EAI Endorsed Transactions
on Digital Transformation of Industrial Processes Research Article EAI.EU

Influencing the SME of PVA films with integrated iron nanoparticles using ultrasound during production

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Abstract

In today's world, shape memory polymers (SMPs) have already found application in a wide range of domains, including medical engineering, control technology, and others. The ability of the polymers to "remember" a stored shape is provoked by different stimuli such as light, pH, temperature or other factors.

A widely studied SMP is polyvinyl alcohol (PVA), which is characterised by biocompatibility, high hydrophilicity, non-toxicity, and efficient shape memory behaviour.

The present study investigates the influence of energy input via ultrasound technology in the polymer mixture on the shape memory effect of PVA with integrated iron nanoparticles. In order to achieve this objective, the strain recovery capacity and strain fixity rate at varying levels of energy input were experimentally determined. Thermomechanical analysis (TMA) was the method of choice for gaining insights into this phenomenon.

A decline in the strain fixity rate was observed in PVA films with integrated iron nanoparticles, as the energy input increased. This renders the process of storing "new" shapes more challenging. No alteration in strain recovery was observed when energy was introduced by ultrasound.

Keywords: shape memory polymers, nanoparticles, ultrasound, strain recovery rate, strain fixity rate, TMA measurement

Received on 21 October 2025, accepted on 31 October 2025, published on 04 November 2025

doi: 10.4108/dtip.10673

1. Introduction

Shape memory polymers (SMPs) are classified as smart materials because of their exceptional ability to change shape in response to external stimuli. This unique characteristic, which can be triggered by a wide variety of factors such as temperature, light, or pH value makes SMPs highly valuable, leading to their widespread adoption across many areas of science, technology, and daily life. [1][2]

The core of this technology lies in the polymer's molecular structure, which allows it to have both a stable, permanent shape and a temporary, deformed shape. When a specific stimulus is applied (the "trigger"), the material undergoes a transition, releasing stored elastic energy to return to its original configuration. This powerful, predictable movement has driven the rapid use of SMPs in biomedical devices like self-tightening sutures and minimally invasive stents, deployable space structures (where they unfurl upon reaching orbit), and smart packaging that seals itself under heat, highlighting their versatility and potential to innovate across virtually every sector. [3][4]

SMPs, despite their versatility, face several intrinsic limitations that restrict their adoption in high-stress and high-performance engineering. Primarily, they exhibit comparatively low tensile strength and stiffness, alongside a relatively low restoring force upon actuation. Furthermore, the material's inherent properties result in low thermal conductivity and poor responsiveness to electric, light, or electromagnetic fields. These factors often combine to produce a slow actuation response and a short

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functional recovery time, which generally impedes their use. To overcome these inherent material weaknesses and leverage the shape memory effect for demanding applications, researchers are increasingly relying on developing Shape Memory Polymer Composites (SMPCs). [2],[5]

Consequently, these material limitations often relegate SMPs to less demanding roles, driving ongoing research focused on material engineering solutions, such as incorporating nanofillers or conductive elements, to bridge the gap between their unique functionality and the requirements of high-performance systems. [1]

Polyvinyl alcohol (PVA) a SMP that has been thoroughly researched, particularly in terms of its use in combination with carbon-based nanoparticles, metal oxide-based nanoparticles, and numerous other nanomaterials. In addition to its shape memory effect (SME), PVA has excellent biocompatibility properties, making it highly desirable for medicine applications such as drug delivery systems, tissue engineering scaffolds, and temporary biomedical implants. [6][7] When used as a 3D printing material for fused deposition modelling (FDM), these properties can contribute to the development of an effective 4D smart drug delivery system.

Triggering the SME of PVA can be achieved by using the physical variable of temperature as a stimulus, as the material is typically programmed and fixed at a temperature above its glass transition or melting point (T_g or T_m) and then returns to its permanent shape when reheated above this transition temperature (T_{trans}).

