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ARTICLE

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# Prestretching effect and recovery process of polyvinyl alcohol film crosslinked with tartaric acid

Altan Bozdoğan[1] | Baki Aksakal[1] | Cenk Denktaş[1] | Yavuz Salt[2]

[1]Department of Physics, Yıldız Technical University, İstanbul, Turkey

[2]Department of Chemical and Metallurgical Engineering, Yıldız Technical University, İstanbul, Turkey

**Correspondence**
Altan Bozdoğan, Department of Physics, Yıldız Technical University, Esenler, 34210, İstanbul, Turkey.
Email: abozdog@yildiz.edu.tr

**Abstract**

The tartaric acid (TA)/polyvinyl alcohol (PVA) composite films were prepared with various TA concentrations from 5 to 20 wt%. The crosslinking due to TA improved the tensile characteristics such as tensile strength and the Young's modulus, and thermal stability of the films. The addition of TA in PVA led to a decrease in the crystallinity. Application of prestretching or preliminary deformation resulted in significant changes in both stress–strain behavior and tensile characteristics of both pure PVA and TA/PVA composite films. Although low preextension levels such as 5% strain did not change much the tensile characteristics, higher preextension levels improved the tensile strength but decreased the extensibility of the films. The recovery processes of the stretched films consisted of a fast recovery process for which most of the recoverable elastic deformation is seen took place within almost 30 min and a time-dependent long-lasting recovery process continued in time very slowly, which resulted in undesirable residual deformation. It was also observed that increasing TA concentration accelerated the recovery process, hence, improved the recovery properties of PVA. The use of TA in the membrane applications can be considered to improve the mechanical properties and reusability of the membrane technology.

**KEYWORDS**

mechanical properties, spectroscopy, thermal properties, thermogravimetric analysis, X-ray

## 1 | INTRODUCTION

PVA is a nontoxic, water-soluble, and semi-crystalline synthetic polymer used in engineering applications such as food packaging, composite film separation, adhesives, textile, paper, drug delivery systems, and so on due to good film-forming, bio-degradable nature, thermal, and chemical resistant properties.[1–5] The chemical and physical properties of PVA produced from vinyl acetate monomer followed by saponification of polyvinyl acetate depend on its degree of polymerization and hydrolysis. Therefore, PVA can be classified into two classes: partially hydrolyzed (87–89%) and fully hydrolyzed (above 98%).[6,7] Also, it was pointed that the chemical and physical properties of PVA may vary depending on the degree of hydrolysis and its molecular weight.[5,8]

PVA shows good mechanical properties in a dry state.[2] Zanela et al. reported that the tensile strength and the elongation-at-break values of a polymeric structure can be improved using PVA with higher molecular weight, and that the rigidity of polymer film can be increased by using higher hydrolysis degree of PVA.[9] However, it has poor stability in aqueous solution due to the existence of hydroxyl groups on its backbone.[2,10] The solubility of fully hydrolyzed PVA in water is lower than that of partly hydrolyzed PVA, and also, the

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solubility of PVA is somewhat decreased with increasing the polymerization degree.[6] For this reason, to provide higher water resistance of PVA especially for the composite film applications, PVA has to be crosslinked chemically using aldehydes, carboxylic acids, and anhydrides to make it resistant to water due to its hydrophilicity and to improve its mechanical strength and thermal properties.[2] However, PVA is a semi-crystalline polymer, and it can exhibit more brittle behavior due to that the segmental motion of polymer chain decreases with an increase in the degree of crosslinking in a polymer. So, Cho et al. indicated that PVA film is too brittle because of high crystallinity.[11] On the other hand, the water resistance of PVA film increases by increasing the crosslinking degree.[12] Depending on the application area, it is necessary to balance the mechanical properties of PVA. For this reason, it is very important to investigate how these properties affect the structural properties of the prepared PVA films.[9]

It is known that chemical crosslinking makes PVA resistant to water as it has poor stability and the large swelling capacity in aqueous solution. The crosslinking reaction between PVA and TA takes place between hydroxyl groups of PVA and carboxylic groups of TA. There are numerous research studies in the literature on the use of carboxylic acids for crosslinking.[13,14] However, there is no specific information in the literature about the advantage and disadvantages of tartaric acid (TA) usage. TA as a carboxylic acid, which occurs naturally in grapes, was used as a crosslinker in this study because it is nontoxic, inexpensive,[15] and easily soluble in cold water.

During the application of PVA as either composite film or thin films, the PVA can be undergone to various deformation or load for different times. Depending on the applied load or deformation, the structural and mechanical properties of materials based on PVA change significantly. Although it is known that the crosslinked PVA materials have better mechanical properties, how the applied load or preextension affects the properties of such materials should be determined to estimate the lifetime and reusability of the crosslinked PVA films especially in membrane applications. Thus, the determination of the effect of various preextensions and deformation on especially mechanical properties is important. In order to obtain pure PVA and TA/PVA composite films with better mechanical characteristics such as high modulus and high-tensile strength, stretching the film at different strain levels, which lead to the alignment and orientation of macromolecules can be used as a mechanical method. It is also important to determine elastic and plastic deformations, which result in remaining or residual deformation considered as undesirable properties on the structure of the crosslinked PVA. The observation of the recovery process is also a crucial point to estimate when the preextended specimen may obtain full recovery from various applied deformations. In the literature, there are few studies about the effect of prestretching on PVA[16] and stress-relaxation process on PVA containing films.[17,18] Fukumori et al. stated that increasing in stretching ratio increased the tensile strength and Young's modulus of PVA.[16] Sharaf's group investigated mechanical and stress-relaxation properties of PVA films doped with ferrous sulphate before and after $\gamma$-irradiation.[17] Karimi and Navidbakhsh investigated the stress relaxation of the PVA sponge for tissue engineering applications.[18] However, there is no any study about prestretching effect and recovery process of PVA crosslinked with TA.

In this study, the effects of uniaxial deformations in the mechanical behaviors of pure PVA and TA crosslinked PVA films containing 5, 10, 15, and 20 wt% TA were investigated after the polymeric films were exposed to various deformations. Thermal, mechanical, and recovery properties in wide strain range of pure and crosslinked PVA films prepared by solution-casting method were analyzed using fourier transform infrared/Attenuated total reflectance (FTIR/ATR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

## 2 | EXPERIMENTAL SECTION

### 2.1 | Materials

#### 2.1.1 | Preparation of TA/PVA composite films

PVA and TA were supplied by Sigma-Aldrich Corp. The TA/PVA composite films were prepared as follows: The PVA was dissolved in distilled water by mechanical stirrer at 90°C for 3 hr in order to produce a PVA solution at 20 wt%. Then, the TA solution was prepared by mixing with distilled water for 1 hr at room temperature. Later, the required amounts of PVA and TA solutions were mixed together at room temperature for 1 hr to obtain TA/PVA composite films (5, 10, 15, and 20 wt%). The each prepared solution at various TA wt% was cast onto plexiglas plates as thin films and the films were left to dry at 40°C in the oven for 24 hr. In order to form to crosslinked films were kept at a constant temperature of 120°C in the oven for 45 min. Finally, all samples were kept in pure water for the removal of unreacted crosslinker, monomer, and impurities at room temperature for overnight. After that the films were dried at 105°C for 2 hr.

## 2.2 | Methods

### 2.2.1 | Thermogravimetric analysis

The thermal properties of the films were carried out on an SII Nanotechnology-SII6000 Exstar TG/DTA 6300 model thermal analyzer instrument. TGA measurements were obtained while heating the films from room temperature to 600°C at a heating rate of 10°C/min in a nitrogen atmosphere at a flow rate of 50 ml/min.

### 2.2.2 | X-ray diffraction

The XRD measurements were performed with a Scintag Irc XRD equipped with Ni-filtered CuKα radiation ($\lambda$ = 1.5418 Å) at 45 kV and 40 mA at ambient temperature. To identify the crystal structure, the films were scanned from 5°–60° at 2°/min.

### 2.2.3 | Scanning electron microscopy

Morphologies of the films were investigated by an SEM (Apollo-300 CamScan SEM). The SEM images from cross-sectional areas of the films were obtained by freeze-fracture method after the films were immersed in liquid nitrogen and then sputtered with gold (SC7620 Mini Sputter Coater/Glow Discharge System at coating current of 10 mA for 90 s).

### 2.2.4 | FTIR/ATR spectroscopic method

The spectroscopic measurements of pure PVA and TA/PVA composite films were obtained on a Thermo Scientific Nicolet iS5 FTIR Spectrometer equipped with an iD7 Attenuated Total Reflectance (ATR) sampling accessory. The spectra of the pure PVA and TA/PVA composite films were recorded in the wave numbers ranging from 4,000 to 650 $cm^{-1}$ at a resolution of 4 $cm^{-1}$ with 32 scans for each measurement at room conditions.

