Production of Prosthetics and orthotics materials with improved tensile strength and elongation at break from venial acetate, low-density polyethylene and additive blends

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Abstract
Polymers including Ethylene vinyl acetate (EVA) and low density polyethylene (LDPE) are some of the useful materials for different engineering applications including artificial legs, hands or prosthetic and orthotics. In most countries in Africa (particularly in Ethiopia) prosthetic and orthotics service is mostly applicable in limited hospitals. Raw materials (pure EVA) are brought from abroad and molding is carried out locally. This time provision of raw materials is reduced due to lack of supplier. Moreover the mechanical properties of these materials have certain draw backs on service properties. Some of the problems are high thermal expansion, poor weather resistance subjected to stress cracking, failure in strength. To alleviate these problems it is required to produce the raw materials locally with improved mechanical properties that prolong the service life, as result of which the foreign currency will be saved. The objective of this research is thus to produce prosthetic and orthotics raw materials from EVA/LDPE blend with improved tensile strength and elongation. To carry out this research thermoplastic LDPE, EVA, color pigment, calcium carbonate, and black carbons were used as charged materials (constituents). Samples were produced in sheet form for further analysis. The research was conducted experimentally. Blending, molding, and testing of the produced material were carried out using different appropriate devices, tools and equipment. It was observed that the addition of additives improve the mechanical properties especially tensile strength. From the gauge reading it was recorded that the maximum tensile strength was 10.5 Mpa and the minimum tensile strength was 2.8 Mpa, at the same time the maximum elongation at break was 469.8% and the minimum elongation at break 40.2%. The other results were in between these ranges, which are better than the material sample produced from pure EVA (maximum tensile strength of 2.3 Mpa and the elongation of 263 %). It is expected that the result of the research will reduce the foreign exchange consumption of the country and satisfy the demand of hospitals and patients.

Keywords: Prosthetic, Orthotic, Blending, Low density poly ethylene, Ethylene vinyl acetate, Mechanical property.

I. Introduction

Every year in the world including Ethiopia, hundreds of thousands of people lose a limb due to diseases including diabetes and cancer, as well as to the trauma associated with automobile collisions, physical damages associated with sports and related exercises as well as violence of different categories. In the United States [11], over 130,000 people had a lower limb amputated in 1997. Of those amputations, 67% were as a result of complications due to diabetes. In 2001, the International Committee of the Red Cross (ICRC) fitted a total 7,418 people with their first prostheses and distributed 9,779 prostheses to land mine survivors in fourteen post-conflict countries. Lower extremity amputation is the most common level of amputation in both civilian and military populations. The correction or improvement of these damages is made using Prosthetics and
Orthotics. As underline in the work of [1], in a narrow sense, prosthetics is a branch of medicine, specifically of surgery, concerned with the replacement of missing body parts (upper and lower limbs, and parts thereof) after amputation. It is related to orthotics, which is a branch of medicine that deals with the support of weak or ineffective joints or muscles using supportive braces and splints. The key task is selecting the proper orthotic, prosthetic materials and designing them into the right device. One of the easiest difficulties to fall into description of materials is selecting rigid or flexible one. This time most prosthetic and orthotics are made from Ethel Vinyl Acetate (EVA).

EVA is low cost, nontoxic material that displays good low temperature flexibility and toughness, moisture resistance, excellent dielectric properties very good chemical resistance, workable by all thermoplastic methods. But the prosthetics and orthotics produced from this materials lack mostly its strength and durability. Thus one of possible method is blending EVA with low cost material, which enhances its strength and durability. One of the preferred material for this purpose is Poly Ethylene (PE) particularly LDPE, which Low cost, ease of process, freedom of odor and toxicity, very good chemical resistance, excellent insulator.

