Journal of Chemistry and Technologies, 2026, *34*(2), 365-374

Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua
editorial e-mail: chem.dnu@gmail.com

UDC 678+547+541; 678.744.72, 547(391.1+39`05+572.1), 541(64+68)

BENZOPHENONE-INITIATED PHOTO-CROSSLINKING OF PVA COMPOSITIONS AND THE PROPERTIES OF THE OBTAINED HYDROGELS

Vasyl O. Vaskiv, Dmytro I. Saiuk, Viktor S. Tokarev*
Lviv Polytechnic National University, 12 S. Bandery str., Lviv 79013, Ukraine
Received 30 January 2026; accepted 15 April 2026; available online 20 June 2026

Abstract

This study aimed to develop photo-crosslinkable hydrogel compositions based on polyvinyl alcohol (PVA), the photoinitiator benzophenone (BP) and functional acrylic monomers, namely acrylic acid (AA), 2-hydroxyethyl methacrylate (HEMA), methylene-bis-acrylamide (MBA). A gradual increase in the content of gel fraction with UV irradiation time was observed for all composite films, indicating progressive crosslinking. PVA compositions with BP and AA, demonstrated the lowest content and the slowest increase in the gel fraction. The addition of MBA resulted in rapid crosslinking and the highest gel fraction content, whereas HEMA-containing compositions required longer irradiation times to achieve comparable levels of crosslinking. Water absorbability depended on both film composition and gel fraction. Films containing BP, AA, and HEMA exhibited the highest water absorbability. Compositions containing BP, AA, and MBA demonstrated the best water resistance, the highest tensile strength and hardness, and the lowest elongation at break, indicating the formation of highly crosslinked hydrogel networks.
Keywords: polyvinyl alcohol; benzophenone; functional acrylic monomer; photo-crosslinking; polymer hydrogel composition; swelling kinetics.

ІНІЦІЙОВАНЕ БЕНЗОФЕНОНОМ ФОТО-ЗШИВАННЯ КОМПОЗИЦІЙ ПВА ТА ВЛАСТИВОСТІ ОТРИМАНИХ ГІДРОГЕЛІВ

Василь О. Васьків, Дмитро І. Саюк, Віктор С. Токарев
Національний університет "Львівська політехніка", вул. С. Бандери, 12, Львів, 79012, Україна

Анотація

Метою цього дослідження було розроблення композиції гідрогелів, здатних до фотозшивання, на основі полівінілового спирту (ПВА), фотоініціатора бензофенону (БФ) та функційних акрилових мономерів, а саме акрилової кислоти (АК), 2-гідроксиетилметакрилату (ГЕМА), метилен-біс-акриламіду (МБА). Для всіх композитних плівок спостерігалося поступове збільшення вмісту фракції гелю з часом УФ-опромінення, що свідчить про їх прогресивне зшивання. Композиції ПВА з БФ та АК показали найменший вміст та найповільніше зростання гелевої фракції. Додавання МВА призвело до швидкого зшивання та найвищого вмісту гелевої фракції, тоді як композиція з ГЕМА вимагала довшого часу опромінення для досягнення порівнянного рівня зшивання. Поглинання води залежало як від складу плівки, так і від вмісту гель фракції. Плівки з БФ, АК та ГЕМА мали найвище водопоглинання. Композиції, що містили ВР, АА та МВА, демонстрували найкращу водостійкість, найвищу міцність на розрив і твердість, а також найменше видовження під час розриву, що свідчить про утворення сильно зшитих гідрогелів.
Ключові слова: полівініловий спирт; бензофенон; функціональний акриловий мономер; фотозшивання; полімерна гідрогелева композиція; кінетика набухання.

*Corresponding author e-mail: viktor.s.tokariev@lpnu.ua

doi: 10.15421/jchemtech.v34i2.351157

Journal of Chemistry and Technologies, 2026, *34*(2), 365-374

Introduction

Polyvinyl alcohol (PVA) is one of the most widely produced and applied synthetic water-soluble polymers, with global production exceeding millions of tons annually for nearly a century [1]. Despite its long industrial history, PVA continues to attract sustained scientific interest, which is reflected in a growing number of recent original papers, reviews and books devoted to its structure, modification, and applications [2–7]. This persistent relevance is explained by a unique combination of properties, including excellent film-forming ability, high enough chemical and thermal stability, pronounced hydrophilicity, non-toxicity, good biocompatibility, and versatility in forming hydrogels under diverse conditions. As a result, PVA is extensively used in engineering materials, medicine and pharmacy, cosmetics, biotechnology, membrane separation processes, water treatment technologies, and the food industry [4–8]. Recently, PVA has also sparked the interest of researchers as a matrix for nanocomposite production [7; 9–12].

