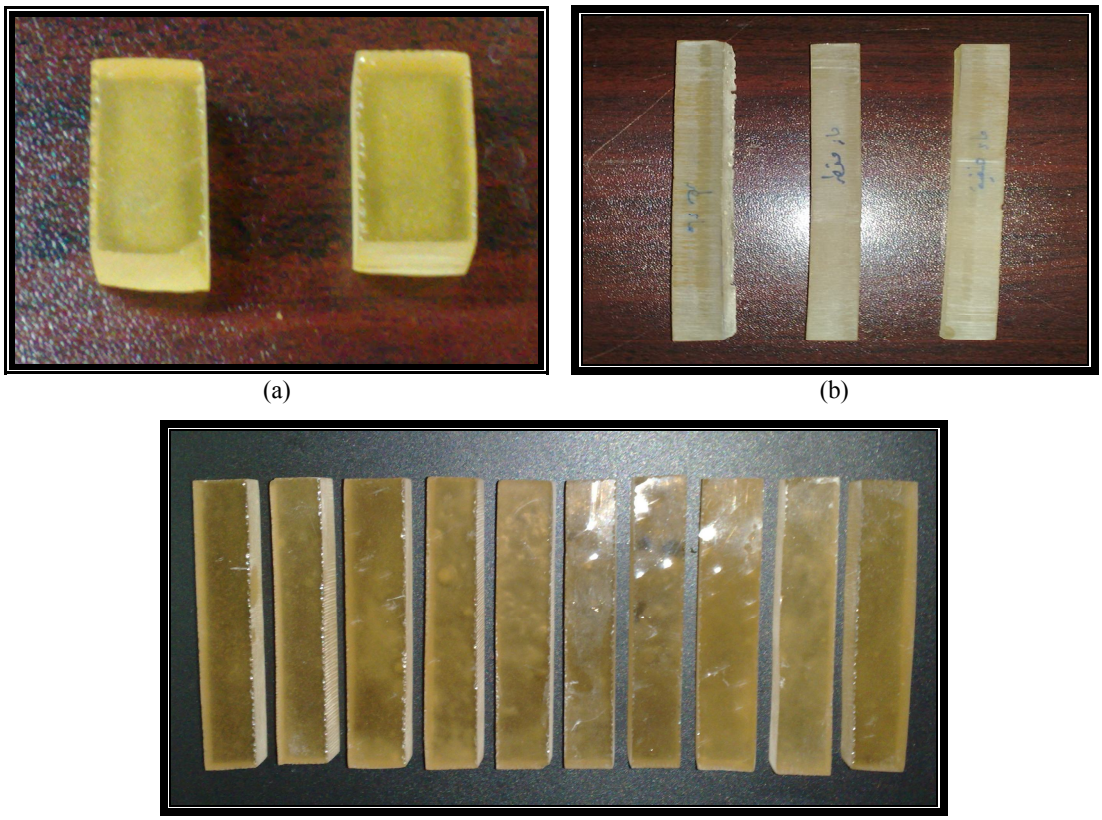
b) The surfaces of all specimens were polished by a grinding machine before testing.

c) The total dissolved salts (TDS) and the (pH) of each type of water were measured and the data presented in Table (1).

TABLE 1. The values of (TDS) and (pH) of each type of water.

Type of water	TDS (ppm) ± 2	pH± 0.1
Distilled water	121	7
Rain water	103	7.7
Tap water	426	7.1

Fig. 1 shows photographic images for some prepared samples under study.



(a) (b)

(c)

FIG. 1. Photographic images of (a) compression, (b) bending and (c) impact test specimens.

Compression test

Hydraulic press type (Leybold Harris/ Germany) was used to perform the compression test; as shown in Fig. 2a. This test was carried out before and after the immersion of the samples into three types (distilled, tap and rain) of water. The relationship between (F-ΔL) was obtained which could be modified to obtain the (σ - ε) relationship; so as to study the mechanical behavior of the blend under the effect of compression loading; where:

F is the applied force on the specimen.

ΔL is the change in the length of the specimen.

(σ - ε) is the (stress- strain) relationship.

Bending test

Three-point bending test was carried out to obtain the Young's modulus values for all specimens at similar conditions. Bending test instrument type (PHYWE/ Germany) was used; see (Fig. 2b).