Polyethylene is characterized as a semi-crystalline polymer, made up of crystalline regions and amorphous regions. The melting point of polyethylene is defined as that temperature at which the plastic transitions to a completely amorphous state. When new requirements with enhanced properties arise [2], newly synthesized polymers may be needed with other additives; however cost increment is one of the problems for many plastic industries. Blending of polymers can readily alter their mechanical properties. When polyethylene (PE) is blended [2] with a high-melting-temperature polymer a substantial improvement of thermal and mechanical properties including toughness, tensile or high-temperature creep resistance could be achieved. As mentioned in the works of[3-4], blending different polymers and yet conserving their individual properties in the final mixture is often a fast, an extremely attractive, and inexpensive way of obtaining new materials with unique properties from existing ones. If considering blending of EVA and LDPE procedurally [2,3], Polyethylene vinyl acetate copolymer (EVA)[3], which is a widely used thermoplastic resin, has been considered to be a good contestant to be used as a biomedical material due to its good physical properties, ease of handling and processing, and moderate biocompatibility. At very low proportion of VA, the copolymer resembles low polyethylene (LDPE) but exhibits the physical properties and processing behavior of tough thermoplastic. The copolymers are more flexible and have higher transparency, lower modulus of elasticity, and improved barrier properties to oxygen and water vapor than LDPE. LDPE [5] is defined by density range of 0.925-0.940 g/cm³. LDPE has a high degree of short and long chain branching, which means that the chain do not pack into the crystal structure as well. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film application such as plastic bags and film wrap. LDPE is more flexible, which makes it good choice for prosthetic devices, most of which are either draped formed or vacuum formed. It has a good impact resistance, easy machinability and is a good choice for fabricated parts where chemical and corrosion resistance is demanded. Moreover, LDPE manifests good compatibility with many other polymers, which leaves enough scope for tailoring desirable properties in the blend. Low density polyethylene (LDPE)[4] represents the majority of thermoplastics currently used in food packaging materials or in other industrial application. Blending two or more polymers is an effective strategy to improve polymeric material performance. Among the existing polyolefin’s, low density polyethylene (LDPE) is a suitable polymer for blending with EVA to improve the mechanical properties such as tensile strength, flexure modulus, abrasion resistance, toughness, and hardness for prosthetic application. LDPE [7] is a non-polar molecule with all its hydrogen
atoms tightly bound to carbon atoms and commercial products have a degree of crystallinity of about 40 to 50 %. Compared to LDPE, EVA is more polar and less crystalline due to the acetate groups and the amorphous depends on the content of VA.

While blending some additives can be added to it in order to reduce cost and enhance physical and mechanical properties of prosthetic and orthotic materials. To improve physical properties and mechanical properties fillers and reinforcement can be used. These include titanium dioxide calcium, carbonate (CaCO3), wax, and stabilizer. Plastics with non-fibrous fillers such as glass spheres or mineral powders generally exhibit higher stiffness characteristics than unfilled resins, but not as high as fiber-reinforced grades. Considering these properties of LDPE and EVA, it can be said that products made from LDPE/EVA blends would have many improved properties. The VA content [6] has two main effects on the polyethylene (PE). Increase VA content decreases the crystallinity of PE. Although PE crystallinity could reach 65%, EVA with about 50 wt% VA is completely amorphous and, the polarity of EVA increases as VA content increase as a result of polar nature of acetoxy side chain. This permit manipulating important properties to suit diverse application, including flexible shrink wrap, coating, footwear sole, hot melt and heat seal adhesives, flexible toys and tubing, etc. This time using prosthetic and orthotics materials are a key issue in many countries including Ethiopia.

Prosthetic and Orthotics used in Ethiopia, currently, are pure EVA and Poly Propylene (PP), which are supplied by ICRC (International Committee of the Red Cross) for developing countries. Today the supply of these materials is reduced and is not produced in the country yet. More over the supplied materials lack strength and durability. Patients being invalid due to different reasons suffer lack of prosthetic and orthotics materials. The cost required to purchase this devices is sufficient enough for invalids. Thus producing prosthetic and orthotic materials with improved properties and low cost locally is a critical issue to solve the mentioned problems. The current research dealt only on preparing orthotic and prosthetic material with improved mechanical property (tensile strength) from the blend of EVA and LDPE with additives type like black carbon, CaCO3, TiO2 and color pigments.

II. Material and method
A. Materials
To carry out this research the following raw materials were used. Two types of base polymers that include EVA- density 1g/cm^3 and LDPE 1g/cm^3 density with different additives were used.

| TABLE I |
| Raw MATERIALS | MFI\(^{a}\) g/10m | Total Weight |
| Raw material | | |
| EVA | 3 | 16g |
| LDPE | . | 16 kg |
| CaCO3 | 9 | 12 kg |
| Carbon black | 3 | 5 g |
| TiO2 | 4.77 | 955 g |
| Color Stabilizer(lead) | | 40 g |
| | | 3 kg |

MFI\(^{a}\) = Melt flow index (190°C, 2.16 kg)

**Fig1.** Base polymer :(a) LDPE resin,(b) Granular EVA resin

For the research conducted 9 samples of different composition ratio of the raw materials (base polymers) were taken and displayed in table II.
TABLE II