### 2.2.5 | Methods for tensile test and recovery process

Uniaxial tensile tests of pure PVA and TA/PVA composite films were carried out by using a tensile testing machine LF plus (AMETEK Lloyd Instruments Ltd., UK) with a crosshead speed of 30 mm $min^{-1}$ (100% per min) at room conditions (T = 25°C; Relative Humidity = 60%). The initial gauge length of the samples was chosen as 30 mm and the test specimens had the same width of 4 mm. The thicknesses of pure PVA films and TA/PVA composite films were measured by using a digital micrometer (Mitutoyo Corp., Japan, Digimatic Micrometer; MDC-25SX Model, No 293–821-30). The data reported here were averaged over at least six to eight specimens. In order to see the effect of prestretching on the stress–strain curves, each sample was first stretched to a strain level ranging from 5% to very high levels and the composite film was hold at a stretched position for 10 min during which a stress-relaxation process occurs. After the stress-relaxation process, the stretched composite film was tested in the same tensile testing equipment at the same experimental conditions. In order to examine the recovery process, following the stress-relaxation process as soon as the composite film was released from that stretched position, the residual length (strain) on the composite film was carefully measured in the same equipment for the recovery times up to around 1 hr. Then, for longer recovery times, the residual deformations were determined by measuring the length of the composite film in that present state in time with a digital Vernier Caliper (Mitutoyo Corp., Japan, Digimatic Caliper; CD-S15CK Model, No 550–450).

## 3 | RESULTS AND DISCUSSION

### 3.1 | Thermal and structural characterization of TA/PVA composite films

#### 3.1.1 | Thermal analysis

The TGA thermograms of pure PVA and the crosslinked PVA films with different TA ratios are illustrated in Figure 1 and thermal parameters are given in Table 1. It is seen in Figure 1a that pure PVA has three major regions of weight loss. The first region at a temperature of 30–160°C ($T_{max,1}$ = 88.92°C) is due to free and bounded water, respectively, and the weight loss in this region is about 7.141 (wt%).[19,20] The second region at temperature extending from 200 to 400°C ($T_{max,2}$ = 319.05°C) was associated decomposition of the side chains of PVA with the formation of volatile products[20] and the total weight loss is about 77.620 (wt%).[21] The third region at temperatures greater than 400°C ($T_{max,3}$ = 443.09°C) corresponded to the decomposition of the main chains of PVA and the total weight loss is about 12.830 (wt%).[20,22] After 475°C, the small weight loss is due to charred residues of black carbon only.

The TGA curves of TA/PVA composite films with various TA concentrations also exhibited three weight loss

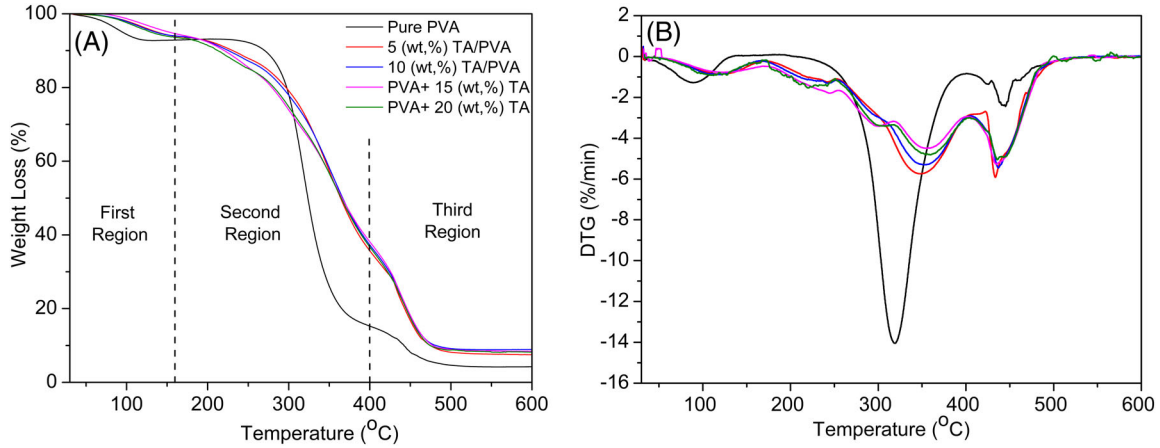



**FIGURE 1** (a) Thermogravimetric analysis (TGA) curves of TA/PVA composite films and (b) corresponding derivative TGA curves. PVA, polyvinyl alcohol; TA, tartaric acid; TGA, thermogravimetric analysis [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 1** Thermal degradation parameters of all films

| | $T_{max}$ (°C) | | | Weight loss (%) | | |
|---|---|---|---|---|---|---|
| **Specimen** | **First region** | **Second region** | **Third region** | **First region** | **Second region** | **Third region** |
| Pure PVA | 88.9 | 319.1 | 443.1 | 7.1 | 77.6 | 12.8 |
| 5 (wt%) TA/PVA | 119.5 | 348.0 | 433.2 | 6.2 | 58.1 | 22.5 |
| 10(wt%) TA/PVA | 118.2 | 352.1 | 437.2 | 6.0 | 51.3 | 27.4 |
| 15(wt%) TA/PVA | 123.4 | 354.9 | 434.7 | 6.1 | 30.8 | 28.6 |
| 20(wt%) TA/PVA | 112.6 | 357.5 | 436.0 | 6.5 | 33.4 | 27.6 |

Abbreviations: PVA, polyvinyl alcohol; TA, tartaric acid.

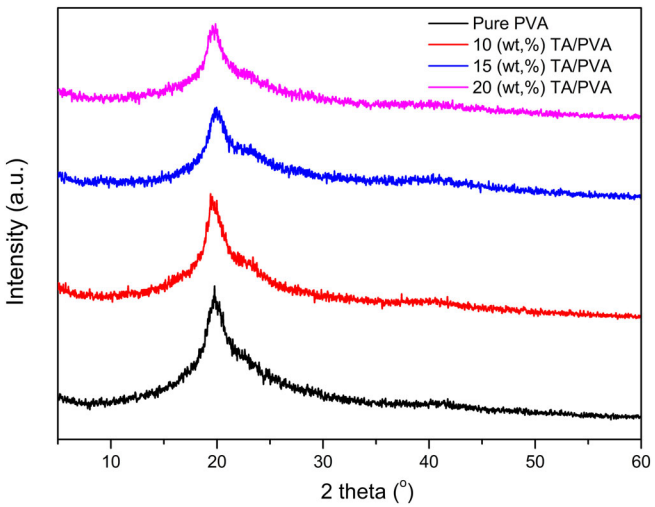



**FIGURE 2** XRD spectra of TA/PVA composite films. PVA, polyvinyl alcohol; TA, tartaric acid; XRD, X-ray diffraction [Color figure can be viewed at wileyonlinelibrary.com]

regions. As seen in Figure 1b, $T_{max,1}$ values of the first regions were shifted to higher temperatures (111.26–123.36°C).[23] In this region, the weight loss of TA/PVA composite films was less than that of neat PVA, due to the presence of less amount of adsorbed water on crosslinked PVA films. In the second degradation region attributable to the degradation of side chains and TA crosslinks with PVA, the $T_{max,2}$ of the TA/PVA composite films were shifted from 348.03 to 357.48°C as TA concentration increased from 5 to 20 (wt%). Besides, weight loss of films decreased dramatically with increasing TA concentration as seen in Table 1. These results can be attributed to stronger intermolecular interactions due to crosslinking between the polymer chains.[13,24] The third region is attributed to the main degradation and cleavage of polymer backbones. It can be concluded that the thermal stability of pure PVA is improved due to the crosslinking formation between pure PVA matrix and TA molecules.