The values of Young's modulus (E) were calculated from the following equation [9]:

$$E = \frac{MgL^3}{48(I)S} \quad (\mathrm{N/m^2}) \; ; \qquad (1)$$

where (M) is the applied mass on the sample, (S) is the elastic deflection of the sample, (M/S) is the slope of the curve obtained from the

relationship between the mass and the deflection of each sample, g = 9.81m/s^2, L is the distance between two supports of the instrument. (I) is the area moment of inertia:

$$I = \frac{bd^3}{12} \quad (\text{mm}^4) \quad ; \qquad (2)$$

where (b) is the width; while (d) is the thickness of the specimen.

Impact test

Charpy impact tests were conducted on the specimens at room temperature before and after immersion into the mentioned three types of water. The standard specimen was held as a horizontal cantilever beam, broken by a single swing of a pendulum, the energy to failure was measured by the measurement fixed on an instrument.

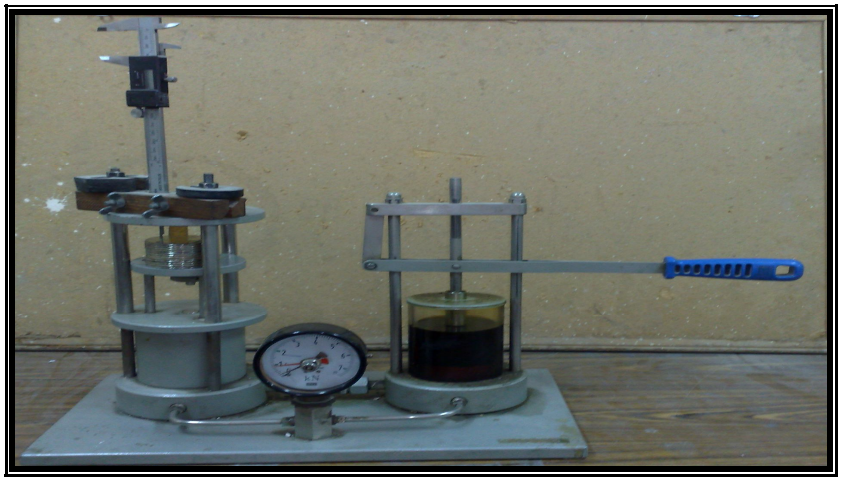
The impact strength ($I.S$) was calculated as follows [3]:

$$I \cdot S = \frac{Uc}{A} \quad (\text{J/m}^2) \; ; \qquad (3)$$

where (Uc) is the required energy for breaking the specimen, (A) is the cross-sectional area of the specimen.

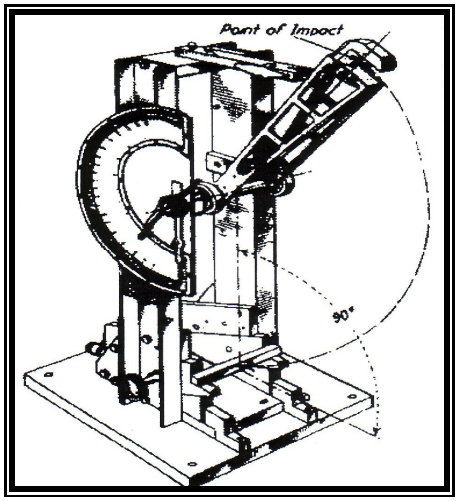
$$A = b \times d \;\; (\text{m}^2) \; . \qquad (4)$$

Fig. 2c is a schematic drawing of Charpy impact test instrument.



(a)

(b)



(c)

FIG. 2. Photographic images of (a) compression, (b) bending test instrument and (c) schematic drawing of Charpy impact test instrument.

Optical microscopy

Optical microscope (15X) type (73346/digital camera, Japan) was used to study the morphology and microstructure of specimens before and after immersion into the three types of water.