PVA is a hydrophilic linear copolymer primarily composed of vinyl alcohol and residual vinyl acetate units, since it is produced by partial or complete hydrolysis of poly(vinyl acetate). The physicochemical properties of PVA, such as solubility, crystallinity, mechanical strength, and swelling behaviour, are mainly governed by two key parameters: the degree of polymerization and the degree of hydrolysis. Owing to the presence of hydroxyl groups along the macromolecular backbone, PVA is capable of forming extensive intermolecular and intramolecular hydrogen bonding networks. This feature makes PVA particularly suitable for the preparation of hydrogel materials – three-dimensional polymer networks capable of absorbing and retaining large amounts of water. However, linear PVA chains alone lack structural integrity in aqueous environments, and PVA solutions remain viscous sols prone to dissolution.

For the formation of stable PVA hydrogels, crosslinking of polymer chains is required. Various physical and chemical crosslinking approaches have been developed and extensively studied [2; 8; 13–18]. Physical crosslinking methods, such as freeze–thaw cycling and crystallization technique are attractive owing to the absence of potentially toxic reagents. However, physically crosslinked PVA hydrogels are generally characterized by limited stability and may undergo structural degradation or dissolution under changes in temperature, mechanical stress, or prolonged swelling. This significantly restricts their use in applications requiring long-term stability and reproducible properties.

Chemical crosslinking provides a more reliable route to obtain stable PVA hydrogels. Various chemical agents, including aldehydes, acids, and multifunctional crosslinkers, have been employed to form covalent interchain bridges. Among chemically crosslinked systems, hydrogels formed via radical mechanisms are of especial interest, since the resulting carbon–carbon crosslinks are resistant to hydrolysis and ensure enhanced mechanical and chemical stability. In this context, the use of polymer peroxides for crosslinking water-soluble polymers, including PVA, has been demonstrated to be an effective strategy for achieving high crosslinking densities and robust network structures [18]. The disadvantages of the peroxide-initiated thermal crosslinking are necessity applying quite high temperatures for quite long time, which increases energy consumption and limits the compatibility of the process with thermally sensitive additives or biological components.

An attractive alternative to thermal radical crosslinking is photo-induced crosslinking initiated by ultraviolet (UV) irradiation. Photo-crosslinking processes offer several important advantages, such as spatial and temporal control of network formation, relatively mild reaction conditions, and reduced energy input [13; 19–21]. These features make UV-initiated crosslinking to be perspective technique for the fabrication of hydrogels intended for biomedical, pharmaceutical, and advanced technological applications. To enable efficient photo-crosslinking, suitable photoinitiators must be incorporated into the PVA compositions. Among them, benzophenone and its derivatives are well-known type II photoinitiators capable of generating reactive radicals upon UV exposure through hydrogen abstraction reactions [22]. Due to their commercial availability, relatively low cost, and established photochemical behaviour, benzophenone-based systems represent a promising platform for the development of photo-crosslinked PVA hydrogels.

In addition to performance characteristics, modern materials science puts increasing emphasis on the simplicity, cost-effectiveness, and environmental sustainability of production technologies. The availability of starting materials, low energy consumption, and the possibility of avoiding harsh reaction conditions are critical factors for the large-scale implementation of

Journal of Chemistry and Technologies, 2026, *34*(2), 365-374

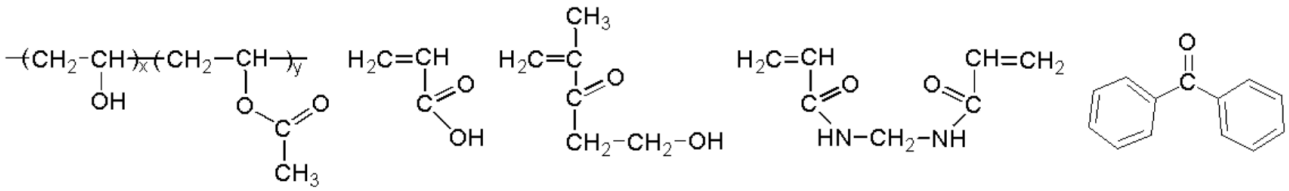
hydrogel materials. In this regard, photo-crosslinking of PVA appears to be a highly relevant approach that combines technological simplicity with the ability to tailor hydrogel properties by adjusting composition and irradiation parameters. Therefore, the development and investigation of PVA hydrogels obtained via UV-initiated photo-crosslinking remains an urgent and practically significant task.