### 3.1.2 | XRD analysis

The XRD spectra of all the films are illustrated in Figure 2. As shown in Figure 2, for neat PVA, the XRD spectrum exhibits a prominent broad peak at 19.75° (2$\theta$)

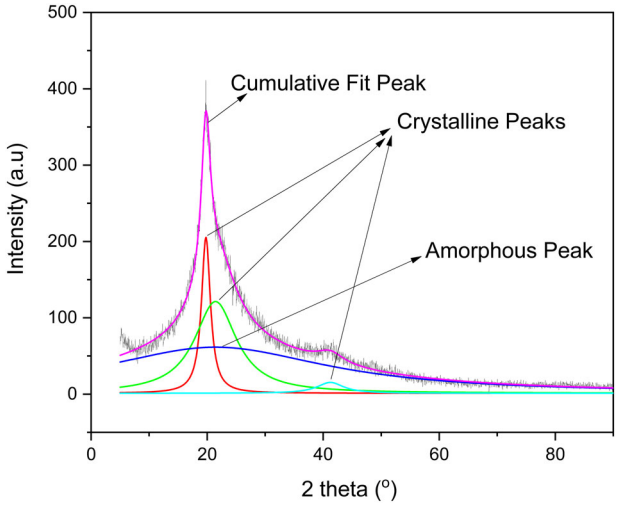



**FIGURE 3** XRD pattern of pure PVA film deconvolved into crystalline and amorphous peaks. PVA, polyvinyl alcohol; XRD, X-ray diffraction [Color figure can be viewed at wileyonlinelibrary.com]

and its *d*-spacing value is 4.48961 *Å*.[25] This peak is in agreement with (101) reflection plane.[26] In addition to this peak, the other two peaks at 22.8 and 41° belong to the polymer crystalline phase of PVA.[27] Deconvolution into components of the diffraction pattern of pure PVA films is seen in Figure 3. The crystallinity of pure PVA and TA/PVA composite films was calculated using the following relation:

$$\chi_C(\%) = \frac{A_{cr}}{A_{cr} + A_{am}} \times 100, \quad (1)$$

where $A_{cr}$ is the summation of the areas of crystalline peaks and $A_{am}$ is the area of the amorphous peak. The degree of the crystallinity of pure PVA and TA/PVA composite films is given in Table 2. It was determined that as TA concentration increased, the degree of the crystallinity decreases from 34.4 to 14.8%, whereas the amorphous phase increases from about 65 to 85%. Thus, disorderliness in the crystalline regions increased. As a result, the decrease in the crystallinity is supposed to be associated with an increase in the number of defects and in free volumes existing in the crosslinked films and the changes in the intermolecular interactions between TA molecules and hydroxyl groups of the PVA.[28–30]

### 3.1.3 | SEM analysis

SEM images from the surface of pure PVA at different magnification show that the unstretched PVA has a smooth surface without any crack as shown in Figure 4a,

**TABLE 2** Crystallinity ($X_C$) of TA/PVA composite films

| Specimen | $X_C$ (%) |
|---|---|
| Pure PVA | 34.4 |
| 10 (wt%) TA/PVA | 19.5 |
| 15 (wt%) TA/PVA | 16.3 |
| 20 (wt%) TA/PVA | 14.8 |

Abbreviations: PVA, polyvinyl alcohol; TA, tartaric acid; $X_C$, crystallinity.

b. However, when the pure PVA composite film was stretched at 100% strain, the roughness of the composite film slightly increased as shown in Figure 4d,e without any crack formations. As shown in Figure 4c–f, from the comparison of the images taken from the cross-sectional area as the composite film was stretched, similar changes in the roughness on the cross-sectional area, that is, an increment in the roughness was observed.

As shown in Figure 5, the 20 wt% TA/PVA composite film has a rougher surface structure than that of pure PVA. The TA formations deteriorated the homogeneity of the composite film's surface leading to some agglomerations. From the comparison of SEM images of the pure PVA and 20 wt% TA/PVA composite film, the effect of TA additions to the PVA structure was also seen as an increment in the roughness on the crosssection. When the 20 wt% TA/PVA composite film was stretched, a significant change on the surface of the composite film was seen in Figure 5d,e. At higher magnification, it is seen that due to stretching the composite film, some crack formation was apparently seen on the surface structure, which leads to some changes in the mechanical properties. From Figure 5c,e, when the composite film was stretched, although the depth of the cracks decreased, the number of cracks along the vertical direction obviously increased.

### 3.1.4 | FTIR/ATR spectral analysis

Figure 6 shows the FTIR/ATR spectrum of pure PVA and TA/PVA composite films in the wave number regions of 650–1,800 and 2,400–3,700 $cm^{-1}$. Band frequencies[13,31–38] and assignment of the characteristic peaks of PVA and TA are listed in Table 3. It is seen that some peaks of TA overlapped with other peaks in the same wave number range of pure PVA in the spectrum of TA/PVA composite films. However, some distinctive peaks of TA due to wagging mode of O—C—O[13,37] at around 670 $cm^{-1}$ and combination of C—O symmetric stretching and —OH[13,37] bending at around 1,129 $cm^{-1}$ are seen in Figure 6, although these peaks are absent in

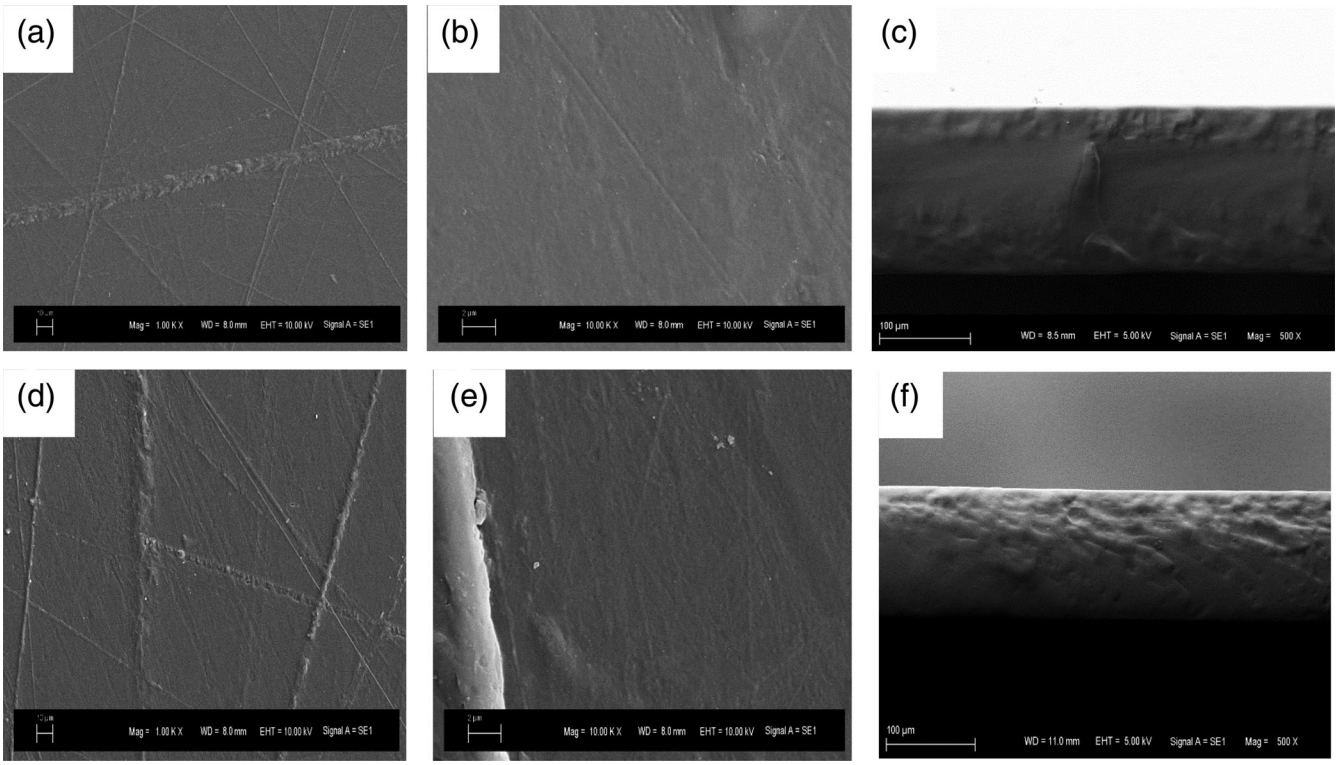



**FIGURE 4** SEM images from the surface (a,b) and the cross-sectional area (c) of unstretched pure PVA, SEM images from the surface (d,e) and the cross-sectional area (f) of pure PVA extended at 100% strain. PVA, polyvinyl alcohol; SEM, scanning electron microscopy