Results and discussion

(Stress- Strain) curves

To study the mechanical behavior under the effect of compression load, (stress-strain) relationships were obtained for all prepared specimens. Fig. 3 shows this relation for the blend before immersion into water; while Fig. 4 illustrates the effect of immersion into three types of water (distilled, tap and rain water) for periods of time ranging from (1-5) weeks. From those curves, the effect of water type and period of immersion can be clearly noted. These behaviors were already expected due to the plasticization phenomenon of the polymer resulting from immersion into water; however, the results clearly indicate that the changes in stress-strain behavior were not proportional to the immersion time. When Figs. (3, 4) are compared with the typical (stress-strain) curves of polymer materials generally [10,11], it can be noticed that the behavior of material transformed from (hard and tough) to (soft but tough) with increasing time of immersion. This means that the polymer blend under work transformed from a material with high modulus, high strain and high stress at break to behave as a material with low modulus but high strain and high stress at break [10, 11].

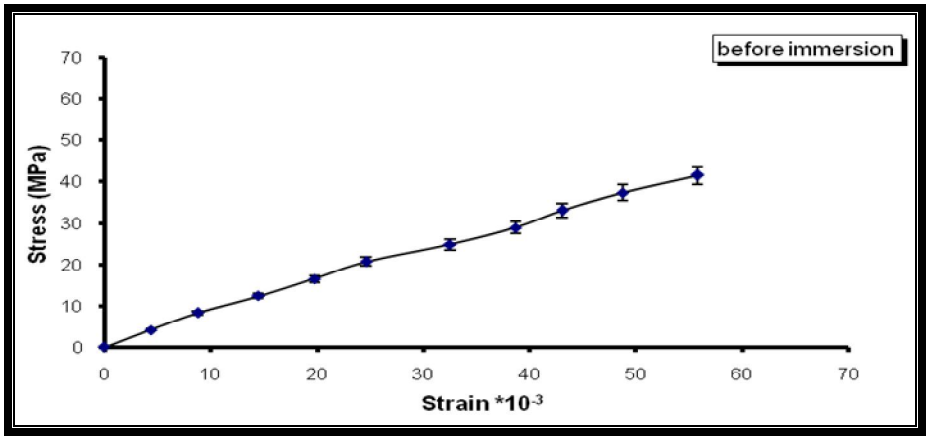


FIG. 3. (Stress-strain) curve for (UPE/NR) blend under the compression load before immersion.

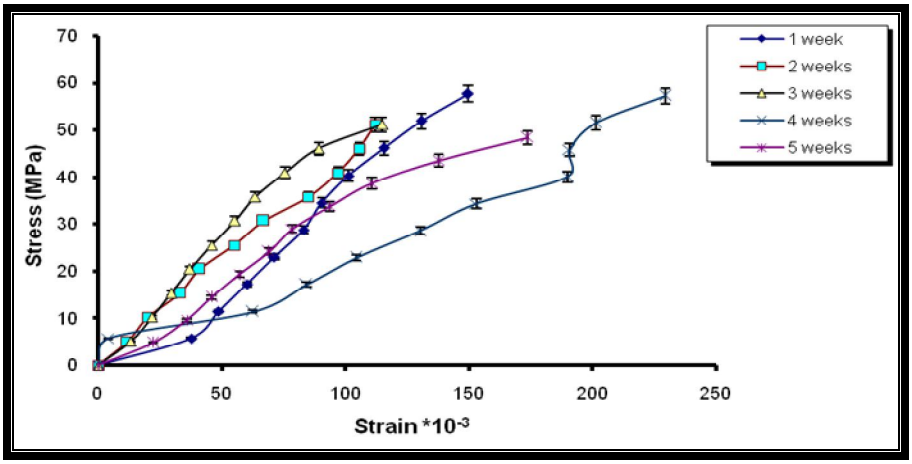
Young's modulus

Young's modulus is indicative of the property called stiffness; small values of (E) indicate flexible materials and large values of (E) reflect stiffness and rigidity [3]. Fig. 5 illustrates the change in the Young's modulus values as a function of immersion time. It can be noticed that the Young's modulus values had a remarkable drop after 4 weeks of immersion for all three types of water. This may be attributed to the influence of water which acts as plasticizer factor for polymer, which decreases T_g and elasticity moduli [9, 12].

