The Effect of PVP Addition on the Mechanical Properties of Ternary Polymer Blends

S I Salih¹, A R Jabur¹ and TA Mohammed²

¹Materials Engendering Department, University of Technology, Baghdad, Iraq
²Central Organization for Standardization and Quality Control Baghdad, Iraq

Abstract. One of the problems associated with polymeric blend composites is how to make the components adhere. In this work, the effect of introducing polyvinylpyrrolidone (PVP) to binary polymeric blends was studied. Two sets of ternary polymeric composites were prepared using twin-extruders: the chemical composition of the first set consisted of Polypropylene (PP) with 15%; linear low-density polyethylene (LLDPE), x% Polyvinylpyrrolidone (PVP), and 1% basalt particle (B.P.), where x values were 0, 4, 8, 12, and 16; whereas the samples of the second set were prepared by substituting the LLDPE material with HDPE material at the same weight ratios, giving a chemical composition of PP with 15% HDPE, x% PVP and 1% B.P. The mechanical characteristics and morphology results were studied, and the results showed general mechanical property enhancement with increased PVP content in the two groups of prepared samples, with the exception of elongation which decreased with the addition of PVP to the blends. The highest values of the tensile strength, modulus of elasticity, impact strength, and fracture toughness were recorded at an 8% ratio of PVP content in the first group samples, while the highest values for the same properties in the second group samples was at a 4% ratio of PVP content in the blend. Moreover, the samples of the first group had the highest values of impact strength and fracture toughness (0.45 kJ/m²) and (4.58 Pa√m) respectively, whereas the samples in the second group gained the highest values of fracture strength and Young's modulus. SEM images indicated that the addition of PVP gave better interfacial adhesion between the constituents of the polymeric blends.

Keywords: Ternary polymers blend; polymeric composites; PVP; PP; HDPE; LLDPE.

1. Introduction

Polymeric materials have become important to a variety of industrial applications; the basic reasons behind the great popularity of these materials are their enormous range of characteristics and ease of manufacture. Blending chemically different polymers is an important tool in industrial production for creating products with high-performance properties. The major feature of such a process that the resultant properties are in most cases better than those shown by any of the components [1]. Execution of polymeric blends depends on how they are arranged in space and the characteristics of their components, represented by their chemical structure, molecular weight, concentrations, and intermolecular interactions [2]. Polymeric blending must thus be carried out under particular thermal, mechanical, electrical, and chemical conditions imposed by application requirements [3, 4].

One of the most basic questions about the morphology of polymer blends is their miscibility. Generally, chemically different polymers create immiscible blends, and this blending leads to polymeric materials with weak bonding strength and low mechanical integrity [5]. Studies have suggested that improving the properties of immiscible polymeric blends by adding a third component to acts as a compatibility agent improves the compatibility between the constituents of polymeric blends. This process leads to modification of the adhesion properties in the interfacial boundary of immiscible polymeric blends, reducing the tension at the interfacial boundaries of blend components and thus promoting adhesion between the components of the blends through interphase formation, creating fixation of the morphology [6].

There is extensive literature on the blending of polymeric materials, especially on blends of polypropylene (PP) with polyethylene (PE) [7,8]. One of the reasons for the addition of PE to PP is
improvement in mechanical properties, such as fracture toughness and modulus of elasticity, especially at low temperatures, as well as the improvement in environmental stress cracking properties. The weak properties of polypropylene can receive considerable improvement by blending with other polymeric materials [9,10].

However, the miscibility of PP with LLDPE is limited by preparation conditions and composition ratios. For example, when a polymeric blend of LLDPE and PP is cooled from the state of a miscible melt, the construction morphology breaks apart into two phases, leading to the creation of an immiscible blend [3]. Studies elsewhere have shown that such un-immiscible polymer blends provide a synergy of mechanical properties only when the processing and compositional parameters are near optimum values [11].

Another way to promote polymeric properties by cooperative interaction is by using filler as a reinforcement material. By encouraging cooperation in more than one organic or non-organic material, it can act as an agent to produce combined effects greater than the sum of the materials' effects in their separate states [12,13].

The present study thus aimed to investigate the effects of PVP content on the mechanical properties of two groups of ternary polymer blend composites, PP/LLDPE/PVP and PP/HDPE/PVP, reinforced with basalt particles.

