Study of weathering effects on binary and ternary polymer blends

Rana M Salih
Applied Science Research Unit, Department of Applied Sciences
University of Technology, Baghdad-Iraq

Emails: 100166@uotechnology.edu.iq, ranamahdi1@gmail.com

Abstract. Composite materials were prepared using polypropylene (PP), polycarbonate (PC) and polyethylene terephthalate (PET). The three polymers were manufactured into binary blends (PP+PET) and ternary blends which consist of (PC+PP) together as the major constituent, and PET as the minor constituent. The optimum mixing ratio (OMR) of the polymers mentioned previously decided by the tensile test results, so the blend with the highest tensile strength chosen as the composites matrix material to be prepared. The blends employed as composite matrix materials by the addition of 1% wt. of titanium oxide, to assess their resistance to weathering effects (UV spectrum in the current work). Mechanical tests (tensile and impact) conducted to assess the change in properties before and after exposure to the mentioned effects. The reinforced binary and ternary blends showed a higher resistance to U.V. spectrum compared to unreinforced blends, such that the tensile strength and impact strength were higher using TiO2-reinforced specimens than the unreinforced ones.

Keywords: polypropylene, polyethylene terephthalate, polycarbonate, thermoplastics, polymer blends, tensile strength, impact strength, weathering, ultraviolet spectrum, titanium oxide

1. Introduction
Polymer blends received a great deal of study and research in the last decades because of their properties and potential uses. The term implies the combination of two or more types of polymers into one structure, in order to get the desired properties not usually obtainable with a single polymer, or reduce the costs. Polymer blends are not new though, as they have been in use in rubber industries and polymer coatings for decades. Anyway, this approach comes with its own difficulties, as it’s hard to combine two polymers in a fully miscible blend, since they tend to segregate, nevertheless they are still used as compatible blends, although separated into two or more phases down to the molecular level, they are still useful and could be used in many technological and industrial aspects [1].
Polymers are sensitive to weather elements like U.V. radiation from the sun. As these effects have the energy and power to be in contact with the exposed parts of polymers and interact, possibly in a negative manner with the polymer chains which leads to break into small portions, in a process called “scission”. The extent at which this process occurs depends on the structure of polymers and the dose of exposure [2], that’s why researchers have developed certain additives (such as titanium oxide), to be mixed with polymers in order to reduce such effects. Titanium oxide is a naturally occurring oxide known for its versatile uses whether in pigments, cosmetics and U.V. absorber in polymers, which converts the latter destructive radiation into heat [3].

Many works have been devoted to study the influence of weather elements on the properties of polymers due to the importance of this objective in deciding the final properties of the plastic products: A.L. Andrady et.al. Studied the combined effects of U.V. spectrum, with other weather factors like temperature on the life of plastic coatings for outdoor applications, the researchers studied the usefulness of the some photostabilizers in preventing the damage caused by the U.V spectrum. So, the results showed that the amount used for this purpose must be optimized according to the dose of spectrum in which the plastic is used in, since more or less addition percentage may not give the desired protection against U.V. [4]. In 2003, a study carried out by Hongying Y. et.al. To assess the use of TiO2 as a U.V. retardant in fabrics and films, especially for outdoor products. As they used TiO2 in the Nano-scale additive and a pigment, they found that the Nano additive is more efficient in blocking the U.V. spectrum than the as it pigment, as it has more absorbency [5].

The current work studied the effect of ultraviolet light on the mechanical properties (tensile, impact) of polymer binary and ternary blends of (PP, PET and PC), and how to reduce this effect by the addition of TiO2.

2. Experimental

2.1 Materials

Polypropylene, polyethylene and polycarbonate chosen to work with in the current work, all produced by Exxon Mobil®, they are thermoplastic materials that were chosen to achieve optimum ductility and higher tensile strength.

2.2 Procedure

Blending was carried out according to different percentages: such that for binary blend, polypropylene was the major constituent while polyethylene terephthalate was the minor constituent, and for the ternary blend: PP and PC together were the major constituents and PET was the minor constituent.

