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# Investigation of Thermal, Microstructure and Shape Memory Behavior of PLA-PEG-PHA Ternary Polymer Blends

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**Abstract**

Instead of blending two polymers to make a blend, a "ternary polymer blend" is typically created by adding a third polymer. In recent years, triple polymer blends have found a wide field of study in order to improve and change the properties of traditionally obtained binary blends. In this study, a blend was created by adding Polyhydroxy Alkanoate (PHA) polymer to Polylactic Acid (PLA) and Polyethylene Glycol (PEG) polymers, which are known to be compatible with each other. The aim of this study is to examine the effect of changing PHA amount on the blend of the triple shape memory alloy. The thermal properties, shape memory and scanning electron microscope (SEM) images of this blending were examined. It was investigated which of the samples prepared with three different percentages would give the most ideal results. Although the thermal analysis results are generally close to each other, differences were observed in the shape memory of the material due to the change in the amount. In particular, it can be said that the decrease in the percentage of Polytactic Acid (PLA) polymer, which has binding properties, causes a delay in shape transformation.

**Keywords:** Ternary polymer blends, shape memory polymers, polylactic acid, polyethlene glycol, polyhyroxy alkanoate

# PLA-PEG-PHA Üçlü Polimer Karışımlarının Termal, Mikroyapı and Şekil Hafıza Davranışlarının İncelenmesi

**Öz**

Bir karışım oluşturmak için iki polimeri karıştırmak yerine, tipik olarak üçüncü bir polimer eklenerek "üçlü bir polimer karışımı" oluşturulur. Geleneksel olarak elde edilen ikili karışımların özelliklerinin iyileştirilmesi and değiştirilmesi amacıyla son yıllarda üçlü polimer karışımları geniş bir çalışma alanı bulmuştur. Bu çalışmada birbiriyle uyumlu olduğu bilinen Polilaktik Asit (PLA) and Polietilen Glikol (PEG) polimerlerine Polihidroksi Alkanoat (PHA) polimeri eklenerek bir karışım oluşturulmuştur. Bu çalışmayı yaparken üçlü şekil hatırlamalı alaşımın, değişen PHA miktarının blend üzerindeki etkisini incelemektir. Bu karışımın termal özellikleri, şekil hafızası and taramalı elektron mikroskobu (SEM) görüntüleri incelenmiştir. Üç farklı yüzdeyle hazırlanan örneklerden hangisinin en ideal sonucu vereceği araştırıldı. Termal analiz sonuçları genel olarak birbirine yakın olsa da miktar değişikliğine bağlı olarak malzemenin şekil hafızasında farklılıklar gözlemlenmiştir. Özellikle bağlayıcı özelliğe sahip olan Politaktik Asit (PLA) polimerinin yüzdesindeki azalmanın şekil dönüşümünde gecikmeye neden olduğu söylenebilir.

**Anahtar Kelimeler:** Üçlü polimer karışımları, şekil hafızalı polimerler, polilaktik asit, polietilen glikol, polihidroksi alkanoat

## INTRODUCTION

It is the process of combining at least two polymers under suitable conditions and obtaining a new material, known as polymer blend. It is desirable to choose one of the polymers as the compatibilizer when obtaining the blend. The most famous polymer blends that have been studied extensively in the last decade are; Polypropylene/Polyamide (PP/PA) is Polystyrene/Polymethyl Methacrylate (PS/PMMA) and Polypropylene/ Polystyrene (PP/PS). It is available in our previous shape memory polymer blend works (Koulic et al., 2001; Tomic and Marinkovic, 2019; Wang et al., 2011). It is not preferable to combine the blend, which is generally preferred in pairs, and triple or more polymers. The reason for this is that it is thermodynamically

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immiscible and the technological difficulty of combining polymers harmoniously. Since the word "polymer blend" refers to the combination of two polymers, the term "ternary polymer blend" is used for triple blends. Although increasing the number of polymers while obtaining the blend causes various complications, it is an area that needs to be studied and developed. It is thought that adding various properties to the traditional polymer blend material and the desire to obtain higher performance products will increase the popularity of such materials (Adedeji et al., 2001; Folkes and Hope, 1993; Macosko et al., 1996; Sperling, 2005).