2. Experimental Work

2.1 Materials
In this research, four types of polymer materials were used; these polymer materials were polypropylene (PP), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and polyvinylpyrrolidone (PVP). Suppliers and selected physical property data for each polymer is given in Table (1). Basalt particles (B.P.) were used as a filler material for the polymer blend; these were produced from basalt stones which obtained from That Al-Sawary State Company for Chemical Industries. The basalt stones had different colours ranging from grey to black.

| Material Information | Polymers | HDPE | LLDPE | Polyvinylpyrrolidone (PVP) |
|----------------------|----------|------|-------|---------------------------|
| Supplier company     | Sabic    | Sabic| Dow Company | "Sinopharm chemical reagent company" |
| Trade name           | 520LPP   | M80064| "Dowlex 2042/2045" | type (K-30) "Luviskol or Kollidon" |
| Melt flow index       | 10       | 8    | 1.0 – 2.0 | |

2.2 Samples Preparation
The basalt stones were washed thoroughly with detergent powder and then rinsed with hot distilled water in order to remove any dust and mud; after that, these stones were dried in a desiccator at 60 °C for 3 hours, and then crushed with a cracking machine. Then, the basalt grains were ground using a porcelain mill several times, each time for three hours, until the grains became fine particles. These ground particles were graded using a sieving process to obtain very fine particles. The particle size distribution of the basalt particles was assessed using a laser diffraction particle size analyser type SHIMADZU SALD—2101. The results of particle size distribution testing are shown in Figure (1). The mean diameter was 4.848 μm, and the median value was 5.872 μm; the chemical composition for these particles was assessed by the Iraq Geological Survey, as shown in Table (2).
Table 2. The chemical composition for basalt particles

| Oxides% | SiO₂ | Fe₂O₃ | Al₂O₃ | TiO₂ | CaO | MgO | Na₂O | K₂O | P₂O₅ % |
|---------|------|-------|-------|------|-----|-----|------|------|--------|
| Proportions | 45.85 | 12.67 | 17.93 | 2.83 | 10.16 | 4.91 | 3.25 | 1.26 | 0.61 |

| Figure. 1. Particle size analysis of basalt. |

To prepare the batches for extrusion, pellets of polymer materials and basalt particles were weighed into the selected ratios displayed in Table (3). To ensure optimum distribution of polymer materials and basalt particles, they were mixed together in a dry condition at room temperature for 20 minutes using a mill made of porcelain material. The first group was prepared according to the formula PP: 15% (LLDPE: x% PVP): 1% basalt particle (B.P.) with weight ratios selected for x values 0, 4, 8, 12, and 16. The second group was prepared with a chemical composition of PP: 15% (HDPE: x% PVP): 1% B.P., and both sets were melted in double screw extruder machine with a screw L/D of 30:1 and an extrusion speed of 50 rpm, with barrel temperatures of 170 °C, 180 °C, and 160 °C from the feed to die zone, respectively.

The extruder product was long strips of polymer blend of thickness ≈ 1.5 mm.

To prepare samples of suitable thickness according to ASTM specifications, a compression technique was carried out on the strips at pressure 350 kgf/cm² at 150 °C for 10 minutes.

Table 3. compositions of polymeric blends.

|                | PP      | LLDPE: PVP | Basalt particle |
|----------------|---------|------------|----------------|
| First group    |         |            |                |
| 84%            | 15%LLDPE| 1%         |
| 84%            | 15% (96%LLDPE+4% PVP) | 1% |
| 84%            | 15% (92%LLDPE+8% PVP) | 1% |
| 84%            | 15% (88%LLDPE+12% PVP) | 1% |
| 84%            | 15% (84%LLDPE+16% PVP) | 1% |

|                | PP      | HDPE: PVP  | Basalt particle |
|----------------|---------|------------|----------------|
| Second group   |         |            |                |
| 84%            | 15% HDPE | 1%         |
| 84%            | 15%(96%HDPE+4%PVP) | 1% |
| 84%            | 15%(92%HDPE+8%PVP) | 1% |
| 84%            | 15%(88%HDPE+12%PVP) | 1% |
| 84%            | 15%(84%HDPE+16%PVP) | 1% |