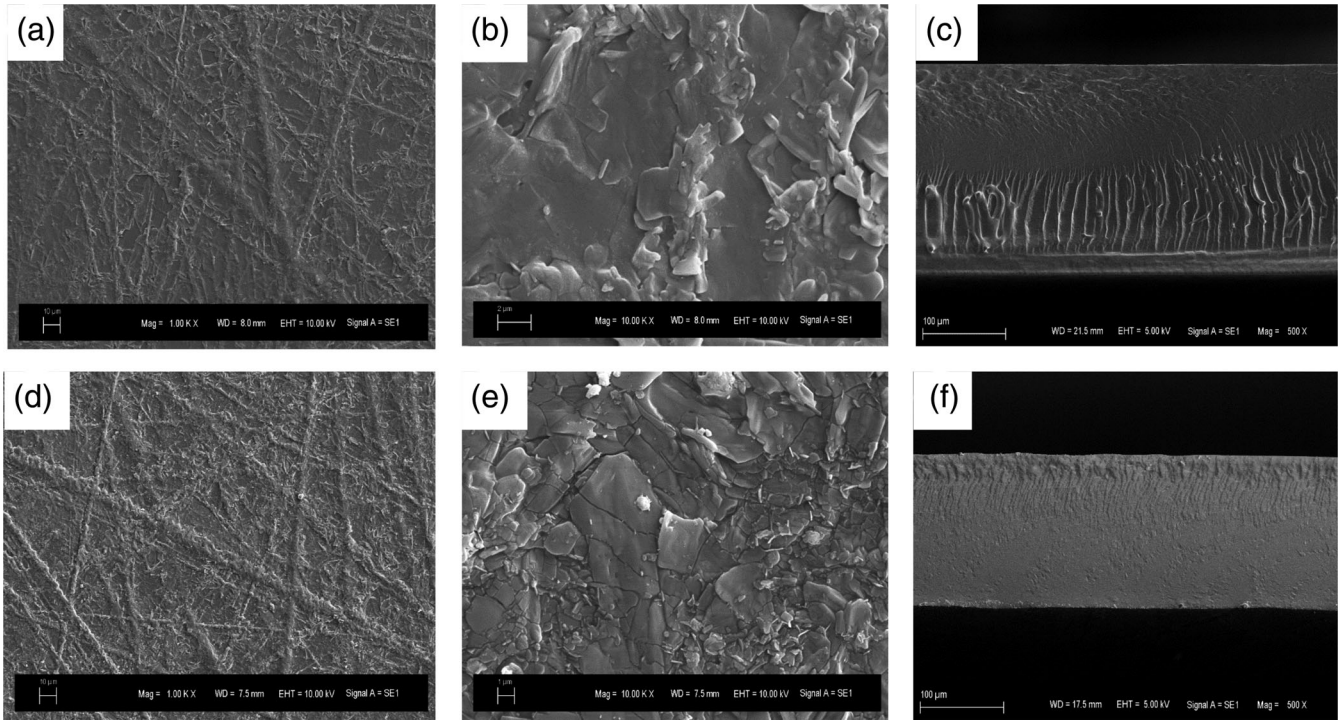



**FIGURE 5** SEM images from the surface (a,b) and the cross-sectional area (c) of unstretched 20 wt% TA/PVA composite film, SEM images from the surface (d,e) and the crosssectional area (f) of 20 wt% TA/PVA composite film extended at 100% strain. PVA, polyvinyl alcohol; SEM, scanning electron microscopy; TA, tartaric acid

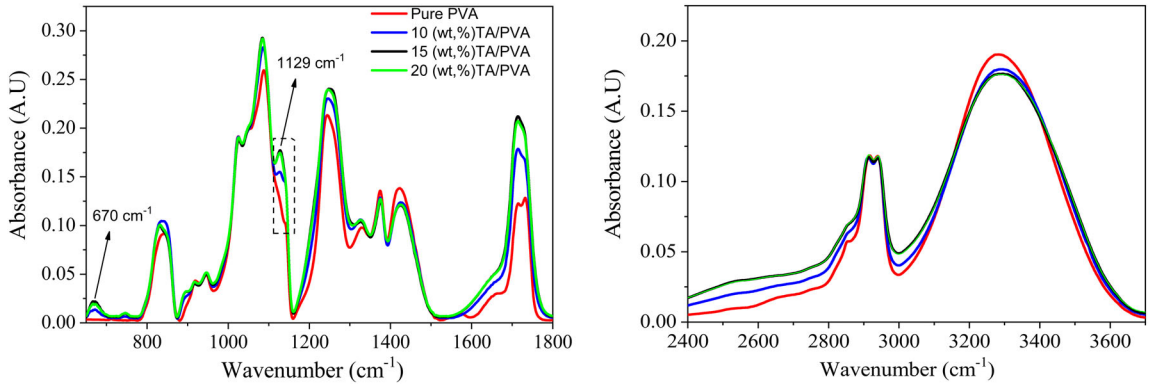



**FIGURE 6** The FTIR/ATR spectrum of TA/PVA composite films in 650–1,800 $cm^{-1}$ and 2,400–3,700 $cm^{-1}$ spectral region. PVA, polyvinyl alcohol; TA, tartaric acid [Color figure can be viewed at wileyonlinelibrary.com]

the pure PVA. The presence of these peaks in the composite film is evidence of TA being in the structure.

As we know due to intermolecular interactions of TA molecules with PVA polymer chains as shown in Scheme 1, some inter and intra-molecular crosslinks occur. As it is seen in Figure 6, the band at around 1,085 $cm^{-1}$ is attributed to the ether band (C—O—C). With increasing TA content, the band position was shifted and absorbance of this band increased significantly, which indicates the increasing crosslinking density in the structure.

The absorbance values of carbonyl (—C═O) groups and hydroxyl groups (—OH) were calculated with an integrated area of the related curves and given in Table 4. It is seen that the absorbance of carbonyl (—C═O) groups increased with increasing TA concentration due to the esterification process. Crosslinking of PVA chains results in the reduction of the hydroxyl groups of PVA chains and the formation of new crosslink ester bonds with a carbonyl stretching at 1,715–1,740 $cm^{-1}$. However, when compared with the absorbance values of ═OH groups of pure PVA, as it is seen in Table 4, the absorbance values of hydroxyl groups of TA/PVA composite films increased little because we think that this little increment may come from the contribution of the —OH groups of some TA molecules, which a make bond to the one of the —OH groups with one end and the other tail becomes free as seen in Scheme 1.

In order to estimate the degree of crosslinking, the absorbance ratio of the (—C═O/—OH) peaks is used to confirm crosslinking between TA and PVA molecules.[13] As represented in Table 4, the crosslinking density increased significantly with increasing TA concentration from pure PVA to 15 wt% TA/PVA and for 20 wt% TA/PVA the crosslinking density did not change much. This increment in the crosslinking density makes the structure more rigid.

### 3.1.5 | Influence of prestretching on the tensile characteristics of TA/PVA composite films

Figure 7 shows how the concentration of crosslinking of TA affects the stress–strain curve of pure PVA and corresponding changes on tensile characteristics were given in Table 5. Here, a significant change was seen on the Young's modulus, that is, it increased almost fourfold and more as TA content increased. Besides, tensile strength also increased by 16–32% compared with that of pure PVA as the TA ratio increased from 5 to 20 (wt%). These results showing an increasing tendency in the tensile strength and Young's modulus and a decreasing tendency in the strain-at-break values agree with the results obtained by Sonker and Verma,[13] which showed the tensile strength increased from 30 to 80 MPa, while strain-at-break values decreased from 184 to 14% strain as TA content in TA/PVA composite films increased from 0 (pure PVA) to 40% (wt/wt).

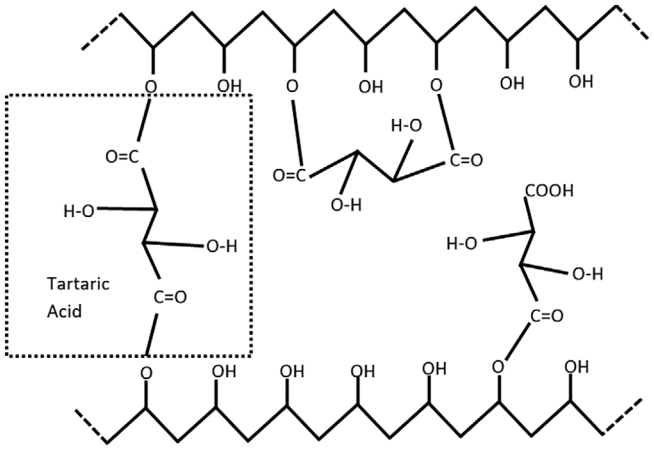
As illustrated in Scheme 1, it is seen that possible molecular interactions of TA molecules between PVA polymer chains form some inter and intramolecular crosslinks. It is assumed that especially intermolecular crosslinking formations lead to a decrease in the extensibility and a significant restriction in the molecular motions in the structure under tensile loading. However, this crosslinking leads to a significant improvement in the Young's modulus and the tensile strength of the TA/PVA composite films. Due to an increase in the tensile strength and the intermolecular interactions, a significant increase in the toughness, which is the required energy per unit volume that a material can absorb before rupturing.