Debolt and Robertson tried the ternary polymer blend in their study and made complex polymers compatible with each other using compatibilizers. It was investigated whether nylon 66 and styrene-block-ethylene-co-butylene could be harmonized with each other and polypropylene was used as compatibilizer (DeBolt and Robertson, 2006). Sprenger and Walheim explains in their study that when there are three liquid phases, the two most incompatible components completely or partially wet the interface. They stated that by changing the balance of the three liquid-liquid interface energies, the morphology of the intervening fluid should also change. In particular, they expected a significant change in the structure of the polymer blend during wetting (Sprenger et al., 2003). V.N. Kuleznev and Yu. P. Miroshnikov et al. in their study demonstrated that some ternary polymer blends were not miscible based on their phase morphology (Kuleznev and Miroshnikov, 2016).

The aim of this study is to examine the differences in the structure and physical properties of the ternary polymer blend by adding Polyhydroxy Alkanoate (PHA) in different proportions and under appropriate conditions to Polyactic acid (PLA), which has a good shape memory feature, and to Polyethylene Glycol (PEG) blend, which is frequently used in the health sector but is fragile.

## MATERIAL AND METHODS

### Materials

Polyactic acid (PLA) and Polyhydroxy alkanoat (PHA) was supplied by ABG filament company in Ankara, Turkey. Polyethylene glycol (PEG) with $M_n$=6000 g/mol$^{-1}$ and anhydrous chloroform (99.9% purity) were purchased from Sigma Aldrich.

### Preparation of PLA/PEG/PHA Blend Film By Solvent Casting Method

Polylactic acid, Polyethylene glycol and Polyhydroxy alkanoate were prepared in 1:1:1 ratio in separate magnetic stirrers, each from 0.15 grams to a total of 0.45 grams in chloroform. The ratio of PHA was changed by keeping the ratio of PLA and PEG constant and not changing the total mass. PHA was added in amounts of 0.05 g, 0.15 g and 0.25 g (11%, 33% and 55% in weight). PLA and PEG in 5 mL chloroform were mixed in a separate mixer and PHA was mixed in a separate mixer for 1 hour and then completely homogenized. The homogeneous solutions were combined and stirred for 1 more hour. Then, the solution poured into the petri dish was kept in the etuv at 40 ºC for 24 hours.

## RESULTS AND DISCUSSION

### Thermal results

Differential Scanning Calorimetry (DSC) measurement was performed to examine the thermal properties and melting/crystallization behavior of the blend obtained by mixing PLA-PEG-PHA ternary polymer. DSC results are given in Fig. 1. The glass transition temperature of PLA is around 65 ºC, which is supported by both our previous studies and the literature (Özen Öner et al., 2022; Qader et al., 2022; Yilmaz at al., 2023). It is known that the melting temperature of PEG roughly coincides with the glass transition temperature of PLA. When the DSC graph is examined, the reason why the first peak is quite obvious is that the melting temperature of PEG and the glass transition temperature of PLA are almost the same values. The second peak seen in the DSC graph is the melting temperature of PLA (177 ºC). As we have confirmed in our previous studies, since the DSC curves are almost the same, they have similar peaks (Matumba, Motloung, Ojijo, Ray and Sadiku, 2023; Sheth, Kumar, Davé, Gross and McCarthy, 1997; Zhang, Wang, Qiao and Li, 2016). Unlike other polymers, PHA has a wide range of melting temperatures. It is known that the melting temperature of PHA is 170 ºC, it is almost the same as the melting temperature of PLA, as seen in the graph. According to the DSC measurement results, it was observed that the melting temperatures and crystallization temperatures increased before 50% PHA ratio and also the enthalpy values of the peaks increased. After the PHA ratio exceeded 50%,

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melting and crystallization temperatures and enthalpy values were found to decrease.

Thermogravimetric analysis results are given in Figure 2. Thermal degradation of PVC and PEG polymers occurs in two stages. The first decomposition temperature occurs at 275 °C, and the second decomposition temperature occurs at 375 °C. It has been determined that the thermal stability of the polymer composite material decreases slightly depending on the changing PHA amount.