2.3 Mechanical test: -
The tensile strength test was carried out according to ASTM D638 [14], using a testing machine model WDW 200 E. The test was done at a constant crosshead speed on the order of 1 mm/min. The bending test was accomplished using a three-point loading technique; this test was performed according to
ASTM D-790-78 [15], with velocity 5 mm/min using a testing machine model WDW 200 E. Compression testing was accomplished according to ASTM-D695 [16] with dimensions 8 x 4 x 4 mm³; a computerized universal testing machine (WDW 200E) was used. The impact fracture testing technique was established according to ASTM standards (ISO 179) [17] and an Izod Charpy testing instrument was used. Hardness testing was accomplished according to ASTM standard D2240 [18]. This method is suitable for thermoplastic polymers and thermoset polymers; the hardness test was done utilising a Durometer hardness instrument 3120, Shore D type. A Scanning Electron Microscope (SEM) model TESCAN VEGA-SB was used to analytically examine the fracture surface morphology. To achieve good electric conductivity, all samples were sputtered with gold from the surface along the edge. All tests mentioned above were carried out at ambient temperatures.

3. Results and Discussions

3.1. Mechanical Tests Results

Tensile inspection was carried out mainly to investigate the effect of adding PVP on the behaviour of stress-strain curves for ternary polymeric blend composites. Figure (2) illustrates the effect of PVP content on the behaviour of the stress-strain curves of the first group of composite samples, which consisted of PP: 15% (LLDPE: x% PVP): 1% basalt particle (B.P.), with different ratios of PVP (0, 4%, 8%, 12%, and 16%) relative to the LLDPE content, and Fig. (3), shows the behaviour of the stress-strain curves of second group of samples, which consisted of PP: 15% (HDPE: x% PVP): 1% B.P., with a different ratios of PVP (0, 4%, 8%, 12%, and 16%) relative to the HDPE content. As shown from the figures, all the stress-strain curves show plastic behaviour in terms of tensile stress and significant decreases in the elongation at break for all prepared samples as PVP content increased in the polymer blend. This may be related to the PVP content obtaining stronger linkages between the components of the polymer blends and the polymeric chains. These, in turn, would reduce the motion of the molecules, reducing the sliding of polymer chains when the sample is subjected to tensile load and thus reducing of the percentage of elongation [8].

![Stress-Strain curves of PP: 15% (LLDPE: x% PVP): 1% basalt particle as a function of PVP content in the blend.](image-url)
Figures (4) and (5) illustrate the effect of PVP content on the fracture strength and modulus of elasticity of polymer blend composites. As shown in these figures, there was an increase in the fracture strength and Young's modulus values of the two groups of composites with increasing PVP ratios, reaching maximum values of 34.60 MPa and 0.832 GPa, respectively, at an 8% ratio of PVP content in the first group; in the second group of samples, the maximum values were 34.11 MPa and 0.81 GPa respectively at a 4% ratio of PVP content. These values decreased with further increases in PVP ratio in the polymer blend, falling below their values in the basic blend free of PVP content. This is related to the characteristics of PVP which show good compatibility between the constituents of polymer composites at lower ratios of PVP content, as well as promoting optimum dispersion of basalt particles in such composites [2,7]. However, higher amounts of PVP (larger than 8%) accumulate in the dispersal phase, and this creates a disadvantage in terms of the mechanical properties of the prepared samples. It can also be noted from Figures (4) and (5) that the fracture strength and Young's modulus values of the second group which contained HDPE material were higher than in their counterparts in the first group which contained LLDPE material, except at the 8% ratio of PVP. This is related to HDPE material containing chain structures with few branching structures as compared to blend samples with LLDPE materials, which have many branching structures that lower the tensile strength in the polymer blend matrix [8]. In addition, the highest values of fracture strength and Young's modulus for the sample with an 8% ratio of PVP in the first group may be related to the good interfacial reaction between the constituents of this blended material; the 8% ratio of PVP gave optimum compatibility to this sample.
Figure 4. Fracture strength of PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle as a function of PVP content in the blend.

Figure 5. Young's modulus of PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle as a function of PVP content in the blend.

Figure 6 shows the elongation at break for the two groups of prepared polymer blends; it can be noticed that the elongation decreases with an increased PVP ratio in both groups, which is related to the properties of PVP that increase the interfacial adhesion between the blend components and improve stability and decrease chain sliding [20].
From Figure (7) it can be observed that there is an increase in compressive strength with increasing PVP content ratio in the polymeric blends, compared with blends free from PVP material; the compressive strength values reached to maximum values at the 8% PVP ratio, then decreased with further increased PVP content, becoming nearly stable at less than 12% PVP ratios for both groups of polymeric blends. These values remain higher than the values of the blend at a zero% ratio of PVP. It can also be noted from Figure (7) that the compressive strength for the second group of samples was slightly higher compared with the values of their counterparts in the first group of samples; this was due to the difference in the chains' structure for both HDPE and LLDPE materials. The structure of LLDPE has linear chains with short side branches, whereas the structure of HDPE has linear chains with fewer short branches on the main chains, allowing these latter chains to pack more closely together to increase strength [19].