The aim of this research was the development of photo-crosslinkable polymeric hydrogel compositions based on polyvinyl alcohol, a photoinitiator, and functional monomers; the study of their crosslinking under UV irradiation. Special attention was paid to the influence of the composition formulations and crosslinking conditions on the swelling behaviour, mechanical characteristics, and overall stability of the formed polymer networks, which are crucial for their potential application in advanced functional materials.

Materials and Methods

Polyvinyl alcohol (**PVA**) supplied by "JAPAN VAM&POVAL Co" brand JP-18 with the following characteristics: degree of hydrolysis x = 87.0–89.0 %, molecular weight – 80 kDa.

Acrylic monomers: acrylic acid (**AA**), 2-hydroxyethyl methacrylate (**HEMA**), methylene-bis-acrylamide (**MBA**), and the photoinitiator – benzophenone (**BP**) were obtained from Merck & Co. AA was vacuum distilled prior to use, other reagents were used as received.



PVA **AA** **HEMA** **MBA** **Benzophenone**

x = 88±1% x =12±1%

Photo-crosslinkable compositions were prepared by mixing a 10 % aqueous solution of PVA with a solution of BP in AA. The ratio of these components PVA : BP : AA was preferably 100 : 1 : 5, respectively. The compositions exhibited the necessary rheological properties that ensure the formation of uniform films. The compositions were coated onto glass substrates, dried, placed in a PE bag under an inert atmosphere, and then irradiated with a DRT-400 UV lamp at a distance of 10 cm. Experiments were conducted at room temperature; to prevent the samples from being heated by a UV lamp, they were cooled with a fan (see Fig. 1). After irradiation for a certain time, the samples were removed from the PE bags and subjected to tests for sol-gel fraction content, swelling ability, surface hardness, tensile strength, and maximum elongation.

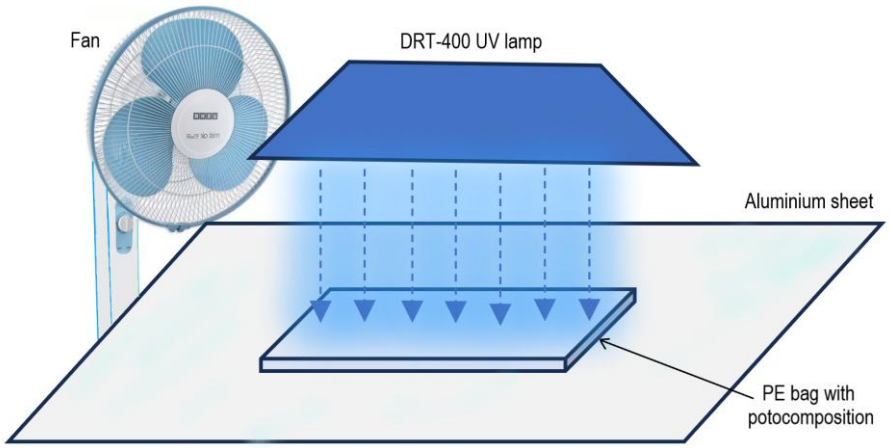


Fig. 1. Setup for photo-crosslinking of PVA film

To determine the sol-gel fraction, the samples were extracted using a Soxhlet extractor for 8 hours using distilled water as the extraction solvent. Subsequently, the samples were dried in an oven at 333 K until a constant weight was achieved. The gel fraction (G) was determined using the following equation:

$$G = \frac{Wf}{Wi} \times 100\% \qquad (1)$$

where: G – gel fraction content in the crosslinked polymer film, %; W_i – initial weight of

Journal of Chemistry and Technologies, 2026, *34*(2), 365-374

the polymer film before extraction, g; W_f – the weight of dried film after extraction, g.

The swelling of polymer hydrogels in distilled water was studied over a certain period of time. The swelling degree (S) was calculated using the following equation:

$$S = \frac{m_s - m_d}{m_d} \times 100\%, \quad (2)$$

where S is the swelling degree, %; m_s – weight of a hydrogel polymer film soaked with water, g; m_d – weight of a dry polymer film, g.