**SEM images**

SEM images and EDAX results of 11PHA, 33PHA and 55PHA samples are given in Fig. 3, Fig. 4 and Fig. 5, respectively. When the SEM images are examined, it is seen that the porous structure is formed. It is known that the polymer forming the porous structure originates from PEG, and it is seen that PEG causes an increase in chain movement and the formation of voids in the polymer structure. Similar results were obtained in our previous study (Yilmaz et al., 2023). Chen et al. suggested that PEG infiltrates the PLA chains, increasing the particle size. Darabian et al. stated that the hydrogen bond is formed between the carbonyl group in PLA and the hydroxyl group in PEG (Chen et al., 2014). Therefore, PLA and PEG are suitable polymers for blending. The biggest reason for being a suitable polymer is the bond formation between them. Based on our previous studies, it is examined what changes occur in the structure of the polymeric material by keeping the PLA and PEG ratios constant and adding PHA at certain ratios. When the EDAX results are examined, it is seen that carbon and oxygen amounts are encountered. It is known that the content of polymeric structures is based on carbon and oxygen bonds. For this reason, it is expected to be reflected in the EDAX results.

**Shape memory effects**

Fig. 6 shows the shape memory effect of 11%, 33% and 55% samples of PLA-PEG-PHA ternary polymer blend. The shape memory properties of PLA-PEG-PHA polymer blends prepared with three different percentages were examined. Shape memory polymers are materials that can change their properties such as shape and color with external factors. To observe the shape memory effect, the glass transition temperature of the polymers is taken into account. Above the glass transition temperature, the material is given a temporary shape and then it is expected to maintain its temporary shape by providing suitable conditions. The polymeric material, which retains its temporary shape, returns to its original shape by rising above the glass transition temperature again. Similar results were obtained as in previous studies (Özen Öner et al., 2022; Pekdemir et al., 2023; Pekdemir, Öner, Kök and Qader, 2021; Pekdemir, Qader, et al., 2021). In this study, it is investigated how PHA, which varies by 11%, 33%, and 55%, will have an effect on the material. In order to make a correct interpretation between the three, comparisons were made at the same time and in the same environment. The materials were cut in the same dimensions and immersed in hot water. Polymers softening in hot water were temporarily formed and then immersed in cold water (below the glass transition temperature). It is observed that the polymeric material, which is observed to retain its temporary shape, returns to its original shape in a short time after being immersed in hot water. If three materials are compared, it is seen that 33% sample is difficult to form. In addition, it can be said that the time to return to its former shape is longer than the others and its structure is more opaque than the others. Since the proportions of the 33% sample are equal, it can be interpreted that the amount of PLA polymer acting as a binder is low. On the contrary, it is seen that the high PHA ratio in the 55% sample neutralizes the low amount of PLA. That is, PEG, which does not have the ability to memory and is fragile. It can be interpreted that the binder of the polymer is PHA.

