

Poly(vinyl alcohol) – poly(vinyl acetate) composite films from water systems: formation, strength-deformation characteristics, fracture

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Abstract. The object of investigation was thin ($< 200\ \mu\text{m}$) films, formed by casting from water based mixtures of poly(vinyl alcohol) (PVA) water solution and poly(vinyl acetate) (PVAc) water suspension. Starting systems hence were suspensions of plasticized PVAc particles in PVA water solution. Systems with full range of PVAc volume fraction ϕ_{PVAc} were studied. Kinetic relationships of several parameters which characterize film formation in drying process were compared and scrutinized. It revealed that the main factor which restrains coalescence of PVAc particles in the composite is high viscosity of PVA water solution at the final stage of composite structure formation. In tensile deformation conditions PVA/PVAc systems behave as being PVA matrix composites in a whole range of PVAc content. Use of *Kerner* approach, based on the self-consistency idea, for the analysis of $E_{\text{COMP}}(\phi_{\text{PVAc}})$ relation, confirms the continuity of PVA matrix.

1. Introduction

Poly(vinyl alcohol) (PVA) is the most widely produced water soluble polymer today. PVA is a polymer of a great interest because of its many desirable characteristics: high mechanical properties, biodegradability, excellent gas barrier properties, transparency. Creating of blend systems with other polymers is promising way of modification of strength-deformation properties of PVA. Blends of PVA with different linear polymers were investigated for different purposes [1-4].

In the present study, blends of PVA with the plasticized poly(vinyl acetate) (PVAc) were investigated. PVA/PVAc film specimens were manufactured by casting blends of a PVA water solution and a PVAc water suspension. At room temperature the components form separate phases [5]. The purpose of the present study is to estimate the structure and its correlation with certain strength- deformation characteristics of PVA/PVAc blend films.

2. Materials and Investigation Methods

PVA with a molecular weight of 133,000 Da and a content of acetate groups 0.98%, as well as a PVAc (containing 10% of a dioctyl phthalate as plasticizer) water suspension were used as initial materials. A water solution of PVA was mixed with a PVAc suspension (10% of polymer in both cases) in different proportions providing the specified volume fraction of the components (ϕ_{PVA} and ϕ_{PVAc}) in the blend. The films were obtained by casting: the blends were poured into *Petri* dishes 140 mm in diameter (the initial thickness of the layer was 2mm) and dried at 17°C up to a constant content of water ($\approx 3\%$). The thickness of obtained films was $150 \pm 10\ \mu\text{m}$. Water content $W_{\text{H}_2\text{O}}$ in the drying system were determined by continuous weighing. Viscosity μ of PVA water solution as function of $W_{\text{H}_2\text{O}}$ was determined using Thermo HAAKE VT 550 rotary viscometer at 25°C with cylinders SC4-18, SC4-34, ULA-34.

The films were tested in tension on a Zwick/Roell universal machine at room temperature according to ENISO527. The speed of the mobile crosshead was 20mm/min. The data obtained were processed by using the test XpertV11.0 program. The stress-strain relationship σ - ϵ was determined up

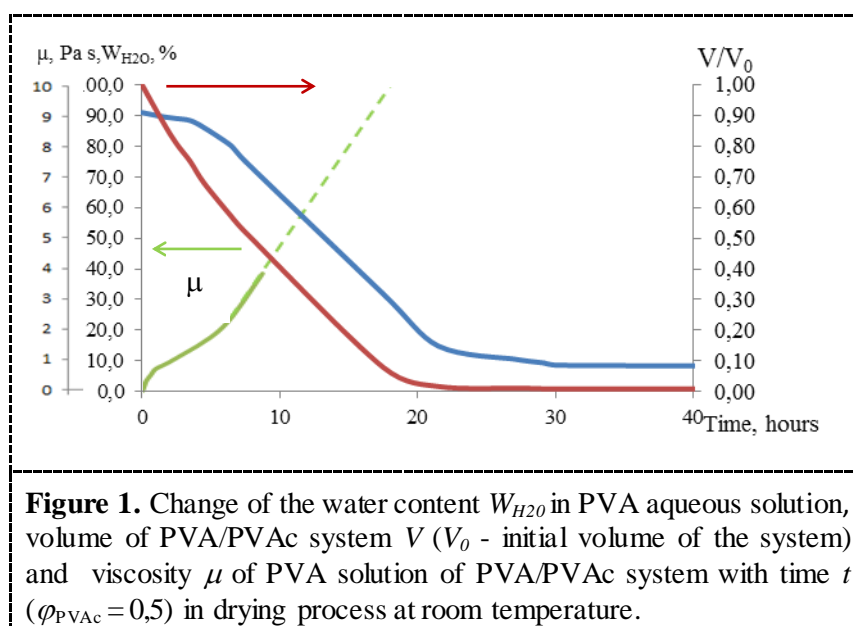


to the failure of specimens. All mechanical characteristics were found on the basis of five parallel measurements.