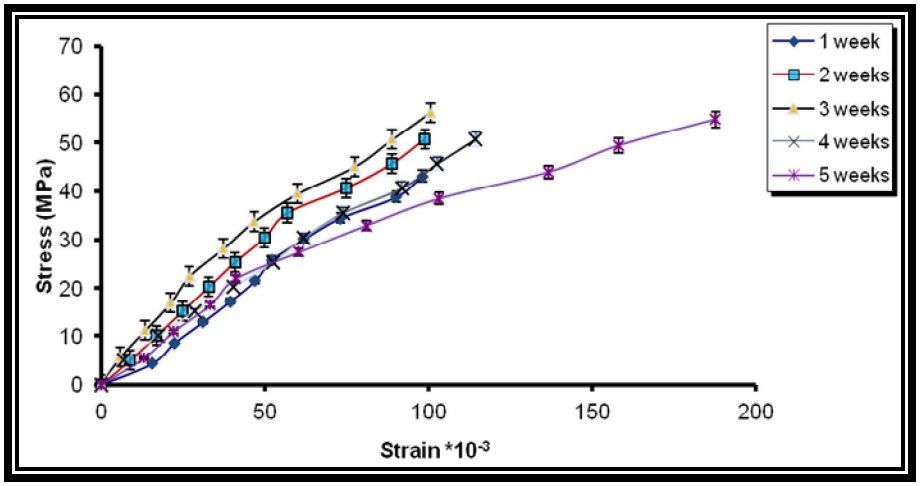
Impact strength

Fig. 6 shows the values of impact strength for all specimens as a function of immersion times. It can be seen that at the first stage of immersion, the prime effects of distilled and tap water are similar and decrease the impact strength value which then increases gradually with increasing the immersion time; while this behavior is different for specimens immersed into rain water; where the value of impact strength increases at the first stage of immersion and then decreases at the second stage and finally returns to increase again. This behavior may be related to the nature of rain water (weak alkaline medium, pH = 7.7 as shown in Table (1)), this medium attacks the ester linkage, thus breaking the polyester chain [13], this phenomenon reflects negatively on the impact strength of polymer blend after 2 weeks of immersion; whereas it is interesting to note that the immersion into tap water (salt environment as shown in Table (1)) records higher impact strength at the same period of immersion. This could be possibly explained, if NaCl molecules act as an interphase between the two phases (UPE/NR) causing the reduction in interfacial

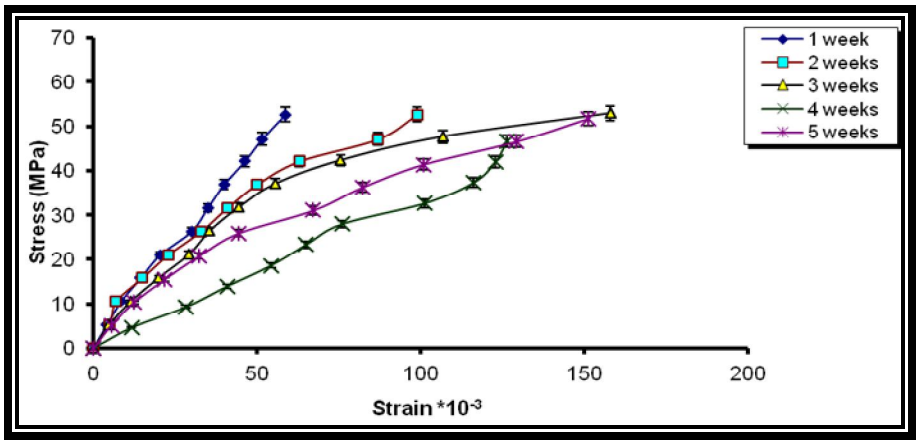
shear. This will increase the energy absorption capability at the interface resulting in the increase of fracture energy and then the impact strength will be increased [14]. Other previous studies indicated that the increase in the impact strength of polymers after the immersion into water is expected as a result of the plasticization when partially saturated with moisture [7, 12].



(a)



(b)



(c)

FIG. 4. The effect of immersion into (a) distilled water, (b) tap water and (c) rain water on (stress-strain) behavior for(UPE/NR) blend under compression load.