The deformation induced by loading and extension to which PVA films and other products based on PVA are exposed in its various application can change many

**TABLE 3** The vibration frequencies and band assignments of observed peaks in neat PVA and TA/PVA composite films

| Vibration frequency ($cm^{-1}$) | Band assignment | References |
|---|---|---|
| 670 | [a]OCO wagging | [13,37] |
| 901 | [a]Bending –COOH | [13,37] |
| 1,085–1,096 | [b]COC stretching (ether band) | [13,31,35,37] |
| 1,129 | [a]CO symmetric stretching + -OH bending | [13,37] |
| 1,246 | [a]CC symmetric stretching | [13,37] |
| 1,242, 1,257 | [c]CH wagging | [34,35,38] |
| 1,329, 1,340 | [b]CH + OH, the bending vibration of bond COH | [13,32,35,37] |
| 1,374 | [c]$CH_2$ wagging | [33,37] |
| 1,408 | [a]COOH stretching | [13,37] |
| 1,424 | [c]Symmetric bending mode of ($CH_2$) | [33–35,38] |
| 1,640 | [c]Bending vibrations of absorbed water molecules | [13] |
| 1,715, 1,740 | [b]CO stretching | [13,37] |
| 2,852 | [c]CH stretching | [34,38] |
| 2,914 | [c]$CH_2$ symmetric vibration | [32,35,38] |
| 2,939 | [c]$CH_2$ antisymmetric vibration | [32,35,38] |
| 3,210 | [a]OH stretching, free water | [13,37] |
| 3,200–3,400 | [c]OH stretching vibration of the PVA hydroxyl groups | [32,35] |

[a]TA.
[b]TA + PVA.
[c]PVA.
Abbreviations: PVA, polyvinyl alcohol; TA, tartaric acid.




**SCHEME 1** Possible interaction of TA molecules with PVA chains. PVA, polyvinyl alcohol; TA, tartaric acid

**TABLE 4** Absorbance values of CO, OH bands and the degree of crosslinking ($A_{1715}/A_{3290}$)

| Specimen | $A_{1715}$ (CO) | $A_{3290}$ (OH) | $A_{1715}/A_{3290}$ |
|---|---|---|---|
| 0 (pure PVA) | 6.77 | 67.53 | 0.100 |
| 10 (wt%) TA/PVA | 10.31 | 67.74 | 0.152 |
| 15 (wt%) TA/PVA | 12.70 | 69.04 | 0.184 |
| 20 (wt%) TA/PVA | 12.41 | 69.02 | 0.180 |

Abbreviations: PVA, polyvinyl alcohol; TA, tartaric acid.

properties of such products. It is important to determine what extend the preextension or deformation influences the tensile behavior and characteristics of PVA films.

As a result of the application of various preextension levels on pure PVA, obtained stress–strain curves indicating how the tensile behavior changes after stretching was given in Figure 8. Changes in the tensile characteristics caused by preextension at various levels from 20 up to 300% strain were tabulated in Table 6.

It is seen that for the preextension up to around 100% strain, tensile strength, and Young's modulus did not change significantly and a relative increase in the strain at break or extensibility was seen. This can be due to the opening of the entanglements and relative movement and extension of the polymer chains in especially amorphous regions in PVA structure during extension up to around 100%. For the preextension level higher than 100% strain, although a great improvement was seen in the tensile strength and Young's modulus, a dramatic decrease was seen at the strain-at-break value. These results are in good agreement with the results obtained by Fukumori et al., which stated that when the PVA films were stretched up to 800% strain, the Young's modulus increased from 5.2 GPa for the 200% stretched film to 20.2 GPa for the 800% stretched whereas corresponding tensile strength values increased from 230 to 460 MPa.[16]

During the extension up to very high-strain levels, it is thought that the straining of molecular chains and the orientation of structural units such as crystalline domains along the loading direction occur. Thus, the molecular chains are more strained and stressed and less extensible. Therefore, a prominent improvement was obtained on tensile strength and Young's modulus as seen in Table 6. The change in the stress–strain curve indicates that the

structure changed from more amorphous and flexible to a more rigid and oriented one.

In order to see the effect of preextension on stress–strain behavior and tensile characteristics of PVA films crosslinked with TA at various contents, preextension or deformation starting from very low strain value corresponding to that in linear and initial region of stress–strain curve to very high-strain level up to 200–300% was applied to the specimens. The changes due to the application of preextension at different levels on the stress–strain curves and tensile characteristics of TA/PVA composite films are given in Figure 9 and Table 7. In the literature, there is not any study about prestretching effect on the tensile properties of TA/PVA composite films. However, a similar experimental method, that is, the stress-relaxation process was applied onto PVA films and film samples including PVA, but not TA.[17,18] In these studies, after the films were stretched and let to undergo stress relaxation, the tensile tests of the stretched films were not done.

Considering the 5% TA/PVA composite film, as the $\varepsilon_{pe}$ increases up to around 50%, the shape of stress–strain curves did not change much. However, with the application of $\varepsilon_{pe}$ higher than 50%, it obtained that of more rigid and stiffer structure. For the $\varepsilon_{pe}$ up to 200%, although there was a gradual improvement in the tensile strength and a great increase in the Young's modulus, almost twofold to threefold compared with that of an unstretched 5% TA/PVA composite film, a significant decrease, that is, about 28% and more for $\varepsilon_{pe}$ equal to 300%.

On the other hand, after the application of $\varepsilon_{pe}$ in the linear region, for example, 5% strain, for 10 wt% TA/PVA composites, because the deformation is mostly elastic and recoverable, the structure of the composite film did not change much and preextended composite film showed a very similar stress–strain curve and tensile characteristics to that of undeformed one. However, it is seen that some stress–strain curves are placed under that of an unstretched composite film with lower mechanical properties. As the $\varepsilon_{pe}$ increases from 5 to 100%, although there is a slight decrease in the tensile strength, Young's modulus decreased to one-fourth of that of the unstretched composite film. Prominent decrease was also seen on the toughness. It is thought that during the extension up to such high-strain levels as 100% because the most of the crosslinking bonds between PVA chains are assumed to be broken, it leads to a significant decrease in the Young's

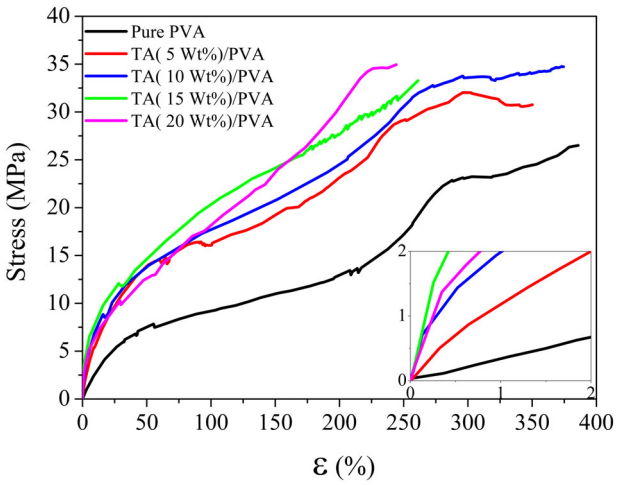



**FIGURE 7** The influence of TA concentration (wt%) on the stress-strain curves of PVA. PVA, polyvinyl alcohol; TA, tartaric acid [Color figure can be viewed at wileyonlinelibrary.com]

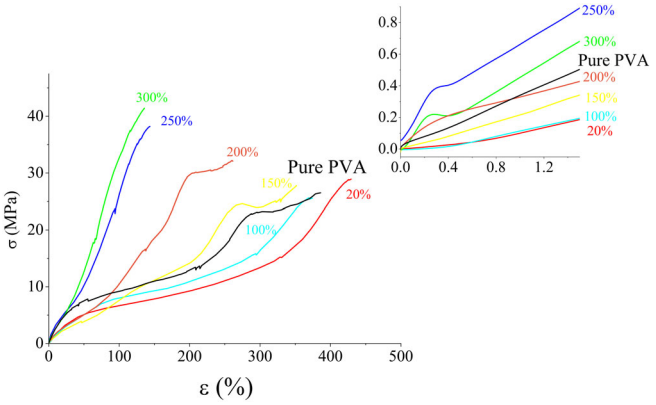



**FIGURE 8** The influence of prestretching on the stress-strain curves of pure PVA films. PVA, polyvinyl alcohol [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 5** The influence of TA concentration on the tensile characteristics values with *SD* of PVA

| Specimen | $\sigma_T$ (MPa) | $\varepsilon_r$ (%) | $E_y$ (MPa) | $U_T$ ($10^4$, J/m$^3$) |
|---|---|---|---|---|
| 0 (pure PVA) | 26.51 ± 2.90 | 385.85 ± 34.46 | 32.34 ± 4.65 | 5,435.49 ± 175.65 |
| 5 (wt%) TA/PVA | 30.76 ± 1.27 | 350.17 ± 36.55 | 128.73 ± 31.77 | 6,940.38 ± 158.35 |
| 10 (wt%) TA/PVA | 34.73 ± 3.20 | 374.98 ± 31.86 | 150.51 ± 18.68 | 8,959.64 ± 361.88 |
| 15 (wt%) TA/PVA | 32.59 ± 1.69 | 261.13 ± 21.83 | 189.57 ± 1.00 | 5,678.72 ± 248.26 |
| 20 (wt%) TA/PVA | 34.94 ± 3.40 | 244.24 ± 22.45 | 206.05 ± 12.63 | 5,084.57 ± 188.61 |