SEM was used to determine morphology of PVA/PVAc systems. The specimens were cooled in liquid nitrogen and subjected to a brittle fracture. The fracture surfaces were gold covered (Emitech,K550X). Samples were examined on a Tescan, Mira/LMU Schottky, scanning electron microscope at 3000 \times and 10,000 \times magnifications and a voltage of 25 kV.

3. Discussion of the Results

Change in time of the most important parameters of the drying PVA/PVAc (for $\phi_{PVAc} = 0,5$) layer with is shown in figure 1 as an example.



In a course of drying the water content in PVA solution decreases, content of PVAc particles in the suspension grows, the distance between particles decreases. The greater is the volume fraction of PVAc (ϕ_{PVAc}) in PVA/PVAc system the smaller the final average distance between the PVAc particles. Up to $\phi_{PVAc} < 0.7$ plasticized PVAc particles are more or less evenly dispersed in PVA medium. Associates PVAc particles did not observed. Evidently closer merger of particles is hindered by large viscosity of PVA solution. Particles retain the original spherical shape (figure 2 a - e).

The situation changes when ϕ_{PVAc} value is greater. The same complex of interfacial and capillary forces, which determines the PVAc film formation from pure suspension, begins to play a decisive role. The difference is that instead of water there is PVA water solution, which viscosity and surface tension are changing during the drying process. PVAc particles are gradually deformed while moving towards each other, resulting in a form that is close to polyhedron. Thickness of PVA interlayer decreases (see figure 2 e,f).

From figure 2 f it is seen that direct contact particles and coalescence of PVAc does not happen, even at $\phi_{PVAc} = 0,9$ and the PVA interlayer between PVAc particles remains. SEM micrographs of PVA/PVAc system with $\phi_{PVAc} = 0,9$ (figure 2 f) and pure PVAc (figure 2 g) shows that the morphology of corresponding systems differs. In the system with $\phi_{PVAc} = 0,9$ PVA particles are less compactly arranged and PVA interlayer persists.

The values of tensile elastic modulus E of composites are between the E values of rigid PVA ($E_{PVA} = 2,3$ MPa) and compliant PVAc ($E_{PVAc} = 0,3$ MPa). E value decreases with an increase of ϕ_{PVAc} : namely, increase of content of compliant component in the rigid matrix (figure 3).