COMPOSITION OF BASE POLYMER

<table>
<thead>
<tr>
<th>Mix Code</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(W/W) %</td>
<td>20/40/40</td>
<td>42.86/28.57/28.57</td>
<td>50/25/25</td>
<td>40/20/40</td>
<td>33.33/33.33/33.33</td>
<td>28.57/42.86/28.57</td>
<td>25/50/25</td>
<td>60/40</td>
</tr>
<tr>
<td>Thickness (mm)</td>
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<td>1.4</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.8</td>
</tr>
</tbody>
</table>

III. Method of Research

The research was carried out experimentally and purposive sampling method was chosen. To carry out the research, selecting the material EVA, LDPE and additives, measuring weight of EVA, LDPE and additives by using beam balance, combining the additives by using XINXING compounding machine, measuring steady state melt viscosity of raw material by using Zwik D-7900 melt flow index, Blending the raw material and additives by using extruder to produce samples in the form of sheet. Testing the mechanical properties were done. The research was carried out using single extruder machine marked LENTATES.s (ml) available at Ethio- plastic factory located in Addis Ababa. The single extruder machine was heated for one hour. Charging of raw thermoplastic materials (EVA/LDPE) according to the amount listed table II, in pellet form displayed in Fig1, and additive was done through the extruder barrel; the additives added were used as filler, processor and provide good dispersion in the blends. The material was heated on the heated barrel surface and also by mechanical action of screw, and melts. This screw, which turn inside the extrusion barrel, convey the polymer forward a hot region of the barrel, where a combination of external heating and frictional heating melted the polymer. The screw moved the molten polymer forward until it exited through the die. The melt was compressed by the taper of screw and was ultimately extruded through the shape die to the form of sheet and cooled in water faced ring die.

The temperature in the feeding for samples was 140°C and transition sections were kept in all runs respectively. Mixing of the sample was used for all samples and temperature setting of metering section and die of the extruder were 190°C and 165°C. Sheet samples were produced (fig2).The thickness of the materials (sheets produced) were slightly different but widths of samples are the same 57.5 cm. Finally, the samples were cut according to requirements for tests.
IV. Experimental analysis

The experimental analysis and testing were carried out at Lather Industry Development Institute Testing and Research Laboratory of Ethiopia. The tests carried out were tensile test and elongation at break for determining the mechanical properties of samples. The tensile properties of the blend were carried out on INSTRON tensile testing machine designed according to the specifications of ASTM D 638-03. The tensile strength was expressed as the maximum force at break divided by the initial cross-sectional area of the sheet strip and the elongation at break as a percentage of the original length. Two metallic grips were attached for gripping both ends of the specimen of the stripe. The lower grip was stationary and the upper grip moves upward with constant rate of extension for all samples. The sheets were cut into strips with width of 6.00 mm and different thickness. Experiments were carried out at 100 mm/min test speed and 5N pretension load at room temperature of 23°C and 50% humidity.

In analyzing the mechanical properties of the material, the concept of mechanical characteristics of polymers are related to molecular weight, crystallinity, orientation, morphological structure and other parameters. Stress-strain curves were recorded using the commonly known simple equations for the calculation of stress (σ) and strain (ε).

Tensile strength of all samples was tested in two directions measured in axial direction and transversal (90° of axial direction). Test results are displayed in Table III below.

As seen in the table the tensile strength and elongation at axial and transversal directions are various. In case of tensile strength the axial direction results are higher than the transversal and the vise versa for elongation. This is due to the fact that the pulling of material up ward results in increasing elongation in the horizontal direction with time until ultimate tensile strength is reached due to plastic deformation. Each sample in table III, and fig. (4-12), showed values of tensile strength and elongation due to the effect of concentration of constituents in the blend.
TABLE III
TENSILE STRENGTH AND ELONGATION

<table>
<thead>
<tr>
<th>Test code</th>
<th>Tensile strength(N/mm²)</th>
<th>Elongation at break (%)</th>
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<td></td>
<td>axial</td>
<td>transversal</td>
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</tr>
<tr>
<td>R</td>
<td>2.4</td>
<td>2.3</td>
</tr>
</tbody>
</table>

V. Result and discussion
Eight samples from the blend and one sample of the original type were taken for tensile testing. All tests were conducted on both axial and transversal (90° of axial or machine) directions and have different results due to molecular arrangement, dispersion of additives, tie entanglement of branched and crystalline LDPE and influence of polar EVA. The mechanical performance of all specimens was investigated in tensile and elongation at break test.