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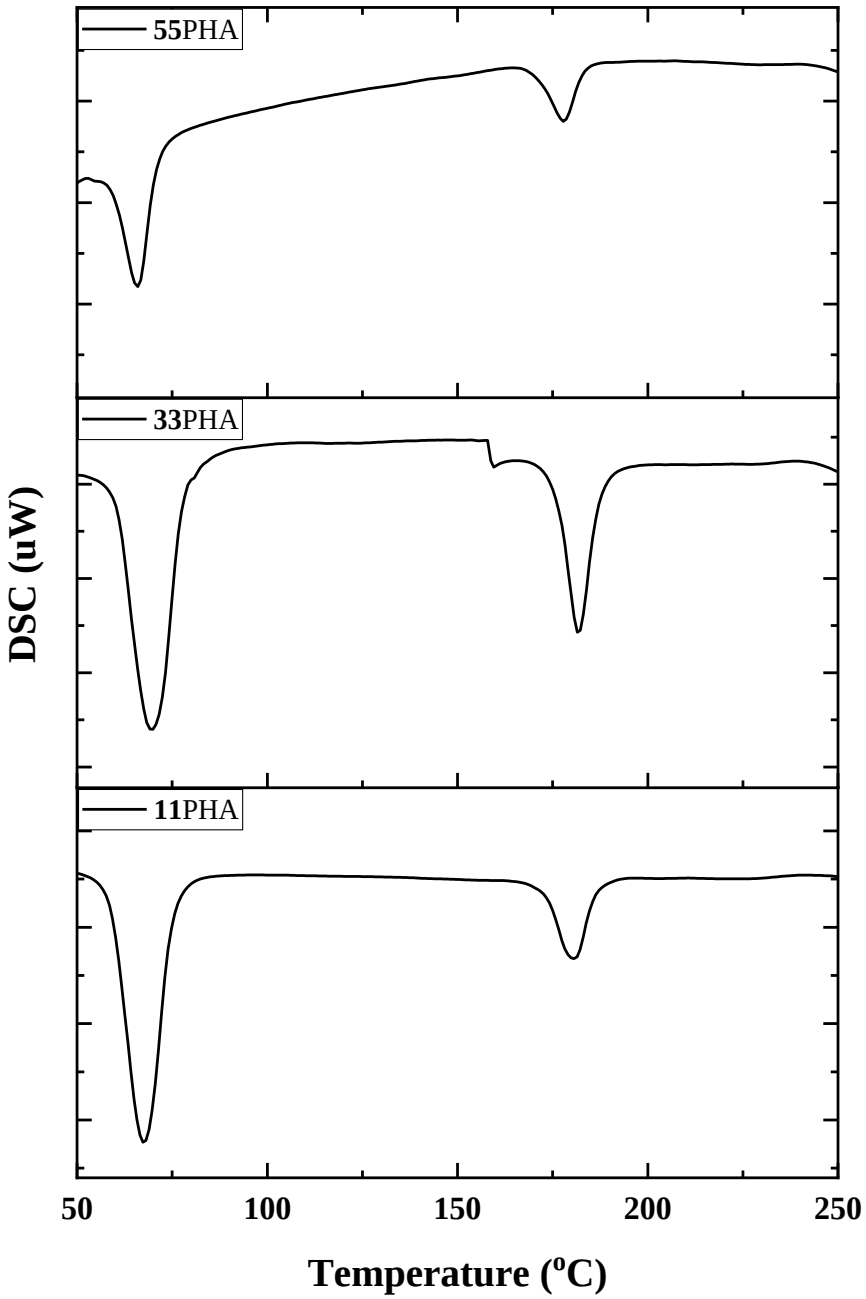