To determine the swelling rate constant (K) and the equilibrium (maximum) swelling degree (S_∞) of hydrogels, the equation (3) derived from the Schott's second-order diffusion model, which demonstrated good agreement with experimental results, obtained for many diverse polymer hydrogels [23, 24], was used:

$$\frac{dS}{dt} = K \cdot (S_\infty - S_t)^2. \quad (3)$$

Its integration with the limits of $S_0 = 0$ at time $t_0 = 0$ (at the beginning) and S_t at time t gives the following equation:

$$S_t = \frac{S_\infty^2 \cdot K \cdot t}{S_\infty \cdot K \cdot t + 1} \quad (4)$$

After rearrangement, equation (4) can be written in the linear form:

$$\frac{t}{S_t} = \frac{t}{S_\infty} + \frac{1}{S_\infty^2 \cdot K} \quad (5)$$

It was used for estimation of two main parameters characterizing the swelling behaviour of the hydrogel materials obtained, namely K and S_∞.

The relative surface hardness of the films (T, RU) of the samples was measured on an M-3 pendulum device in line with the EN ISO 1522:2022 standard [25]; the calculation was carried out according to the following equation:

$$T = \frac{t_{p.f.}}{t_{g.p.}} \quad (4)$$

where $t_{p.f.}$ and $t_{g.p.}$ are the oscillation periods of the pendulum on the crosslinked polymer film and glass plate (as reference) in seconds, respectively.

The breaking strength (P, MPa) and the relative elongation during stretching (ε, %) of the crosslinked polymer films were measured exploiting a TIRA test 2200 tensile machine at a constant speed of 5 mm·min^{-1}, in accordance with the guidelines specified in ISO 527-1:2022 standard [26], and calculated using Equations (5) and (6):

$$P = \frac{F}{A} \quad (5); \qquad \varepsilon = \frac{(l - l0)}{l0} \cdot 100\%, \quad (6)$$

where F is a breaking force, N; A – cross-sectional area of the film, m^2; l_0 – initial length of the film, mm; l – length of the film at break, mm.

Results and Discussion

Study of photo-crosslinking of the PVA compositions with benzophenone and functional acrylic monomers

To obtain photo-crosslinkable compositions based on PVA, a system consisting of photoinitiator BP dissolved in monomer AA was used. The choice of such a system for PVA crosslinking is explained by the following considerations:

- firstly, BP is well soluble in organic solvents, but almost insoluble in water; therefore, it was pre-dissolved in AA, which is well soluble in water; thus, AA serves as a co-solvent for BP allowing it to be introduced into an aqueous PVA solution;
- secondly, as shown by B. Rånby et al. [27] and by other researchers [28, 29], a combination of BP and acrylic monomers, especially AA, is an effective system for polymer crosslinking and polymer surface modification via the photo-grafting mechanism.

Photo-crosslinkable composite films were irradiated with a UV lamp, as described in the '2. Materials and Methods' section. The influence of the film compositions of on the gel fraction content in films after their UV crosslinking was investigated (table 1).

Table 1

Gel fraction content in the photo-crosslinked polymer films

Composition of photo-crosslinkable compositions, weight parts			Gel fraction, %
PVA	BP	AA	
100	1	5	14.9
100	2	10	19.7
100	2	5	7.5

Based on these experimental data, it can be concluded that doubling the weight parts of the photoinitiating mixture of BP and AA (from 1 w.p. and 5 w.p. to 2 w.p. and 10 w.p. per 100 w.p. of PVA, respectively) did not significantly affect the content of the crosslinked polymer, while an increase in the amount of BP alone had a negative impact on this parameter. This phenomenon can be explained if we suppose that AA promoted the running of the grafting reactions as the predominant process, rather than crosslinking of the composition. As a result, mainly graft

Journal of Chemistry and Technologies, 2026, *34*(2), 365-374

copolymers PVA-gr-PAA, well soluble in water, were formed, and a minor fraction of crosslinked PVA constituents. Whereas, an enhanced amount of BP brought about predominantly photo-degradation of PVA matrix via β-scission reactions. Therefore, in subsequent studies, the photo-crosslinking system consisting of BP and AA was used in amounts of 1 w.p. and 5 w.p., respectively, relative to the PVA weight.

The effect of UV irradiation time on the gel fraction content in composition films was investigated; the results are presented in Fig. 2. As can be seen, the content of the crosslinked fraction exhibited a clear trend of increasing with exposure time. However, when using the photo-crosslinking system consisting only of BP and AA, even after 45 minutes of irradiation, the content of crosslinked fraction remains low, reaching values of approximately 15 %.