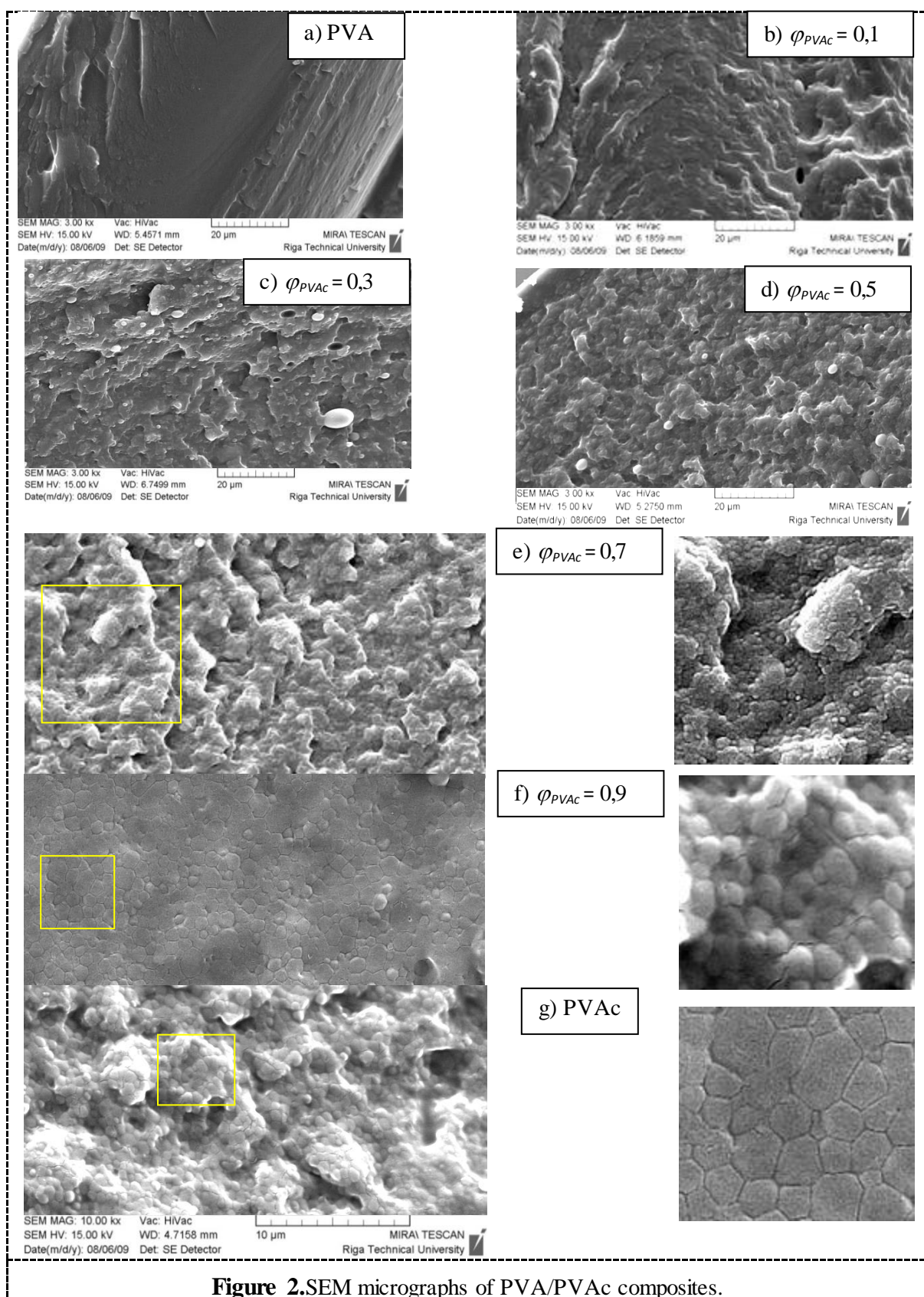
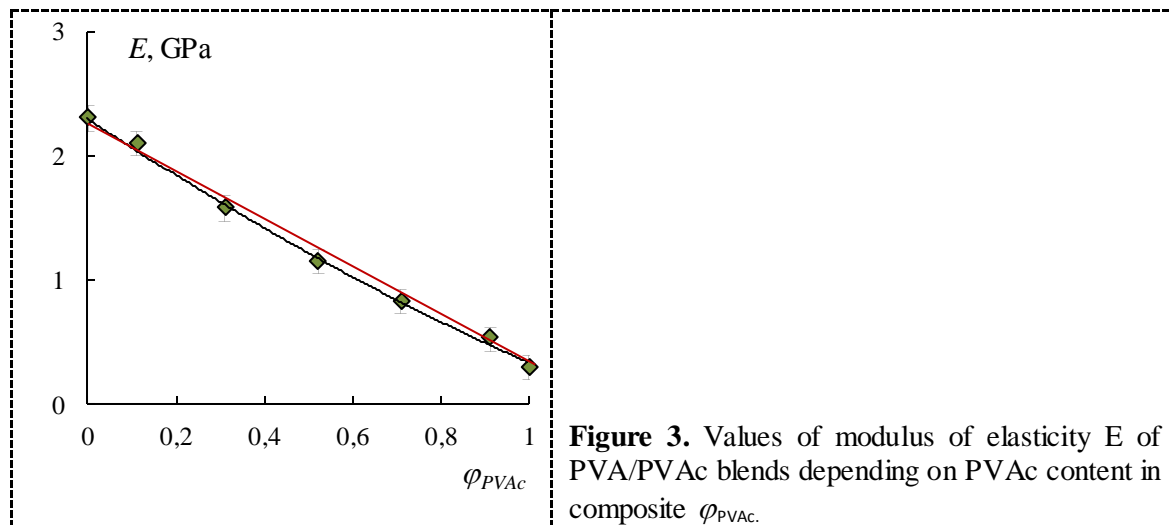


Figure 2. SEM micrographs of PVA/PVAc composites.