Reference specimens of pure polymers (PP, PET and PC) were also manufactured for comparison purposes. The above mentioned polymers all were used to manufacture blends of different ratios. For binary blend: the blending started with (60:40) of PP and PET respectively, then continued with (70:30), (75:25), (80:20), and (90:10) of both respectively. These percentages were blended in a single screw extruder and a flat shaped continuous extradite was gained, from which a tensile test specimen was cut from each blending ratio, and the (60:40) ratio was excluded because of the phase separation and non-homogeneity. Tensile test applied to evaluate the blend of the highest tensile strength.

The procedure mentioned above was performed also on ternary blend, starting with (60:40) of [(PC+PP): PET] respectively, keeping in mind the PC: PP percentage is (80:20) according to previous studies, and as was done with binary blend, tensile test was performed to evaluate the blend with the highest tensile strength. It was found that the (80:20) of [(PC+PP): PET] had the highest tensile strength. For both binary
and ternary blends, the (80:20) percentage has the highest tensile strength, so it was chosen to work with through the current work. After manufacturing the binary and ternary blends, TiO₂ was added to them, with a weight percentage of 1%.

The pellets were dried in a drying oven at 60°C to remove the humidity prior to extrusion, prepared into batches of the designated weights and extruded in a single screw extruder with the temperature set at the melting points of the ingredients. The product then formed into a continuous tape shape, which cooled down at exit with a large water container, later on cut into test specimens according to standard specifications.

2.3 The tests

2.3.1 Tensile test.

The instrument used in the tensile test was Instron-1195® and the test specimens were cut according to the standard specification ASTM D-638, applying a load of 50 kg. and a loading rate (5mm/min) should be applied

2.3.2 Charpy impact test

This test was performed using Charpy impact test instrument by testing machines Inc., Amityville, New York®, according to the standard specification ISO-79. In order to get specimens thick enough for the impact test, thin sheets of the extrudate were hot-pressed together to form a thick specimen.

2.3.3 The weathering test

The weathering procedure was carried out using Hanau Xenotest® by W.C. Heraeus™, using xenon lamp as an ultraviolet radiation source for 24 hours as an accelerated test mechanism, and this process was carried out according to standard specification ASTM G-53.

3. Results and discussion

3.1 Blending effect on tensile strength

The results of tension test for unblended (pure) polymers are shown in figure 1, and for the binary blends in figure 2. The stress-strain behaviors for binary blend (PP/PET) presented an increase in the ultimate tensile strength, i.e. (7.1) MPa, which is higher than each of the PP (3.2 MPa), or PET (4.4 MPa), while the strain found to decrease (i.e. 3.0), which is lower than that for both PP (7.5) and PET (5.5). The binary blend (PP/PET) is immiscible [6] and therefore, under tensile loading, slippage between the ingredients takes place between the two phases such that the PET particles undergo huge plastic deformation. Furthermore, the stretching and elongation of PET particles on the PP matrix, may lead to the formation of longitudinal, stretched particles with oval shape, develops then into microfibers which act as a reinforcement phase. Because of this plastic deformation, a huge amount of energy is needed [6]. Another reason may be that the PET can be crystalline, and this could add to the strength [6]. The ternary blend showed a less tensile strength than the binary blend, and this could be attributed to the immiscibility of this blend of (PC+PP) blend, with low interfacial adhesion between the three phases, leading to a lower tensile strength [7], as shown in figure 3. When the TiO₂ was added to both blends, the strain values shifted towards higher values than the unreinforced blends and in general, and showing higher elongation than the unreinforced blend.
Figure 1. The stress–strain curve for the pure (unblended) polymers.

Figure 2. The stress–strain curves for binary blends, before and after addition of TiO$_2$, and exposure to U.V. radiation.

Figure 3. The stress–strain curves for ternary blends, before and after addition of TiO$_2$, and exposure to U.V. radiation.