**Figure. 1.** Differential Scanning Calorimetry (DSC) result of samples

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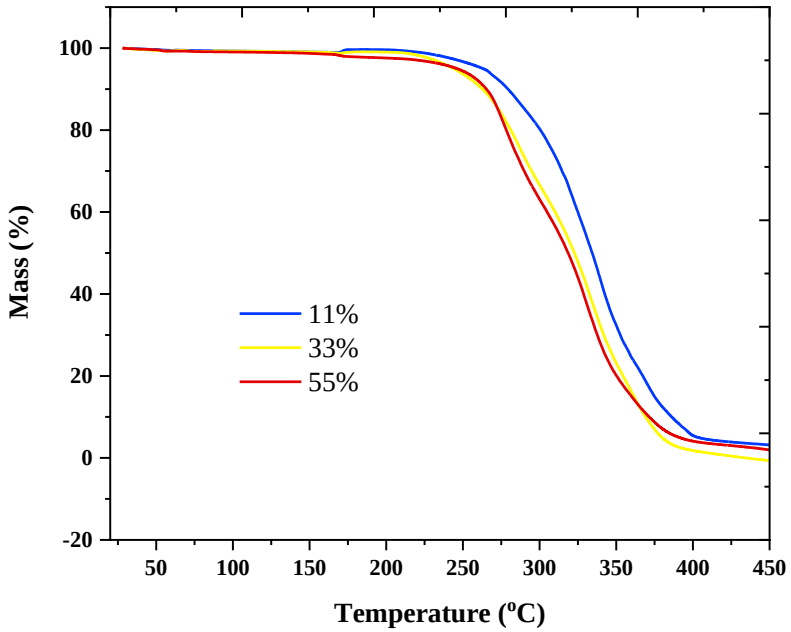
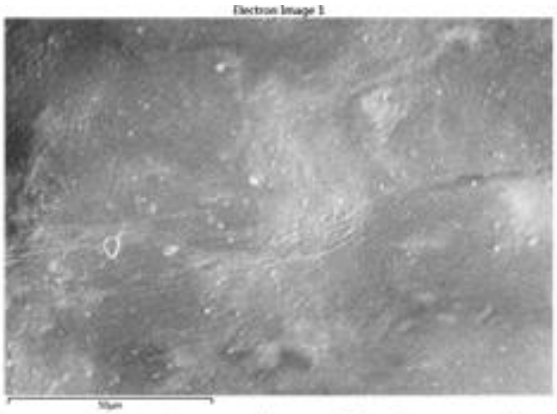
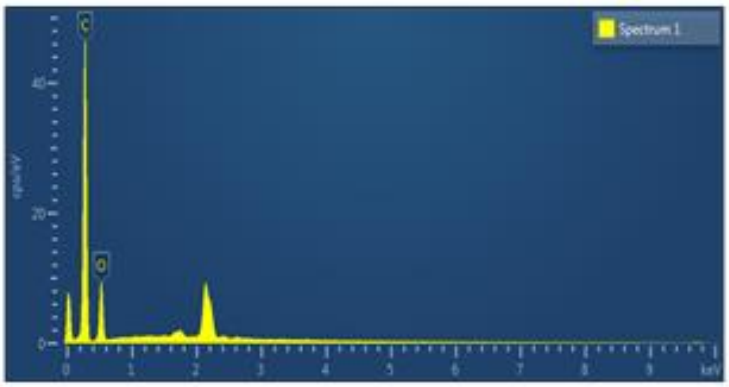



**Figure. 2.** Thermogravimetric analysis (TGA) result of samples






| Element | Line Type | Weight % | Weight % Sigma | Atomic % |
|---|---|---|---|---|
| C | K series | 67.40 | 0.32 | 73.36 |
| O | K series | 32.60 | 0.32 | 26.64 |
| Total | | 100.00 | | 100.00 |