Abbreviations: $E_y$, Young's modulus; $\varepsilon_r$, strain at break; PVA, polyvinyl alcohol; TA, tartaric acid; $\sigma_T$, tensile strength; $U_T$, toughness.

| $\varepsilon_{pe}$ (%) | $\sigma_T$ (MPa) | $\varepsilon_r$ (%) | $E_y$ (MPa) | $U_T$ ($10^4$, J/m$^3$) |
|---|---|---|---|---|
| 0(unstretched) | 26.51 ± 2.90 | 385.85 ± 34.46 | 32.34 ± 4.65 | 5,435.49 ± 175.65 |
| 20 | 29.40 ± 3.67 | 432.84 ± 5.72 | 16.63 ± 0.81 | 5,352.7 ± 263.35 |
| 100 | 25.47 ± 2.40 | 399.38 ± 44.12 | 24.25 ± 1.76 | 4,469.1 ± 263.79 |
| 150 | 27.93 ± 1.40 | 352.11 ± 33.90 | 27.79 ± 3.57 | 4,110.0 ± 302.71 |
| 200 | 30.11 ± 1.59 | 256.63 ± 13.35 | 34.72 ± 2.06 | 3,819.0 ± 377.65 |
| 250 | 36.86 ± 2.57 | 143.03 ± 24.15 | 45.10 ± 1.75 | 3,275.0 ± 578.65 |
| 300 | 40.16 ± 4.20 | 135.81 ± 9.09 | 48.05 ± 0.81 | 2,585.3 ± 272.61 |

**TABLE 6** The effect of prestretching on the tensile characteristics values with *SD* of pure PVA films

Abbreviations: $E_y$, Young's modulus; $\varepsilon_r$, strain at break; PVA, polyvinyl alcohol; TA, tartaric acid; $\sigma_T$, tensile strength; $U_T$, toughness.

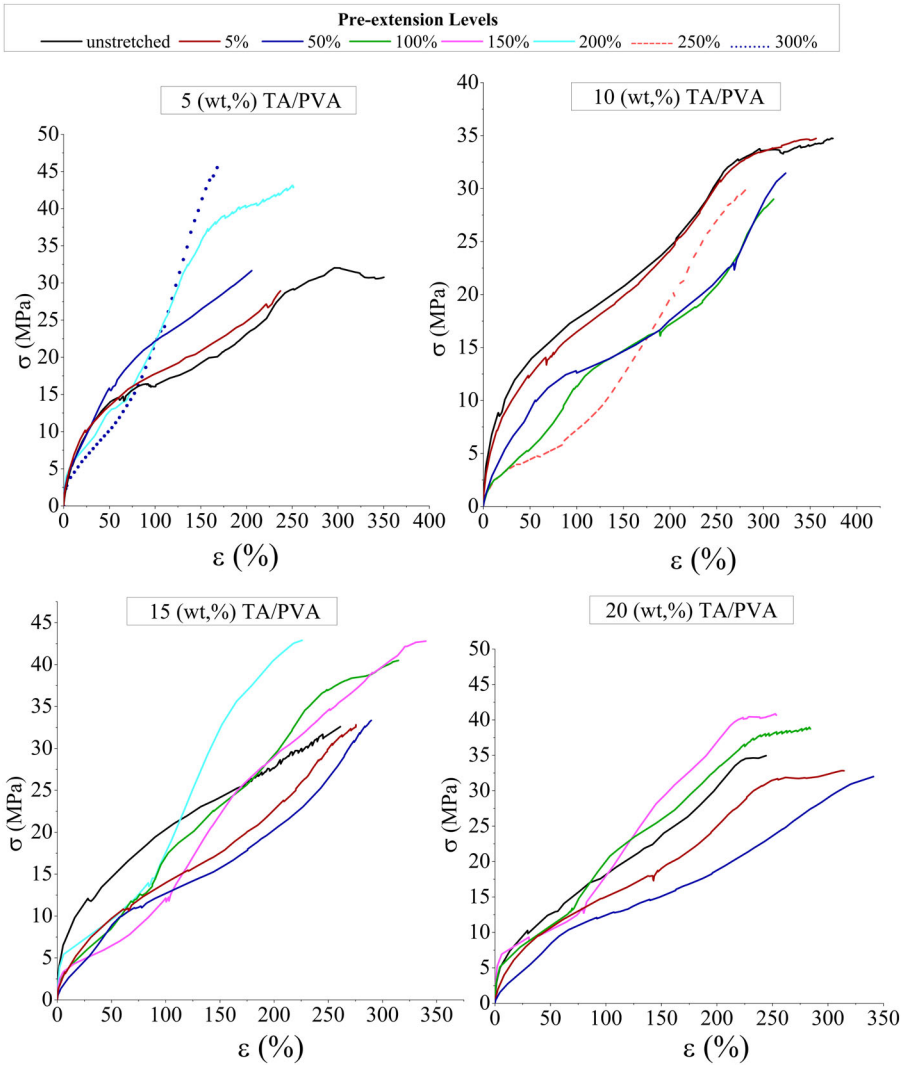



**FIGURE 9** Influence of preextension on the stress-strain curves of TA/PVA composite films. PVA, polyvinyl alcohol; TA, tartaric acid [Color figure can be viewed at wileyonlinelibrary.com]

modulus after the stretched composite film was extended again during the tensile test. It should be noted that the Young's modulus slightly increased and tensile strength tended to increase, because it is assumed that previously extended and stressed at a very high level such as 250%, polymer chains became closer and it led to increase in the strength of intermolecular interactions via hydrogen bonding between especially PVA chains.

When the low preextension level from 5 to 50% is applied to 15–20 wt% TA/PVA composite films, similar characteristics were seen on the stress–strain curves and mechanical properties, that is, corresponding stress–strain curves were placed under that of the unstretched 5–20 wt% TA/PVA composite films with higher extensibility and lower stiffness. Application of $\varepsilon_{pe}$ higher than 50% up to 150% leads to not only breaking of

**TABLE 7** Influence of preliminary extension ($\varepsilon_{pe}$) on the tensile characteristics values with *SD* of TA/PVA composite films

| Specimen | $\varepsilon_{pe}$(%) | $\sigma_T$ (MPa) | $\varepsilon_r$ (%) | $E_y$ (MPa) | $U_T$ ($10^4$, J/m$^3$) |
|---|---|---|---|---|---|
| 5 (wt%) TA/ PVA | 0[a] | 30.76 ± 1.27 | 350.17 ± 36.55 | 128.73 ± 31.77 | 6,940.38 ± 158.35 |
| | 5 | 28.93 ± 1.04 | 237.00 ± 11.23 | 142.72 ± 23.89 | 4,101.76 ± 227.80 |
| | 50 | 31.66 ± 4.47 | 205.63 ± 23.35 | 231.50 ± 32.40 | 5,526.25 ± 320.53 |
| | 200 | 42.49 ± 4.19 | 251.36 ± 22.90 | 337.16 ± 58.23 | 6,658.86 ± 102.59 |
| | 300 | 43.74 ± 3.97 | 168.92 ± 6.188 | 160.18 ± 30.97 | 3,473.57 ± 458.11 |
| 10 (wt%) TA/ PVA | 0[a] | 34.73 ± 3.20 | 374.98 ± 31.86 | 150.51 ± 18.68 | 8,959.64 ± 361.86 |
| | 5 | 34.50 ± 1.62 | 356.38 ± 38.99 | 150.15 ± 15.97 | 7,708.14 ± 376.44 |
| | 50 | 31.45 ± 6.50 | 323.79 ± 3.18 | 92.13 ± 10.24 | 5,135.37 ± 340.40 |
| | 100 | 29.00 ± 0.17 | 310.93 ± 59.63 | 38.63 ± 8.64 | 4,443.23 ± 250.24 |
| | 250 | 30.33 ± 1.76 | 286.13 ± 35.03 | 53.62 ± 4.75 | 4,279.44 ± 211.81 |
| 15 (wt%) TA/ PVA | 0[a] | 32.59 ± 1.69 | 261.13 ± 21.83 | 189.57 ± 1.00 | 5,678.72 ± 248.26 |
| | 5 | 32.81 ± 0.72 | 275.48 ± 15.52 | 114.16 ± 4.20 | 5,445.02 ± 391.42 |
| | 50 | 33.34 ± 3.19 | 289.69 ± 7.26 | 94.97 ± 17.87 | 5,620.58 ± 280.50 |
| | 100 | 40.33 ± 3.36 | 314.70 ± 31.38 | 100.80 ± 14.67 | 6,247.49 ± 350.20 |
| | 150 | 42.34 ± 3.97 | 339.94 ± 21.15 | 138.39 ± 34.04 | 6,663.73 ± 308.60 |
| | 200 | 42.90 ± 5.57 | 225.84 ± 26.15 | 154.27 ± 0.73 | 6,102.11 ± 296.50 |
| 20 (wt%) TA/ PVA | 0[a] | 34.94 ± 3.40 | 244.24 ± 22.45 | 206.05 ± 12.63 | 5,084.57 ± 188.61 |
| | 5 | 32.84 ± 3.92 | 314.63 ± 23.81 | 102.22 ± 11.30 | 5,656.80 ± 525.07 |
| | 50 | 32.00 ± 1.30 | 341.68 ± 30.13 | 62.00 ± 13.76 | 5,726.49 ± 360.40 |
| | 100 | 37.70 ± 4.09 | 284.00 ± 30.60 | 247.04 ± 15.77 | 5,917.04 ± 417.39 |
| | 150 | 40.85 ± 1.43 | 253.66 ± 18.20 | 271.88 ± 17.40 | 6,033.43 ± 770.16 |

[a]Unstretched.