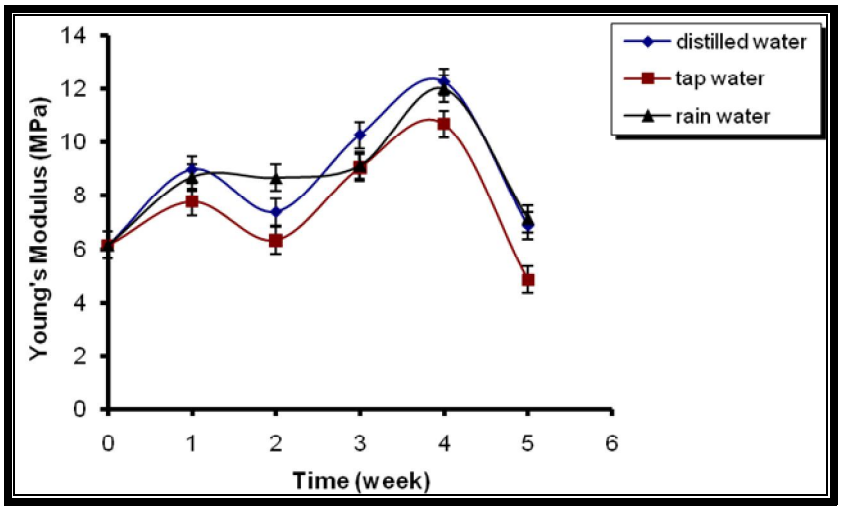


FIG. 5. Effect of immersion time on values of Young's modulus for(UPE/NR) blend.

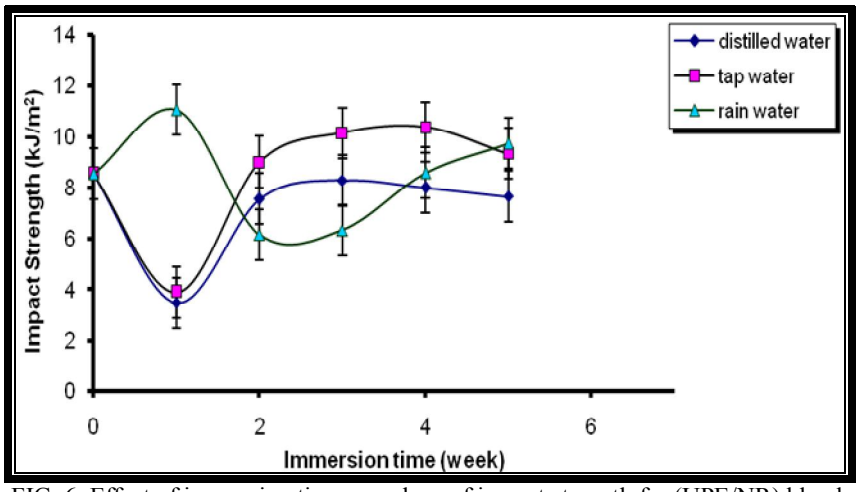


FIG. 6. Effect of immersion time on values of impact strength for (UPE/NR) blend.

Morphology study

Some changes and flaws were noticed after the immersion of the samples into three types of water as shown in Fig. 7. It can be also observed from the optical micrographs that the polymer blend under study seems as a single phase (miscible) which means that the two polymers (UPE and NR) are compatible to form a new material with new properties.

Conclusions

In the current study, UPE resin was used as a matrix material due to its availability at cheaper prices compared with Epoxy resin used in most previous works. In addition to that, the mechanical properties of the prepared blend can compete with that of Epoxy; this would lead to a new industrial material at lower cost. Furthermore, this study is distinguished by the investigation of the effects resulting from absorption of three types of water on the blend's mechanical properties; while previous studies were limited to the behavior at the dry case of material. This work leads to a conclusion that the added value of the present investigation is a significant modification in the properties of the UPE resin resulting from the adding of an optimum percentage of NR, without changing the hardness and rigidity of the original UPE. Other related conclusions are shown below:

1- After blending the two polymers (UPE and NR) with a ratio of (95/5)%, it was found that the blend is homogenous to the eye.

2- It is clear that the deflection rates increase greatly after immersion of the (UPE/NR) blend specimens into the different types of water compared with the case before immersion.

3- The (stress-strain) behavior of the blend under study was found to be affected by the sort of water depending on the (pH) value and the percentage of total dissolved salts (TDS) in each type of water.

4- Rain water has a higher effect on the mechanical behavior of the prepared blend compared with distilled and tap water. The samples immersed in rain water missed their color and became discolored.