Structures of SMPs, which are temperature-stimulated, consist of hard and soft segments. The hard segments contain chemical or physical cross-linking points and crystalline regions, or stiffness chains, which define the polymer chain network's permanent shape. The soft segments of the SMP consist of crystalline regions. The crystallinity and morphology of the soft segments depend on temperature. When the glass transition temperature (T_g) is reached, the soft segments of these SMPs can deform in terms of length and orientation. This allows the SMPs to be fixed in a temporary shape when cooled below T_g. This process minimises the elongation of the SMPs. In this case, strain energy is stored within the polymer chain network. When reheated, the deformed polymer chains regain their mobility, releasing the stored energy. Consequently, the SMP reverts to its original configuration, which is retained by the hard segment. [8][9]

To reduce the above-mentioned limitations when using SMP, various combinations of nanoparticles can be used, as well as the manufacturing process of PVA films, to influence various physical properties and the SMP itself. A good summary of the possible combination of PVA with nanocomposites and the resulting change in properties was described by M. Aslam. For example, ferritic nanoparticles increase saturation magnetization. [10] Several studies have previously observed the effect of nanoparticles or nanotubes on shape memory behaviour, yielding a mixture of favourable and unfavourable results. [8]

This research comprehensively investigates the impact of ultrasonic waves on the SME of PVA films containing iron nanoparticles. The embedded iron nanoparticles are designed to serve as nano-heaters, achieving contactless thermal activation of the polymer by inducing an alternating magnetic field (AMF). This enables the T_g to be exceeded without contact, thereby triggering the SME. The use of ultrasound in the production of PVA film is intended to ensure better distribution of the nanoparticles and to reduce the size of the agglomerates. As H. Abral's paper explains, using ultrasonic waves changes the physical properties of PVA films. For instance, he reports an increase in tensile strength and a decrease in elongation at break, among other changes in properties. The higher lattice strain and crystalline structure are mentioned as the reason for this. [11] In addition to the impact of ultrasound on mechanical properties, one study also revealed an enhancement in the degradability and barrier properties of PVA composite films. [12] In addition to the known mechanical effects of energy input into PVA films using ultrasound, this study aims to investigate the effect on SME.

The strain fixity rate R_f and strain recovery ratio R_r are used to evaluate the impact on SME. These two parameters for evaluating the SME are determined by a thermo-mechanical analysis. During a measurement, the following phases are run through: programming the SMP and triggering the SME.

The strain recovery ratio R_r is a quantitative measure of the material's ability to store its permanent shape and indicates the extent to which a real strain that occurred during programming is reversed in the subsequent shape memory transition.

The total strain recovery ratio ($R_{r,tot}$) is defined as the strain recovery following N cycles relative to the initial shape of the specimen.

The following formula for $R_{r,tot}$ was used to calculate the total strain recovery rate after two cycles (N=2):

$$R_{r,tot}(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m} \tag{1}$$

In the context of this study, the term "ε_m" is used to denote the strain above the switching temperature, which is employed for the purpose of programming the new shape. In contrast, the term "ε_p" is used to describe the permanent strain, which is applied after the memorisation of the permanent shape.

In addition to the strain recovery rate $R_{r,tot}$, the strain fixity rate R_f is also employed for evaluation purposes in this study. The strain fixity rate R_f characterises the capacity of the switching segment to sustain the mechanical deformation that was applied during programming. Consequently, it indicates the precision with which the sample can be fixed in this position after deformation to ε_m. The resulting transient shape invariably deviates from the shape achieved by deformation.

$$R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_m} \tag{2}$$

The term "ε_u" is used to describe the elongation observed in a stress-free state after the programming process. [13]

These two parameters are essential for fully characterizing the SMP behaviour of the SMP and for understanding the influence of processing conditions. Analysing these parameters allows for the description of how methods, such as the dispersion of iron nanoparticles within the PVA matrix, directly impact the material's properties. By correlating the parameters with processing conditions, researchers gain the capability to optimize the composite formulation and thus significantly enhance its overall functional performance. [9]

2. Materials and Methods

The Polyvinylalcohol (PVA), specifically the KURARAY POVAL™ (type 4-98), was purchased from Kuraray Europe GmbH (Frankfurt, Germany).