Abbreviations: $E_{y,}$ Young's modulus; $\varepsilon_{r,}$ strain at break; PVA, polyvinyl alcohol; TA, tartaric acid; $\sigma_T$, tensile strength; $U_T$, toughness.

intermolecular crosslinks but also straining of polymer chains and orientation of ordered regions along stretching direction. Hence, the structure obtained more stressed and strained polymer chains. It is clear that in order to extend such chains during subsequent tensile deformation, more stress is required. That is why the tensile strength and Young's modulus increased.

### 3.1.6 | The recovery characteristics of TA/PVA composite films

Considering the studies in the literature, it is seen that although there are a few studies about the stress-relaxation process of PVA and films not including TA,[17,18] there is not any study investigating the recovery process of not only PVA but also TA/PVA composite films. Thus, the recovery processes of PVA and TA/PVA composite films were carried out in detail in the present study.

The family of recovery curves of pure PVA from different preextension level is represented in Figure 10. In order to understand the velocity of the recovery process, the curves were presented in $\varepsilon$ and $\log t/t_1$ coordinates where $t_1$ was taken as 1 min. It is seen from the curves presented in the logarithmic scale, the recovery process is characterized by two regions, that is, fast and slow recovery regions. Here, fast recovery starts from seconds and continues up to 0.5–1 hr for all applied preextension levels. Beyond this region, a very slow-recovery process takes place and continues up to a very long time. For after the application of preextension level of $\varepsilon_{pe}$ = 5%, because such small deformation in the first linear region of stress–strain curve is fully recoverable, pure stretched PVA sample was completely recovered and it obtained initial length. In order to deduce the information about the velocities of the recovery process, the recovery curves are fitted by linear equations with a simple form.

$$\varepsilon = \varepsilon_i - A_i \log t. \quad (2)$$

Here, $A_i$ is the slope of each curve and indicates the velocity of fast and slow recovery processes. The $A_i$ values for fast and slow recovery processes are given in Table 8.

As $\varepsilon_{pe}$ increases from 50 to 200%, the velocity of the fast recovery process increases approximately 10-fold. However, the velocity of the slow process increased approximately 3.5-fold. We think that the fast recovery is due to elastic and recoverable deformation in the stretched films/structure. However, high deformation leads to great structural changes such as sliding and straining of polymer chains, orientation of amorphous and crystallite regions, and some bond breakages. These structural changes cause the plastic deformation. Since this plastic deformation cannot be recovered completely for long times. Although some part of this deformation is recovered, we obtained some residual deformation, which is time dependent.

In order to comprehend the influence of TA concentration on the recovery process of TA/PVA composite films, the recovery curves of films with TA concentration from 5 to 20% were obtained which are given Figure 11. Similar to that of pure PVA, commonly two recovery regions were seen. The recovery from different strain levels occurred quickly in the first hour and then the recovery continued very slowly. The slopes ($A$) of linear curves are calculated for both regions and are given in Table 8.

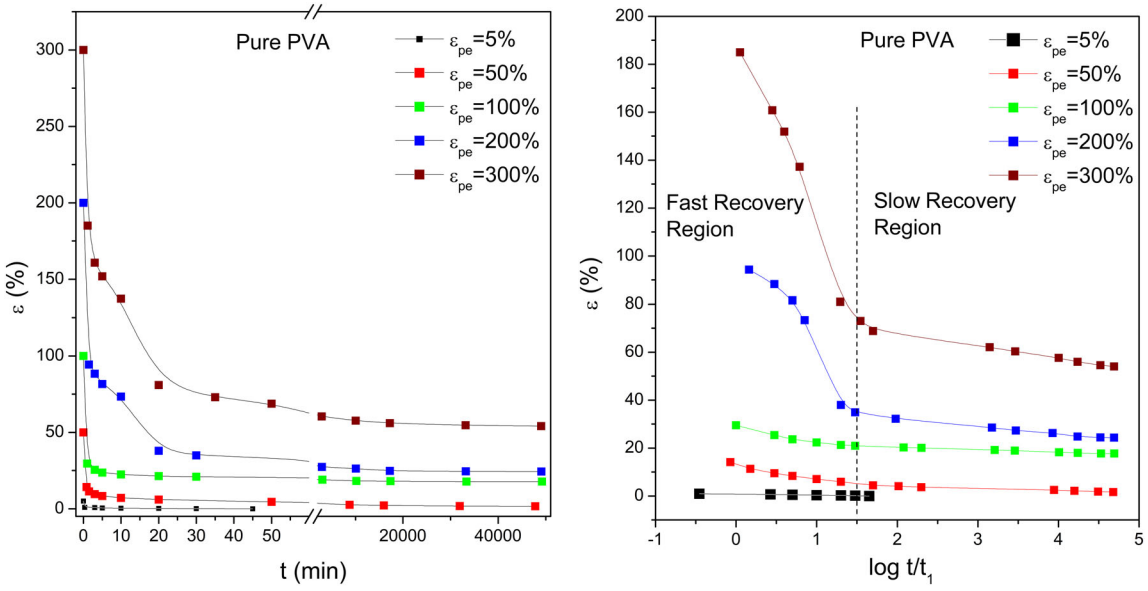



**FIGURE 10** Recovery curves of pure PVA presented in time scale (min) (left) and logarithmic scale (right). PVA, polyvinyl alcohol [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 8** Slopes ($A$) of the linearly fitted recovery curves in fast and slow regions of TA/PVA composite films

| $A_{fast}$ | | | | | |
|---|---|---|---|---|---|
| **$\varepsilon_{pe}$(%)** | **Pure PVA** | **5 (wt%) TA** | **10 (wt%) TA** | **15 (wt%) TA** | **20 (wt%) TA** |
| 5 | 0.443 | 0.576 | 1.057 | 0.852 | 0.702 |
| 50 | 5.183 | 9.789 | 5.344 | 4.313 | 3.824 |
| 100 | 5.721 | 18.157 | 18.602 | 11.210 | 12.607 |
| 200 | 50.428 | 51.248 | 44.628 | 40.636 | b |
| $A_{slow}$ | | | | | |
| $\varepsilon_{pe}$(%) | Pure PVA | 5 (wt%) TA | 10 (wt%) TA | 15 (wt%) TA | 20 (wt%) TA |
| 5 | a | 0.034 | 0.114 | 0.066 | 0.047 |
| 50 | 0.874 | 1.138 | 0.653 | 0.334 | 0.274 |
| 100 | 1.020 | 1.622 | 1.119 | 0.511 | 0.330 |
| 200 | 3.019 | 5.641 | 5.658 | 2.317 | b |

[a]Recovered completely.
[b]Could not be tested.
Abbreviations: PVA, polyvinyl alcohol; TA, tartaric acid.