The dependence of composite tensile elastic modulus E on φ_{PVAc} is close to additive one (red straight line):

$$E = E_{PVA} - (E_{PVA} - E_{PVAc}) \varphi_{PVAc} \quad (1)$$

Thereby from the point of view of rigidity the studied composite essentially is rigid PVA matrix in which more compliant PVAc particles are included.

To confirm the continuity of PVA matrix *Kerner* approach (based on the self-consistency idea [6]), was used for the analysis of $E(\varphi_{PVAc})$ relation.

The value of modulus of elasticity E^* of composite in accordance with *Kerner* model is calculated as follows:

$$E^* = \frac{9KG}{3K + G} \quad (2)$$

Where: K – calculated value of bulk elasticity modulus and G – calculated value of shear elasticity modulus of composite.

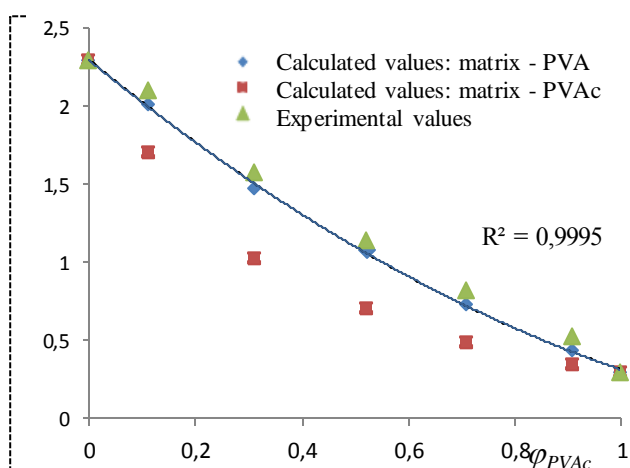


Figure 4. Calculated values (*Kerner* model) of modulus of elasticity E^* compared with the experimentally determined modulus of elasticity E values at different PVAc content in the composite (φ_{PVAc}).

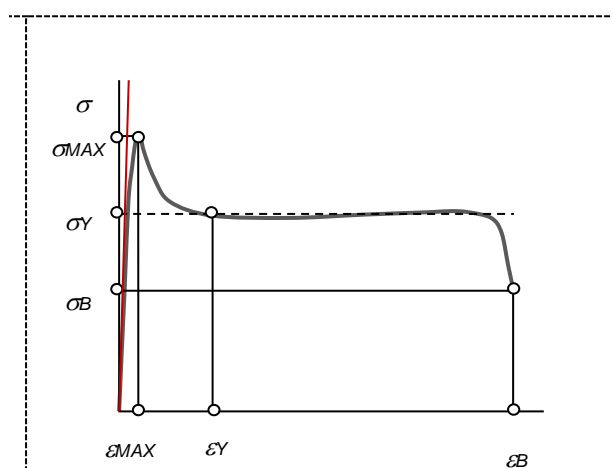


Figure 5. Schematic representation of $\sigma(\varepsilon)$ curve of PVA/PVAc composite and obtainable characteristics: $(E = \lim (d\sigma/d\varepsilon)|_{\varepsilon \rightarrow 0})$.

Calculation of K , G and E^* values were performed in two ways: either assuming that one of the components is a “matrix”(index-m) and the other is “filler”, included in the matrix (index - f) or vice versa (components alternate status).

K and G values of composite were calculated as functions of K_f , K_m , G_m and φ_f (volume fraction of „filler”). K and G values of PVA and PVAc were calculated as follows:

$$K_{PVAc} = E_{PVAc} / 3(1 - 2 \nu_{PVAc}) \quad (3)$$

$$K_{PVA} = E_{PVA} / 3(1 - 2 \nu_{PVA}) \quad (4)$$

$$G_{PVAc} = E_{PVAc} / 2(1 + \nu_{PVAc}) \quad (5)$$

$$G_{PVA} = E_{PVA} / 2(1 + \nu_{PVA}) \quad (6)$$

Where: E_{PVAc} un E_{PVA} – accordingly experimental values of tensile elastic modulus of PVAc and PVA: $E_{PVAc} = 0,3\text{GPa}$, $E_{PVA} = 2,3\text{GPa}$. ν_{PVA} un ν_{PVS} – accordingly PVA and PVS Poisson coefficient values: $\nu_{PVAc} = 0,16$ [7] and $\nu_{PVS} = 0,44$.

Experimental values of modulus of elasticity are very close to the calculated values in the case where the matrix is PVA (see figure 4). This is a serious evidence, that PVA remains as a continuous composite matrix in a wide range of PVA content (at least at $\varphi_{PVAc} > 0,1$).