The nanoparticles SEON^{Dex} were kindly provided by SEON (University Hospital Erlangen, Section of Experimental Oncology and Nanomedicine).

The composition of SEON^{Dex} consists of iron oxide nanoparticles coated with dextran, dispersed in water. The iron concentration of SEON^{Dex} is 25.82 ± 0.15 mg/mL, and its mean hydrodynamic size is 29 nm. [14]

A 16 wt % PVA solution containing 7 vol% iron nanoparticles was used to produce the films. After preparing the solution with demineralized water, it was stirred at 70 °C for one hour. Before the films were applied, 0, 200, 400 and 1600 Ws of energy was applied to the solution using ultrasound. For all composite manufacturing runs, the sonotrode was carefully positioned to a depth of 25 mm within the suspension, and the ultrasonic amplitude was maintained at 60 % of the maximum output throughout the process. The required energy input was achieved by working with the UP200Ht ultrasonic processor and the S26d7 sonotrode both manufactured by Hielscher Ultrasonics GmbH. Figure 1 illustrates the experimental configuration of the ultrasonic device and sonotrode. Subsequently, the cast solution was levelled to ensure uniform thickness and then dried in a convection oven at 50 °C for one hour. The resulting 40 µm film thickness was precisely achieved by controlling the initial casting volume and levelling process.

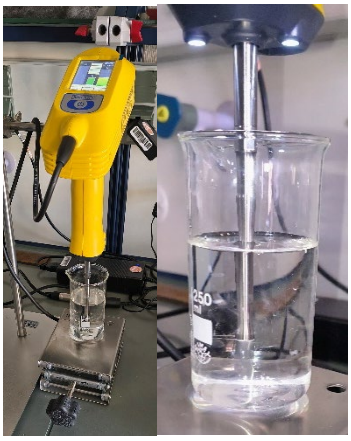

Figure 1: UP200Ht and sonotrode S26d7

To investigate the effect of ultrasound on SME during film production, the total strain recovery rate $R_{r,tot}$ and the strain fixity rate R_f of PVA were measured at different energy inputs. This was achieved by employing a corresponding method utilising thermomechanical analysis (TMA). As demonstrated in previous studies, TMA is recognized as an effective and reliable method for determining the relevant characteristic values (e.g. transition temperatures, coefficient of thermal expansion) of a material. [15] All thermomechanical analyses were carried out using the TMA2+ device manufactured by Mettler Toledo. The resulting TMA samples, along with their respective installations within the TMA device, are illustrated in Figure 2.

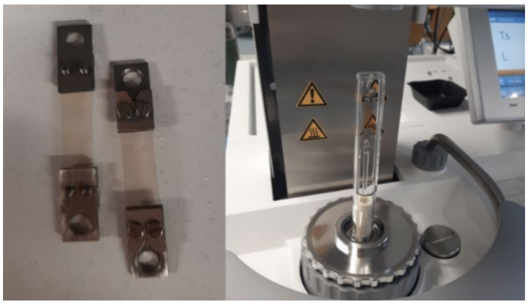

Figure 2: TMA sample on the left, sample inserted in the TMA device on the right.

The experimental thermomechanical cycling procedure is visually detailed in the force-temperature diagram (Figure 3). For rigorous analysis, each sample was subjected to the complete cycle twice, with the process consistently commencing at Step 1 to ensure reliable and comparative data acquisition.