As shown from table II, compositions for the first test contain 20 wt. - % of EVA, 40 wt. - % of LDPE and balance of additives. In this composition the fillers play critical role in increasing tensile strength (fig3). The high conductive polar fillers including CaCO3, TiO2, Carbon black, master batch pigments were loaded in low concentration of polar EVA. The improvement of the mechanical properties depends on content of fillers and composition of the material and compatibilizer. As shown from table III the tensile strength of sample 1 is 4.7 N/mm², which explains that though polar resin interacts with polar filler to stiff material and increasing tensile strength, the increased fillers however reduced the tensile strength as compared to other concentrations where EVA is high. This is also because of rigidity of carbon black particles dispersion in the blend, which made deformation or tenacity to be reduced.
According to [12], the good compatibility of additives with a resin leads to good mechanical properties. In addition the semi crystalline LDPE resist the effect of additives. Author [5] confirmed that increasing carbon black filler content in the LDPE matrix leads to an increase in the mechanical strength and a decrease in the elongation at break. The ductility of material depends on elongation at break and content of coupling agent EVA. While improving mechanical properties of polymers, it should be noted that the ratio of blended polymer components have high effect in trapping the chine of the matrix one.

While performing the second test content of the composition (table II) was 42.86 wt. - % of EVA, 28.57 wt. - % of LDPE and the rest additives. The tensile strength of specimen was 2.8. N/mm², while the elongation at break reached to 38.0%. The result (fig. 4) was reduced as compared to test 1 due to poor dispersion of particles in LDPE matrix. The failure of interfacial adhesion and high interfacial tension were due to mixing time of extruder that decreased degree of dispersion of particle in final product. So mixing time in extruder have role for distribution of the molecules of EVA copolymer between immiscible polymers. The less mixing time decreased stability of blends, coalescence of blends, dispersion, and interfacial adhesion between heterogeneous polymers. As studied in works of [13], the generated inter chain bonding must be stable enough to survive the thermal condition and shearing treatment during the process of blending. That is due to the limit yield of the interfacial reaction due to short extrusion time and low molecular diffusion, highly reactive groups are requiring. The two base immiscible components non polar LDPE and polar fillers become unstable to break the domain and to oppose deformation. The copolymer EVA disperses insufficiently small domains to be solubilized by chain of entanglement and less molecular diffusion cause micelles the base polymer material components. Mixing time and shear imparted during mixing should be optimum for achieving uniform mixing (distribution and dispersion) and avoidance of excessive heat generation. The content of fillers compared to EVA was low which make the material more flexible and decreases tensile strength due to less stiffness and softness of material. While elongation at break and toughness increased due to content of EVA concentration compared to LDPE.

Fig4.Tensile strength of EVA/LDPE/Additives (42.86/28.57/28.57)
While carried out the third experiment the concentration was changed (table II) to 50 wt.-percent of EVA, 25 wt.
-% of LDPE and the rest additives. The tensile strength of sample (table III) was 5.8 N/mm² and elongation at
break was 286.3%. Improved strength (fig. 5) was due to increased content of EVA matrix and interaction with
fillers and LDPE polymer matrix. The more addition of EVA leads the material to better flexible and increased
interfacial adhesion between two immiscible polymers. It is possible to underline that the interpenetrating of
polymer matrix can be governed by increasing content of EVA, as a result of which cross linking between fillers
and LDPE matrix can be increased.

As many authors agreed and test results showed, the good compatibility of additives with resin leads to achieve good
mechanical properties. Thus, the less free volume of EVA due to retention of fillers in comparison with LDPE,
partial replacement of LDPE with fillers without affecting the mechanical properties was resulted. The elongation at
break of blend reveals 172.7% which indicates that ethylene group of EVA interacts with matrix of LDPE. This
indicates the EVA matrix chain entanglement with LDPE and fillers to increase elongation at break during strain of
specimen. The result also confirmed that tensile strength depends on degree of crystallinity.

![Graph of Tensile Strength](image1.png)

**Fig. 5. Tensile strength of EVA/LDPE/Additives (50/25/25)**

Test 4 was conducted with sample concentration of 20 wt.-% of LDPE, 40% wt.-% of EVA and the rest additives.
The tensile strength was 4.5 N/mm² (fig.6). The properties of each individual material have an effect on the
improvement of mechanical properties of blend.

![Graph of Tensile Strength](image2.png)

**Fig. 6. Tensile strength of EVA/LDPE/Additives (40/20/40)**
In test 5 according to table II compositions contain the same content of EVA, LDPE and additives (33.33 wt. %). The tensile strength of composite was 4.1 N/mm² and elongation at break was 114.7 % (fig. 7). According to literatures, the cross linking of fillers and LDPE with EVA depends on content of acetate group and ethylene group. The amount of EVA indicates amorphous zone and LDPE indicates crystalline zone, which means that there is the same amount of EVA and LDPE in both zone. Because of free volume reduction of acetate group, mobility of EVA matrix and ethylene group interaction with LDPE matrix was reduced as a result material (sample) become stiffer and make elongate the matrix when stress applied on specimen. The axial tensile strength and elongation at break were increased comparing to transverse direction was connected with orientation of chain interlock and dispersion of fillers.