The U.V. weathering had a negative impact on the properties of binary and ternary blends, as they became very brittle and lost their elasticity, regarding that the tensile test was carried out under the same conditions for all the specimens. Nevertheless, the addition of TiO$_2$ proved to reduce the effect of U.V. for both binary and ternary blends. The TiO$_2$ naturally has the ability to block the path of U.V. radiation,
which may be attributed to the fact that TiO₂ is a type of semi conducting oxide that has a large band gap separating, it's low and high energy valence, i.e. (3-3.2) eV. These corresponds to the absorption range (413-388) nm, so when U.V. light exposed to TiO₂ with a higher energy than the band gaps (i.e. the wavelength is shorter than the absorption range), then the excess energy absorbed by the electrons and photons that generated between the band gaps. Sequently, an electron-holes produced and the latter will continue with the electron- hole mechanism (which might explain the protection offered by TiO₂) [5].

3.2 Blending effect on impact strength

First, Plain PET showed the lowest value of impact strength comparing to PC and PP, as it’s more brittle, consequently the binary blend became more brittle than the ternary blend, even though both blends showed an improved impact strength value. Binary blend had a noticeable increase in impact strength comparing to PET, which may be attributed to the toughening mechanism due to PET acting as an inclusion, and these inclusions act as stress concentrators, which initiate crazing and plastic deformation in the matrix (PP), hence more energy needed for failure [8]. As for the ternary blend, the toughening mechanism contributed to the growing crazes that initiated by the triaxial stress in front of the crack tip and stabilized by PET domains. The debonding cavitation mechanism occurred at the interface of (PC/PET), which relieved plain strain constraint and promoted shear deformation in both PET and PC. This plastic deformation absorbed tremendous amount of energy. This agrees with the results gained by W. Viratyaporn et. al., who suggested that the tacticity of PP played a role in improving impact properties, since segments of a tactic PP contained in the otherwise polymer (isotactic) may have a compatibilizing effect on the interface between PP and the other polymers, thus increasing the load transfer, energy absorption mechanism and impact strength [9]. The PET domains not only stabilized the growing crazes, but they also bridged crack surfaces after the crack passed by. This effect definitely caused a large plastic damage zone and hence, a high crack resistance. The addition of titanium oxide has further improved the impact strength as these particles acted as crack stoppers to diminish the crack growth [10]. Another possible mechanism for strength improvement was that blending has caused an increase in density, leading to a decrease in free volume, and consequently the movement of chains becomes more difficult at the segment level, resulting in a higher strength [11].

Figure 4. The impact strength values for the pure (unblended) polymers, binary and ternary blends before and after the addition of TiO₂, and before and after exposure to U.V. light.
The U.V. radiation showed a negative influence on the impact strength of the specimens, although the pure polymers showed higher impact strength than their blends. The binary blend reinforced by TiO₂ had an impact strength (0.018 KJ/m²), ternary blend (0.0205 kJ/m²), and both specimens were better than others, while the binary blend which exposed to U.V. radiation was the weakest. As for tensile test, the impact test specimens tested against the exposure to U.V. light in the weather-meter, and the results shown in Figure (4). The degradation of polymer blends depends on the miscibility of phases, thus if the degradation of one component may modified by the pressure and possibly the degradation of another, then diffusion of active species across phase boundaries or direct reactions at the boundary must occur. So to some extent, any interaction between degrading blend components will depend on the degree of dispersion of the phases [12].

Conclusions

In the current work, tensile and impact properties were studied for PP, PET and PC, as pure polymers and as components in binary and ternary blends. TiO₂ was added in a percentage 2% weight fraction to each blend to study its effect as a U.V. blocker. The pure polymers, blends and the blends reinforced with TiO₂ were tested against tensile and impact strengths after exposure to U.V. light for 24 hours. Although the results had shown a decrease in tensile and impact properties of the pure polymers and blends, the blends reinforced with TiO₂ showed better values than the unreinforced blends.

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