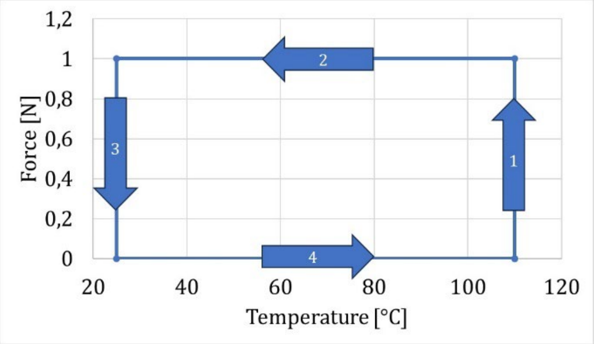

Figure 3: Force-temperature-diagram

As shown in the diagram of Figure 3, the sample is heated to 110 °C and then a force of 1 N is applied. The resulting change in length is documented. The sample is then cooled to 25 °C under the load of 1 N before being released. The sample is then reheated to 110 °C without force while the change in length is being measured. Subsequently, the entire thermomechanical cycle is repeated to verify the reproducibility of the shape-memory characteristics.

3. Results and discussion

Figure 4 shows an example of TMA measurement curves used to determine $R_{r,tot}$ and R_f for films fabricated using various levels of ultrasound energy.

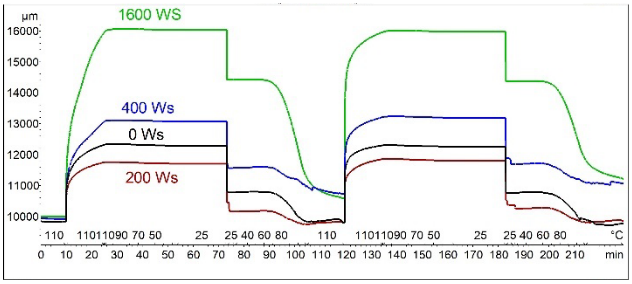

Figure 4: TMA measurement with different ultrasound energy inputs

As illustrated in this figure, the influence of the manufacturing process is obvious: there is a significant difference in the absolute elongation observed under a 1 N load, alongside observable variations in the SMP's performance. Specifically, these variations affect the material's shape fixity (its ability to retain the temporary shape after unloading) and its shape recovery (its ability to return to the original permanent shape). The requisite values for quantifying these effects were extracted directly from the measurement curves and used to calculate the decisive characteristic parameters via Formulas 1 and 2. These calculated values are presented in Table 1 and Table 2. The values indicated in brackets represent the calculated standard deviation from the four measurement cycles.

Table 1: Total strain recovery ratio $R_{r,tot}$

Total strain recovery ratio $R_{r,tot}$ [%]	Energy input with Ultrasound [Ws]			
	0	200	400	1600
With SEON^{Dex}	101 (±6)	101 (±3)	96 (±2)	100 (±1)
Without SEON^{Dex}	97 (±2)	--	--	87 (±4)

The investigation revealed that exposing the composite samples with integrated iron nanoparticles to ultrasound across a range of energy inputs had no statistically significant detrimental effect on the total strain recovery rate $R_{r,tot}$.

Specifically, it was demonstrated that up to a maximum ultrasonication energy of 1600 Ws, the $R_{r,tot}$ of the composite films remained consistently above 95 %. In contrast, the control group, i.e. films without iron nanoparticles, exhibited a distinctly different trend. In this instance, the $R_{r,tot}$ deteriorated, falling to below 90 % at the 1600 Ws energy input, resulting in the films only regaining approximately 87 % of their original shape.

Table 2: Strain fixity rate R_f

strain fixity rate R_f [%]	Energy input with Ultrasound [Ws]			
	0	200	400	1600
With SEON^{Dex}	71 (±8)	58 (±4)	59 (±6)	40 (±8)
Without SEON^{Dex}	36 (±8)	--	--	72 (±2)

The utilization of the ultrasound technique during the production of films incorporating iron nanoparticles resulted in a notable deterioration of the shape fixity ratio R_f. Specifically, it was demonstrated that at the highest energy input of 1600 Ws, the R_f dropped to as low as 40 %. Consequently, films produced under these conditions are only capable of retaining 40 % of their temporary shape following the programming and unloading steps.