**Figure. 3.** SEM-EDAX results of 11PHA Sample

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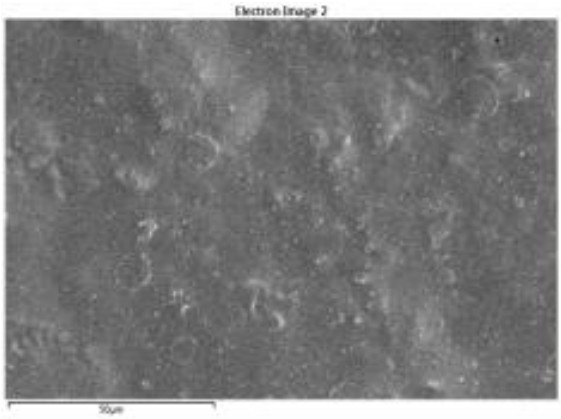
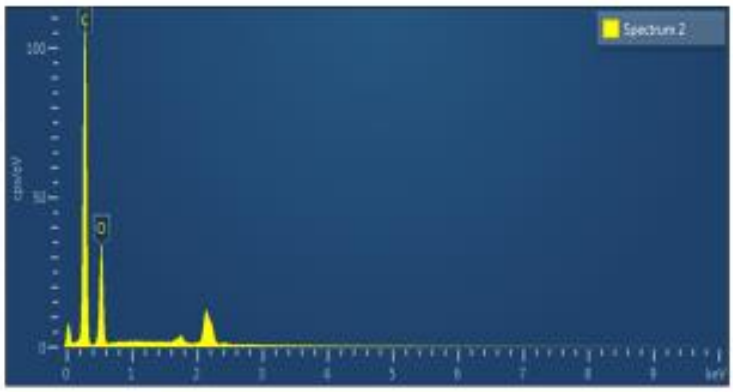
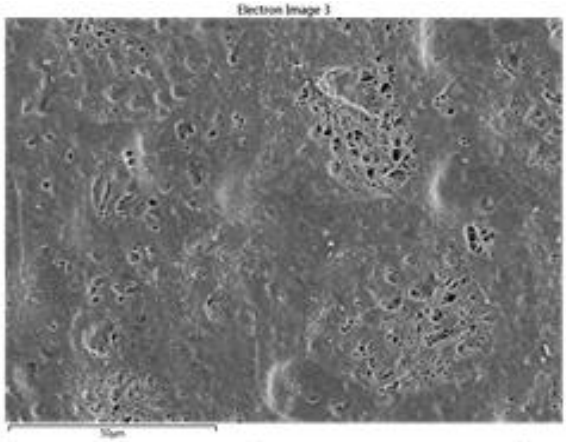
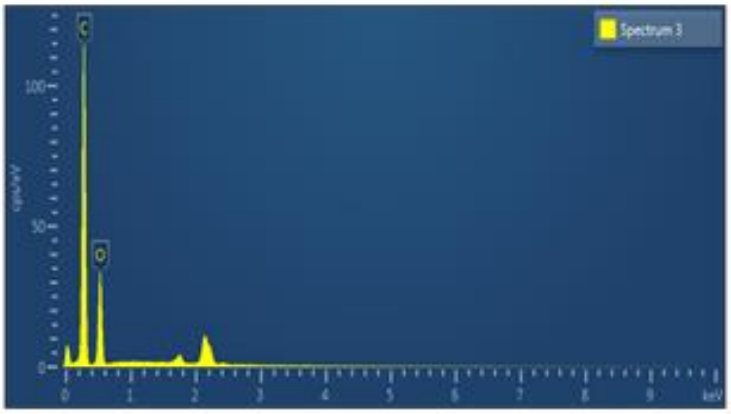



| Element | Line Type | Weight % | Weight % Sigma | Atomic % |
|---|---|---|---|---|
| C | K series | 66.38 | 0.23 | 72.45 |
| O | K series | 33.62 | 0.23 | 27.55 |
| Total | | 100.00 | | 100.00 |

**Figure. 4.** SEM-EDAX results of 33PHA Sample




| Element | Line Type | Weight % | Weight % Sigma | Atomic % |
|---|---|---|---|---|
| C | K series | 67.24 | 0.23 | 73.22 |
| O | K series | 32.76 | 0.23 | 26.78 |
| Total | | 100.00 | | 100.00 |