5- It can be concluded that the penetration of water into the polymer blend has a limited effect on its nature. In other words, the general external appearance of the immersed material reveals that the socked specimens do not undergo any swelling, but they are plasticized.

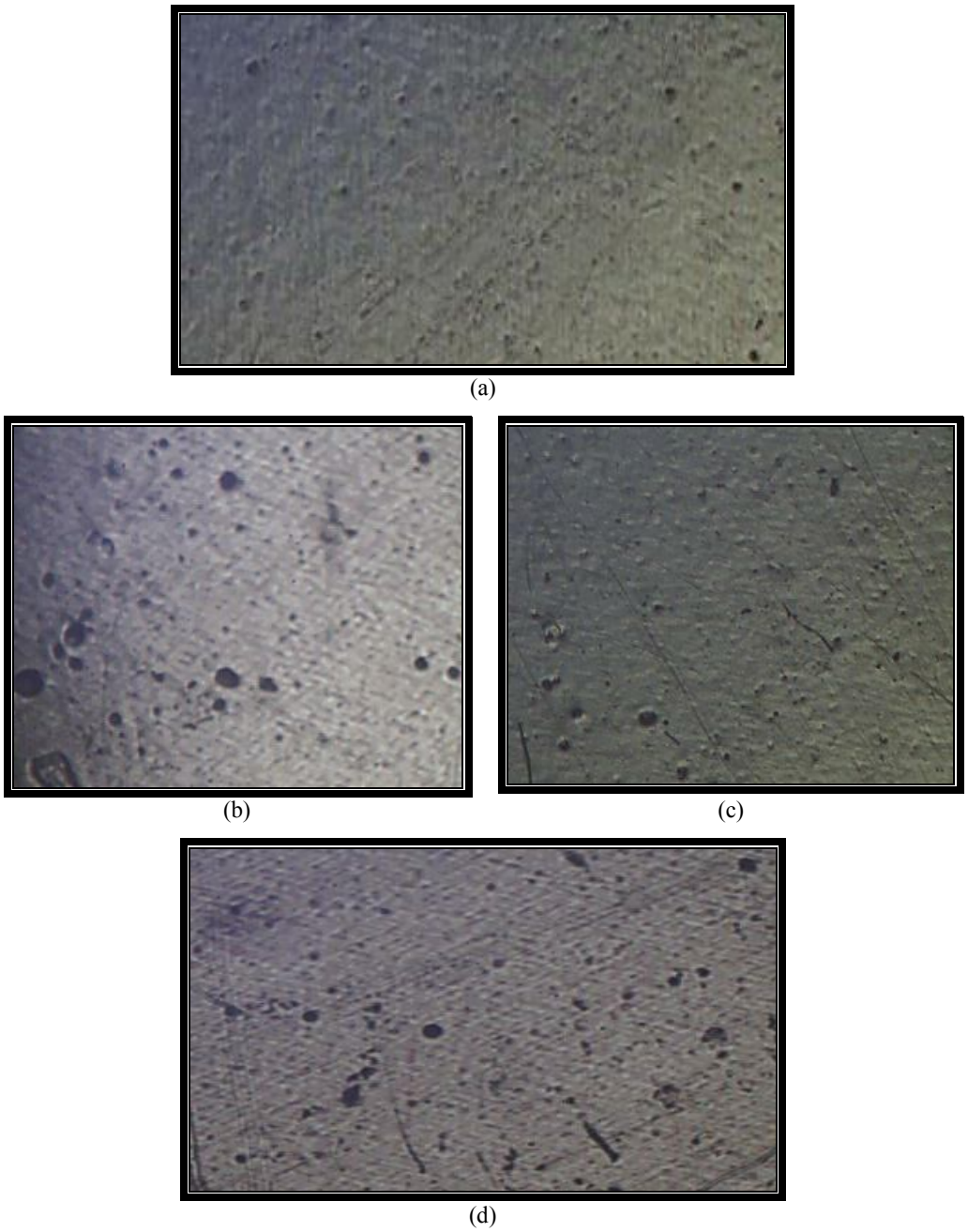


FIG. 7. Optical micrographs (15X) of (UPE/NR) polymer blend (a) before immersion and (b), (c) and (d) after immersion into distilled water, tap water and rain water, respectively.

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