Figures (8), (9), and (10) show the effects of PVP content on flexural strength, flexural modulus, and maximum shear stress, respectively, for both groups of ternary polymeric blends. These figures show...
that the values of flexural strength, flexural modulus, and shear stress increased as the weight ratio of PVP content increased in the blends; this result was related to the nature of the chains’ structure of PVP materials, which acts as an agent to increase interfacial reactions and provides effective compatibility between blend constituents [20]. The increases in rates in these values for the second group were much higher compared with those in their counterparts in the first group, which only slightly increased with increased PVP content in the blends. This is due to the difference in the molecular chain structure for LLDPE and HDPE, as previously mentioned.

Figure. 8. The flexural strength of PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle as a function of PVP content in the blends.

Figure. 9. Flexural modulus of PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle as a function of PVP content in the blend.
Figure. 10. Maximum shear stress of ternary polymeric blends composites PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle as a function of PVP content in the blend.

Figures (11) and (12) show the effects of PVP content on impact strength and fracture toughness, respectively, for both groups of blends. From these figures, it can be noted that impact strength and fracture toughness values increased as the weight ratio of PVP content increased in both sets of blends, reaching a maximum value at a PVP ratio of 4% in the first group of samples. Impact strength and fracture toughness values for a second group saw slight increases at the ratio of 4% PVP content in the mixture, then the values decreased with further increases in PVP content in the blend, falling below the values of the basic blend (free from PVP). Such behaviours may be attributed to two reasons: the first is the nature of the chains' structure in LLDPE, where they are linear with very few side branches in the chain, as compared with HDPE, which has a high degree of crystallinity and strength that reduces sample toughness [2, 19]. Additionally, the nature of the chains' structure of HDPE has a high degree of crystallinity, causing them to be packed more closely together, which may hinder the flow of PVP through the structures of polymer blends containing HDPE materials. This may produce some segregated structures in heterogeneous form, leading to reductions in the toughness of the prepared material [2].
Figure 11. The impact strength of PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle as a function of PVP content in the blend.

Figure 12. Fracture toughness of PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle as a function of PVP content in the blend.

From Figure 13, it can be noted that hardness values slightly increased when PVP was added to the basic composite 84% PP: 15% PE: 1% B.P., and these values increased with increased PVP content in both groups of composites, with the highest values at the 12% PVP ratio. It can also be observed from this figure that the hardness values for the second group of samples were higher than the hardness values for the first group of samples, due to the mixture of HDPE with PVP, which gives high levels of stiffness to the prepared material.
3.2 Morphology test Results

The properties of polymer blends strongly depend on their morphologies. Thus, in order to correlate the mechanical properties of polymer blend samples as a function of the PVP content in the blend with their microstructural morphologies, scanning electron microscopy (SEM) micrograph tests were done at the surfaces (at magnification 1000X) and fracture surfaces (at magnification 2000X) for the ternary polymer blend samples, as recorded in Figures 14 and 15 respectively. The SEM images of the surface morphology of ternary polymer composite samples are shown in Figures (14 a, b). From these figures, differences in the surface morphology and the distribution of basalt particles can be seen to depend on the PVP addition to the composite. It was noted that when adding PVP to the polymer blend, the surface morphology for polymer blends and the distribution of basalt particles becomes more homogenous. This enhances the mechanical properties of the polymer mixture when adding PVP.

![Figure 13. Hardness of Shore D of PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle samples as a function of PVP content in the blend.](image)

**Figure 13.** Hardness of Shore D of PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle samples as a function of PVP content in the blend.

![Figure 14. SEM images showing the effect of PVP content on the surface morphology of polymer blend composite PP: 15% (HDPE: x% PVP): 1% B.P. at magnification 1000X.](image)

**Figure 14.** SEM images showing the effect of PVP content on the surface morphology of polymer blend composite PP: 15% (HDPE: x% PVP): 1% B.P. at magnification 1000X.