**Figure. 5.** SEM-EDAX results of 55PHA Sample

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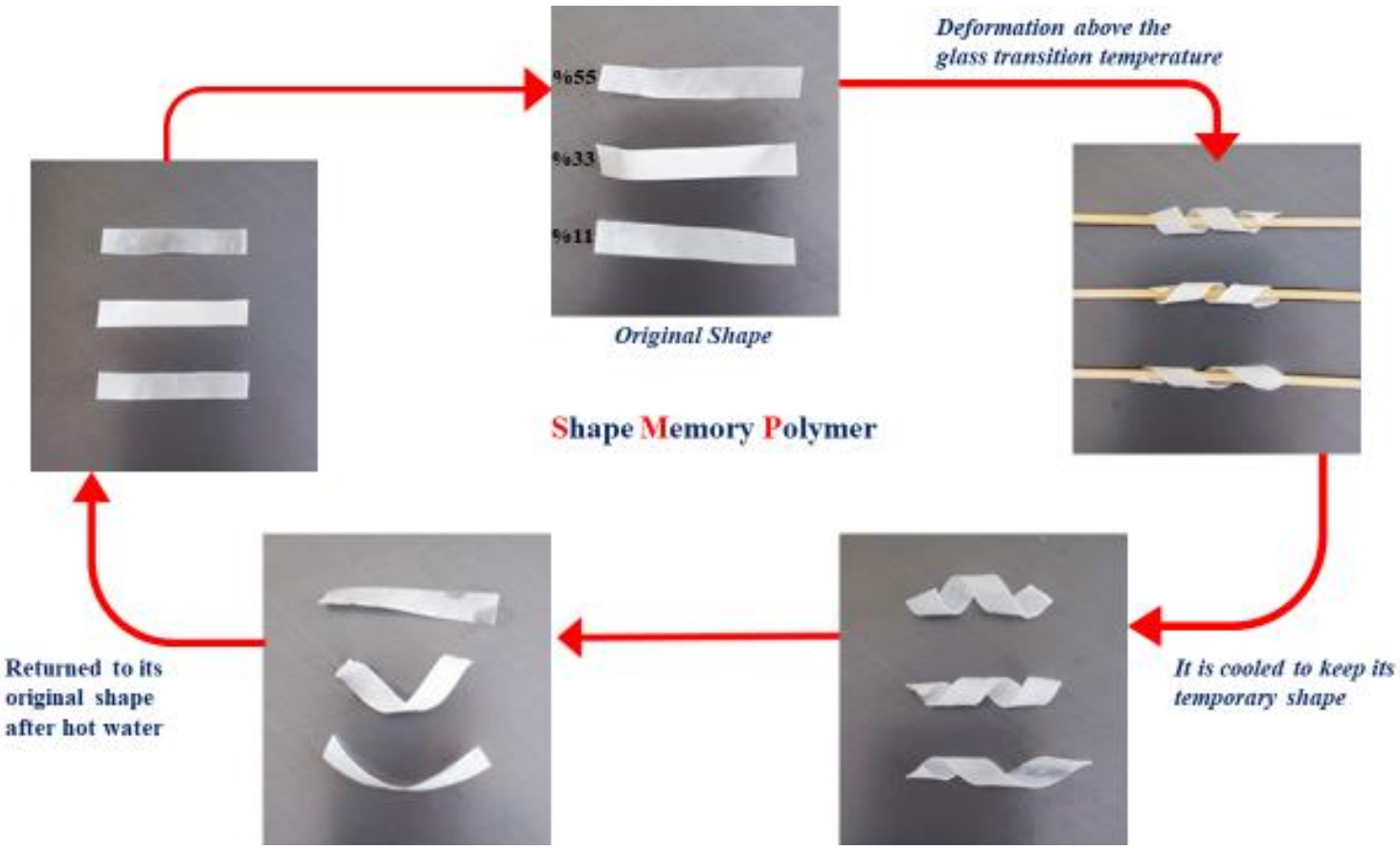


**Figure. 6.** Shape memory effect behavior of samples

**Table.1.** *Weights of polymers in ternary blends*

| **Sample codes** **Polymers** ⬇ ➡ | **11 PHA** | **33 PHA** | **55 PHA** |
|---|---|---|---|
| **PLA** | 0.20 g | 0.15 g | 0.10 g |
| **PEG** | 0.20 g | 0.15 g | 0.10 g |
| **PHA** | 0.05 g | 0.15 | 0.25 g |

## CONCLUSION

The aim of the study is to examine the effect of triple polymer blend and shape memory transformation. Different proportions of PHA were added to PLA and PEG polymers, which are known to be compatible with each other. When the thermal analysis results were examined, it was seen that the values were very close to each other. When the TGA graph was examined, it was observed that thermal stability decreased slightly as the PHA ratio increased. The fact that the melting temperatures of PHA and PLA are very close, caused the peak to be intertwined. When SEM images were examined, it was supported by literature data that the porous structure originated from PEG. This feature of the samples with shape memory feature was examined.

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PLA is known to be a good shape memory polymer. Due to the fact that PEG has a more fragile structure, a very good shape memory effect was observed in the samples with a high percentage of PLA. It was determined that the duration of the shape memory effect was prolonged in the 33% sample with equal proportions compared to the others.

## ACKNOWLEDGMENT

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## CONFLICT OF INTEREST

The Author reports no conflict of interest relevant to this article.

## RESEARCH AND PUBLICATION ETHICS STATEMENT

The author declares that this study complies with research and publication ethics.

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