To carry out the 6th experiment the ratio of the constituents was changed to 42.86 wt. %. LDPE, 28.57 wt. % EVA and the rest additives (table III).

The obtained result it is possible to conclude that LDPE plays a great role in increasing tensile strength of the blended specimen. LDPE is semi crystalline and amorphous and intermolecular tie in the lamella plays dual role in which, in one way the crystalline nature increases the rigidity of (strength) and the amorphous one increases flexibility and thus the tensile strength improvement is obtained from this combined nature of the LDPE (fig. 8). More over LDPE dissolves the EVA and withstand the blocking characteristics of the fillers as a result the elongation at break was high. This gives a benefit to use this blend for prosthetic and orthotic materials, where more rigidity and flexibility together is required in service.

Fig. 7. Tensile strength of EVA/LDPE/Additives (33.33/33.33/33.33)
As observed from composition the content of EVA was small that could be trapped by LDPE matrix and give a chance to fillers to reach to the interfacial face between LDPE and fillers sufficiently to the critical value. The amount of LDPE is then high that the degree of crystallinity is also high enough to develop tensile strength due to more crystalline orientation in the direction of stress.

The seventh experiment was carried out with 50 wt. % of LDPE, 25 wt. % of EVA and additives (table2). The tensile strength was 5.3 N/mm$^2$ and elongation at break was 147.9 %. (table III). Here the concentration of EVA is high, in which the result was depend on it. More amorphous molecular tie increased flexibility. That is why tensile strength (fig.9) was reduced from the previous one (the 6$^{th}$ experiment). The additives were also suppressed by EVA and thus the elongation at break also reduced.

In the 8th experiment the ratio of the polymers was changed to 60 wt. % of EVA and 40 wt. % of LDPE and no additive was used. The tensile strength was increased to 10.5 N/mm$^2$ and elongation at break reveals 469.0 % (table III). As seen from the result(fig. 10) the specimen become more flexible with better tensile strength and resembles rubber characteristics. However the specimen lacks rigidity and thus applying for prosthetics particularly for limb correction is doubt full since more flexible materials are not comfortable to support impact load so that load of human body may not be balanced.
The final experiment was done on the reference material which was produced from 100%EVA.
The tensile strength was 2.3 N/mm² and elongation at break was 265.7 % (fig. 11).
From the result it is possible to conclude that EVA without blending with other materials is more flexible and is not amenable for orthotics and prosthetics used for limbs, hands and sockets.

VI. MOLDING
For validation of the research a prototype of prosthetic was produced by casting. The blend of EVA/LDPE and EVA/LDPE/additives plastic sheet was melt in horizontal oven Teflon sheet anti-adhesive interface ovens melt to pliable forming temperature about 130°C. The plastic sheet pre-cut to the size of mold and draping technique of lower limb was applied. In molding the sheet with particular fillers, the mold (product) showed less warping and shrinkage characteristics, while those without additive showed more shrinkage and lost their shape. The other advantage of filler polymer is in the high tolerance of the molding and
suction. Fig. 12 displays the produced prosthetics for limb replacement.

The molding of prosthetic and orthotic were carried out in Addis Ababa at Medical Faculty of Black Lion hospitals. Before casting the positive and negative cast of the patient was measured.

![Image](a) Suction effect (b) adhesive effect (shrinkage)

**Fig. 12.** The blend of EVA/LDPE/additives (50/25/25) wt.- % human lower limb (with fillers (a), without fillers (b))

**VII. Conclusion**

Based on the research results it is possible to draw the following conclusions:
- Blending of two or more polymeric materials can improve tensile property of prosthetic/orthotic materials;
- Additives blended with EVA and LDPE have significant effect on tensile property of EVA/LDPE blend;
- Prosthetic and Orthotics can be produced effectively from the EVA and LDPE blend with optimum concentration of constituents;

-Better result was achieved when the composition ratio of EVA/LDPE/Additives was 28.57 wt/42.86 wt/25.75 wt% respectively.

-Generally from all result the most important advantageous materials for prosthetic and orthotic were samples 3 and 6.

-The prototype development showed better result if using EVA/LDPE/Additive blends of optimum value.

**References**