The effects of PVP content on the fracture surface morphology of polymeric blends are shown in Figures 15 (a, b, c, and d). The SEM micrographs show differences in the fracture surface morphology which depend on the PVP content in the blend. The fracture surface for the binary polymer blend (Fig. 15 a) and ternary polymeric blends (Fig. 15 b, c, and d) exhibited homogenous morphologies. All of the microstructural morphologies appeared as co-continuous structures, making it difficult to
distinguish the individual polymers in these polymeric blends, which contrasts with previous results [7]. The fracture surface morphology indicates better interfacial adhesion between the constituents of composite samples with PVP content, however.

![SEM images showing the effect of the PVP content on the fracture surface morphology of the polymer blend PP:15%(HDPE:x%PVP):1%BP at magnification 2000X.](image)

**Figure 15.** SEM images showing the effect of the PVP content on the fracture surface morphology of the polymer blend PP:15%(HDPE:x%PVP):1%BP at magnification 2000X.

4. **Conclusion**
The mechanical properties of two groups of composites prepared from of ternary polymeric blends (PP: 15% (LLDPE: x% PVP): 1% basalt particle and PP: 15% (HDPE: x% PVP): 1% basalt particle) were scrutinized to determine the function of PVP ratio content in polymeric composites. Several conclusions can be drawn from this study:

1. The mechanical properties for the prepared composites were enhanced when PVP material was added within limited ratios
2. The prepared blends containing HDPE material had higher mechanical properties compared with other composite materials containing LLDPE, except the properties of fracture toughness and impact strength.
3. The fracture surface morphology indicated better interfacial adhesion between constituents of composite samples with PVP content.
4. The addition of PVP to the prepared composites appeared to act as a good compatibility agent to improve the cohesion forces between the constituents of such composites, especially for certain ratios of PVP content.
References
[1]. Huneault M A, and Hongbo Li 2012 *J. Applied polymer science*, Vol. 126 PP 96-108.
[2]. Donald V R, Marlene G R, and Nick R S 2010 *Plastics Technology Hand Book* Vol 1 Momentum Press, LLC Taiwan.
[3]. Altan M and Yildirim H 2010 World Academy of Science, *Engineering and Technology*, Vol. 70 pp 289-294.
[4]. Michel A H, Hongbo Li 2012 *Journal of Applied Polymer Science* Vol 126 pp. E96-E108
[5]. Nitta K H, Shin Y W, Hashiguchi H, Tanimoto S, Terano M 2005 *Polymer* 46 pp 965-975.
[6]. Jia H L, Yi J P, Chi F L, Chien L H, Chien T H, Chih K C, Zheng I L and Ching W L 2015 *Materials* 8 pp 8850-59
[7]. Dikobe D and Tyyt A S 2010 *XPRESS Polymer Letters* Vol. 4 pp 729-741
[8]. Sihama I AL, Kadhum M S and Rula F. H 2015 *Eng. & Tech. Journal* 33 part (A) (8) pp 1971-85
[9]. Banalia K and Aicha S 2012 *Mater. Des.* 34 pp 313–318.
[10]. Sihama E S, Jawad K O, Rawaa A A 2015 *Eng. & Tech. Journal* 33-part (A) (6) pp 1450-61.
[11]. Sihama E S, Abdullkhalilq F H and Alyaa H A 2013 Modern *Applied Science* Vol. 7 pp 33-42.
[12]. Shujahadeen B A, Rebar T A, Mariwan A R, Omed G A and Hameed M A 2017 *Polymers* 9 p 486
[13]. Qiyan Z, Bo-Yuan Z, Zhao X G and Jian Y 2017 *Polymers* 9 p 404
[14]. Annual Book of ASTM Standard 2003. *Standard Test Method for Tensile Properties of Plastics*. D 638-03, pp 1-12.
[15]. Annual Book of ASTM Standard 2003 *Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials* D 790-03, PP. 1-11
[16]. ASTM, D 2002 *Standard Test Method for Compressive Properties of Rigid Plastics* ASTM materials standards.
[17]. Annual Book of ISO Standard 2006 *Standard Test Method for Unnotched Izod Impact Testing of Plastics* ISO-180 PP 1-2
[18]. Annual Book of ASTM Standard 2003 *Standard Test Method for Plastics Properties-Durometer Hardness* 2240-03, pp: 1-12.
[19]. William F S and Javad H 2011 *Foundation of Materials Science and Engineering* Fifth Edition Mc Graw –Hill
[20]. Yoshida K, Sakurai Y and Kawahara S 2008 *International Archives of Allergy and Immunology* 146 pp 169–73 doi:10.1159/000113522. PMID 18204285