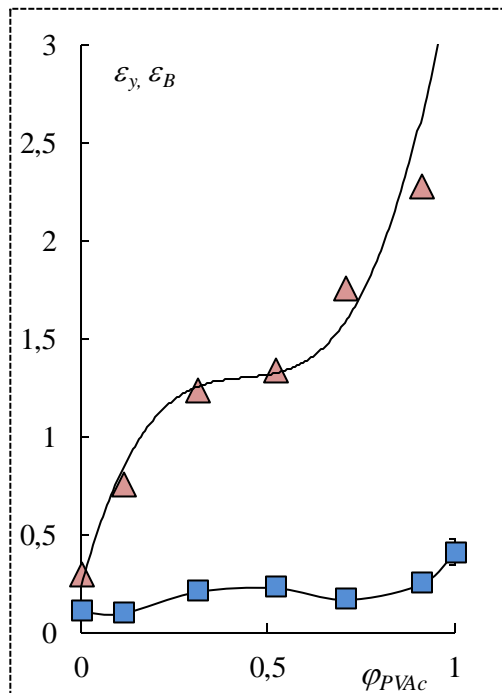


Figure 6. Dependence of relative elongation values on composite content.

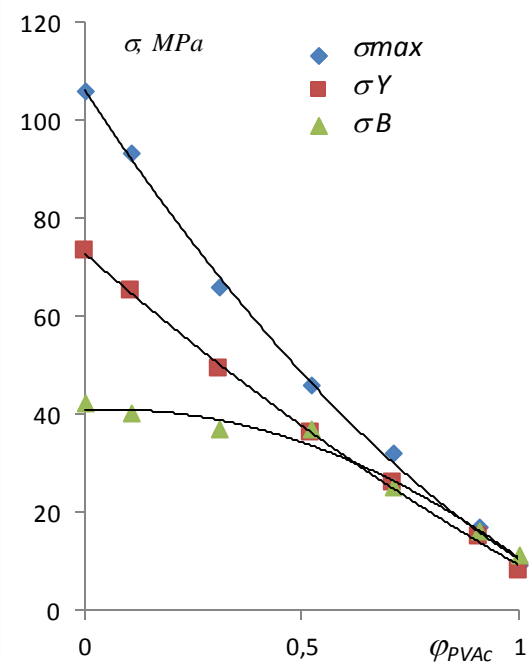


Figure 7. Dependence of σ_{MAX} , σ_Y un σ_B on volume fraction of PVAc in composite.

Deforming the composite over ε_{MAX} and yield elongation ε_Y (see figure 5) the PVA frame gradually locally crashes at stress values between σ_{MAX} (maximum stress,) and σ_Y (yield stress, figure 7). It occurs in locations where the deformation value exceeds the PVA relative elongation at break $\varepsilon_{BPVA} = 0,29$. PVAc particles start to deform (relative elongation at break of PVAc is more than ten times higher $\varepsilon_{BPVAc} = 3,6$) (see figure 6).

The σ_{MAX} and σ_Y values are determined by PVA matrix frame. The lower volume fraction of PVA matrix (φ_{PVA}) in the composite (less effective load-carrying part of frame), the lower are σ_{MAX} and σ_Y values.

At higher ε values composite loses integrity and collapses at comparatively low stress

value (σ_B), either by fracture of PVAc particles or by flinch them from PVA matrix. Obtained results suggest slight change in the data interpretation of paper [8].

4. Conclusions

Up to PVA volume fraction 0,7 PVA/PVAc composite consists of PVA matrix in which not deformed PVAc particles more or less evenly are distributed. At higher content of PVAc interfacial forces deforms spherical particles close to polyhedron. The main factor which restrains coalescence of PVAc particles is high viscosity of PVA water solution at the final stage of composite structure formation.

PVA remains as a composite matrix in a wide range of PVA content ($\phi_{PVAc} > 0,1$). The dependence of composite tensile elastic modulus E_{COMP} on ϕ_{PVAc} is very close to additive one: $E_{COMP} = E_{PVA} - (E_{PVA} - E_{PVAc}) \phi_{PVAc}$. Composite essentially is a rigid PVA frame in which much more compliant PVAc particles are included.

Correlation analysis of characteristics, obtained from stress–strain relations for composites with various PVAc content shows that fracture of composites starts with break of less deformable load-bearing PVA frame at comparatively small elongation and continues with significant deformation of PVAc component. This feature becomes more pronounced with increase of PVAc content.

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