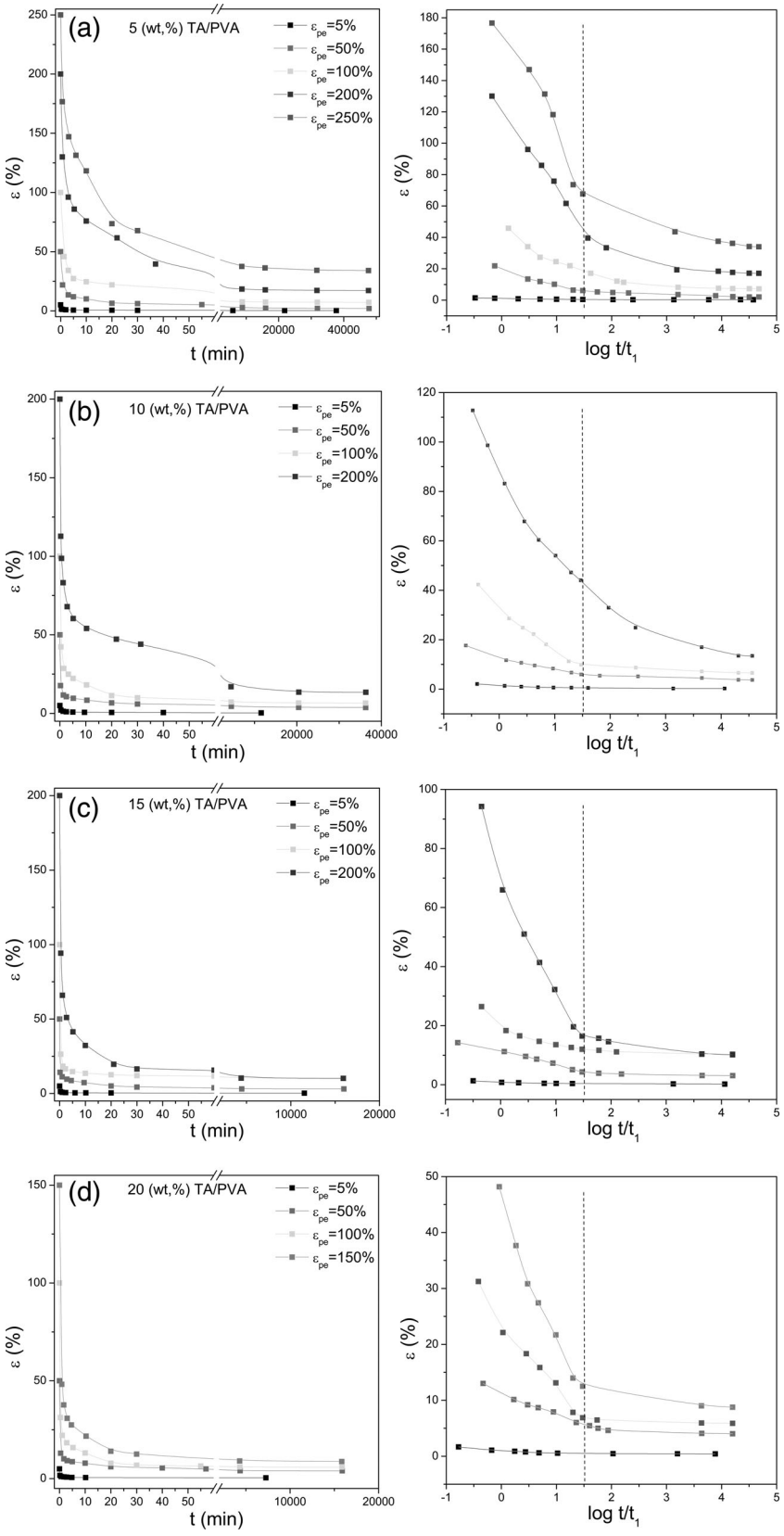



**FIGURE 11** Recovery curves of TA/PVA composite films presented in time scale (min) and logarithmic scale: (a) 5 (wt%) TA/PVA, (b) 10 (wt%) TA/PVA, (c) 15 (wt%) TA/PVA, and (d) 20 (wt%) TA/PVA. PVA, polyvinyl alcohol; TA, tartaric acid

As the preextension level increased, the slopes indicator of the velocity of the recovery process increased for fast and slow regions. It is seen in Table 8 that as $\varepsilon_{pe}$ increase from 50 to 200%, the slopes of the fast recovery process show a similar increasing tendency. For constant strain levels such as 50–100%, it is seen that although the velocity of the slow recovery process has a decreasing tendency, it shows a great decrease for TA concentration

equal and greater than 15 (wt%). It is known from the XRD measurements that the relative crystallinity decreases with increasing TA content. However, the interaction of TA molecules with PVA chains leads to an increase in the rigidity of the structure by the formation of crosslinking. Hence, the decrease in the extensibility of the structure was seen. After stretching the composite film at high-strain levels, in addition to changes in the molecular order and interaction such as orientation, straining, and relative sliding of macromolecules, some bond breakages occur. It is assumed that increasing crosslinking density leads to more networks between PVA matrices. This helps to accelerate the fast recovery including recoverable small deformations in the structure. Although there is a recoverable deformation in the stretched structure, some plastic deformation due to the slow molecular recovery process and some chemical bond breakages take place. This plastic deformation leads to some very high residual deformation on the composite film structure. From the comparison of residual deformations from applied strain levels for TA/PVA composite films, increasing the TA concentration enhances the recovery process and leaves less residual deformations in the structure. It is apparently seen in Figure 12 that with increasing the TA concentration equal and greater than 10 (wt%), residual deformation decrease more. In order to the effect of TA concentration on the recovery process of PVA composite film, as an example, the recovery time for a complete recovery from 200% strain level was calculated for pure PVA and 15 wt% TA/PVA by substituting the parameters from Table 8 in the linear Equation (2). It was determined that the complete recovery at room conditions took a very long time for both specimen, it was estimated approximately as $10^{12}$ min for pure PVA and $10^{8}$ min for 15 wt% TA/PVA composite film. It shows that increasing TA concentration significantly improved the recovery properties of pure PVA.

## 4 | CONCLUSIONS

By considering the results of thermal analysis, the temperature values of the peaks corresponding to each degradation region were shifted to higher values and it can be concluded that the thermal stability of pure PVA is improved due to the crosslinking formation between pure PVA matrix and TA molecules. By using the data of XRD analysis, it was seen that with increasing TA concentration, the crystallinity is decreased from 34.4 to 14.8%. Besides, it was obtained from FTIR spectra that the degree of crosslinking ($A_{1715}/A_{3290}$) significantly increased with increasing TA concentration, which enhanced the mechanical properties.

From the measurements of the tensile characteristics of TA/PVA composite films, the tensile strength was improved from 26.51 to 34.95 MPa and the Young's modulus increased greatly from 32.34 to 206.05 MPa. However, the extensibility of the films was decreased from 385.85 to 244.24%. It was seen that preliminary extension or deformation has an important effect not only on the stress–strain curves but also on the tensile characteristic of both pure PVA and TA/PVA composite films. Although the stress–strain curves and tensile characteristics of the films were similar to those of unstretched films for the low $\varepsilon_{pe}$ value up to 20%. However, higher $\varepsilon_{pe}$ value than 50% lead to significant increase in tensile strength but decrease in extensibility. This is mainly due to straining of polymer chains and orientation of ordered regions along stretching direction, hence, the obtaining more stressed and stretched polymer chains and structure.

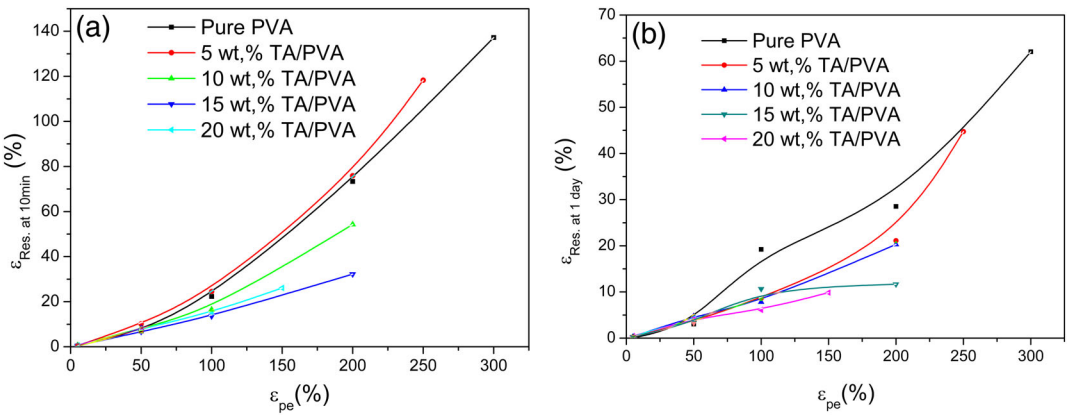



**FIGURE 12** The effect of various TA concentration on the residual (remaining) deformation ($\varepsilon_{res}$) after recovery time of 10 min (a) and of 1 day (b). TA, tartaric acid [Color figure can be viewed at wileyonlinelibrary.com]

By considering the recovery process of the films, the fast recovery process occurs within almost 30 min and the slow process continues in time with a very slow velocity, which results in time dependent residual deformation. It was seen that higher the applied $\varepsilon_{pe}$ level, the velocity of recovery processes gets higher. It was also observed that increasing TA concentration accelerated the recovery process, hence, improved the recovery properties of pure PVA. Thus, the use of TA in the membrane applications with PVA can be advantages in the reusability of these membranes, since the addition of TA enhanced the recovery properties of PVA. Furthermore, by using the obtained linear equation for the slow recovery process, one can estimate the recovered part of the applied deformation and remaining deformation at any time during recovery process.

## ORCID

*Altan Bozdoğan* https://orcid.org/0000-0002-6493-0210
*Baki Aksakal* https://orcid.org/0000-0003-1255-541X
*Cenk Denktaş* https://orcid.org/0000-0001-9255-4374
*Yavuz Salt* https://orcid.org/0000-0002-1375-6953

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