The experimental evaluation indicates that the decline in the shape fixity ratio (R_f) is primarily attributable to a synergistic interaction among the PVA matrix, the iron nanoparticles, and the ultrasound-induced energy. This conclusion is strongly supported by the fact that a wholly distinct image emerges regarding the R_f when control films are produced without iron particles, suggesting the nanoparticles mediate the detrimental effects of ultrasound mixing. As demonstrated in Table 2, the strain fixity rate

R_f exhibits a significantly different trend in the absence of iron nanoparticles, increasing to over 70 % at an ultrasonic energy input of 1600 Ws.

The most effective shape fixity rate (R_f) achieved for the composite films was 100 %, observed when the films containing iron nanoparticles were produced without the application of ultrasonic energy. This substantial enhancement in the R_f of the PVA when combined with iron nanoparticles corroborates the findings of an earlier independent study. [16]

4. Conclusion

The investigation revealed that the use of ultrasound during the fabrication of PVA films with integrated iron nanoparticles has a particularly significant, detrimental impact on the shape fixity rate (R_f), leading to a substantial deterioration of approximately 30 %. This characteristic behaviour of the PVA matrix (the sharp decline in R_f) is only observed when the iron nanoparticles are additionally treated with ultrasound during film production. This allows us to extrapolate a direct interaction between the ultrasonic energy and the iron nanoparticles that disrupts the chemical and physical network points (cross-links) of the PVA. It is hypothesised that the nanoparticles hinder the formation of the crystalline structure, leading to the predominance of amorphous regions. Consequently, fewer interactions can develop that are necessary for fixing the new form. This theory is supported by the comparison sample devoid of nanoparticles. In this instance, R_f increases to approximately 70 %, which can be attributed to the utilisation of ultrasound during the manufacturing process. Moreover, the decline in R_f is assumed to be irreversible, meaning that healing over several cycles of the deformation process is not possible. Based on the SME of PVA with the formed hard and soft segments, only the soft segment is dissolved during the programming of the SMP. The higher-level structure, the hard segment, remains intact, and thus also the possible number of interactions. Further investigations are necessary here to strengthen the statement and determine the influence of other nanoparticles on the structure of PVA. Consequently, this constraint must be a primary consideration for the utilization of these composite films, as the diminished precision in temporary shape retention will inevitably lead to errors in forming novel shapes during application.

However, the effects on the total strain recovery rate ($R_{r,tot}$) were negligible. Specifically, no significant changes were observed when iron nanoparticles and ultrasound were combined. This consistency in performance is a positive and advantageous finding, as it confirms that the polymer's ability to recover its permanent shape (the 'memory' function) is not compromised by the nanoparticle/ultrasound interaction. Consequently, the design and fabrication processes of the PVA films do not need any special measures to compensate for a potential $R_{r,tot}$ deterioration.

In addition to their influence on the final total strain recovery rate ($R_{r,tot}$) and the strain fixity rate (R_f), the kinetics of the shape recovery process are of considerable interest across many application areas. An improvement in this recovery rate has been previously demonstrated when water is used as a solvent, a phenomenon attributed to the favourable interaction and structural compatibility between water and the PVA matrix, which collectively contribute to a shorter overall recovery time. [17]

This raises the critical question of the extent to which the ultrasonic energy input can influence the shape recovery rate in the composite films. The time required for the SME is of paramount importance across all application sectors utilizing PVA films, including the medical, sensor/control technology, and automotive industries. It is also pertinent to emphasize the inherent water solubility of PVA, a feature that is highly advantageous in fields like drug delivery. In this specific application, two crucial trigger points can be strategically combined: the functional shape change enabled by the SME and the ultimate detachment and dissolution facilitated by water, offering enhanced control over drug release profiles.

Acknowledgements

The authors would like to express their gratitude to SEON (Section for Experimental Oncology and Nanomedicine) of the University Hospital Erlangen for providing the iron nanoparticles.

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