To form films with highly crosslinked polymer structures, an additional functional monomer acting as a crosslinking agent, namely MBA or HEMA, was added to the compositions in the amount of 3 w.p. per 100 w.p. of the matrix polymer. The results of photo-crosslinking of these compositions are shown in Fig. 2.

Based on the experimental results, the photo-crosslinkable composition composed of PVA, BP and AC, with 3 w.p. of MBA added, exhibited the most favourable properties in terms of crosslinking rate and gel fraction content. The data revealed that this composition formed a significant amount of crosslinked polymer even after relatively short irradiation times. It should also be noted that the introduction of HEMA in an amount of 3 w.p. also has a positive effect on increasing the gel fraction content in polymer films; however, its growth with the irradiation time was much slower compared to the photo-crosslinkable composition with the addition of MBA. The latter demonstrated a rapid initial increase in crosslinked polymer content, reaching 79.5 % within the first 5 minutes; a longer exposure time caused only its slight increase, reaching 86.9 % after 45 minutes of irradiation.

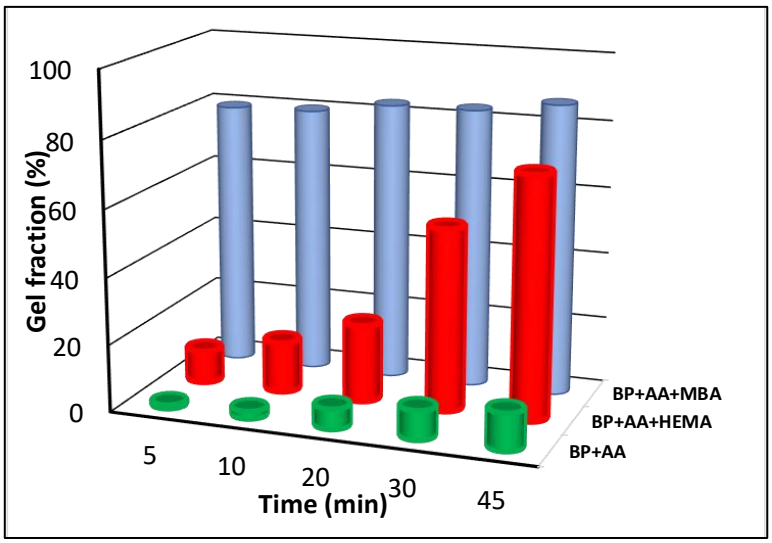


Fig. 2. Dependence of gel fraction content on UV irradiation time of photo-crosslinkable compositions

A comprehensive study of the swelling ability of photo-crosslinkable compositions in water, as well as their physico-mechanical properties, focusing on hardness and tensile strength, was carried out. These properties are crucial for assessing the suitability of the developed materials for potential biomedical applications.

Study of swelling of the photo-crosslinked PVA composition films

The water-absorbability of the films was estimated in terms of the swelling degree and the swelling rate. The swelling ability of PVA-based photo-crosslinkable films in water was found to be significantly influenced by the type of acrylic monomer used and the crosslinking degree. Swelling behaviour of the crosslinked PVA films is illustrated in Fig. 3.

As can be seen from the obtained curves of the swelling kinetics of PVA films, their behaviour was very different when immersed in water and depended on their formulations, as well as on their irradiation time. However, some similarities in their behaviour were also observed. First, all the films readily absorbed water, sharply increasing their weight several times during the first thirty minutes of immersion in water. Then, the swelling degree reached its maximum, and afterwards it began to subside.

The intensity of weight loss by the swollen films was affected by both their composition and

Journal of Chemistry and Technologies, 2026, *34*(2), 365-374

irradiation time. Some basic conclusions can be drawn when analysing the swelling kinetics (Fig. 3)

The highest values of the swelling degree were achieved when photo-crosslinking was performed using a mixture of BP and AA with the addition of HEMA (Fig. 3). Indeed, for these films, the maximum value of almost 2000 % of swelling degree was achieved when this composition was exposed to UV-irradiation for 45 minutes, and a slightly lower value after 30 minutes of irradiation. When films were crosslinked for 20 minutes, the degree of their swelling in water was almost twice as low, and at shorter UV-exposures (10 and 5 minutes), it essentially decreased. Such a decrease in swelling degree can be explained by diffusion of the non-crosslinked PVA macromolecules (sol-fraction) into the surrounding aqueous media, i. e. a part of PVA was apparently washed out of the film. Rapid swelling of the crosslinked PVA films and further washing up sol-fraction were the main reasons for the observed maxima at the swelling curves.

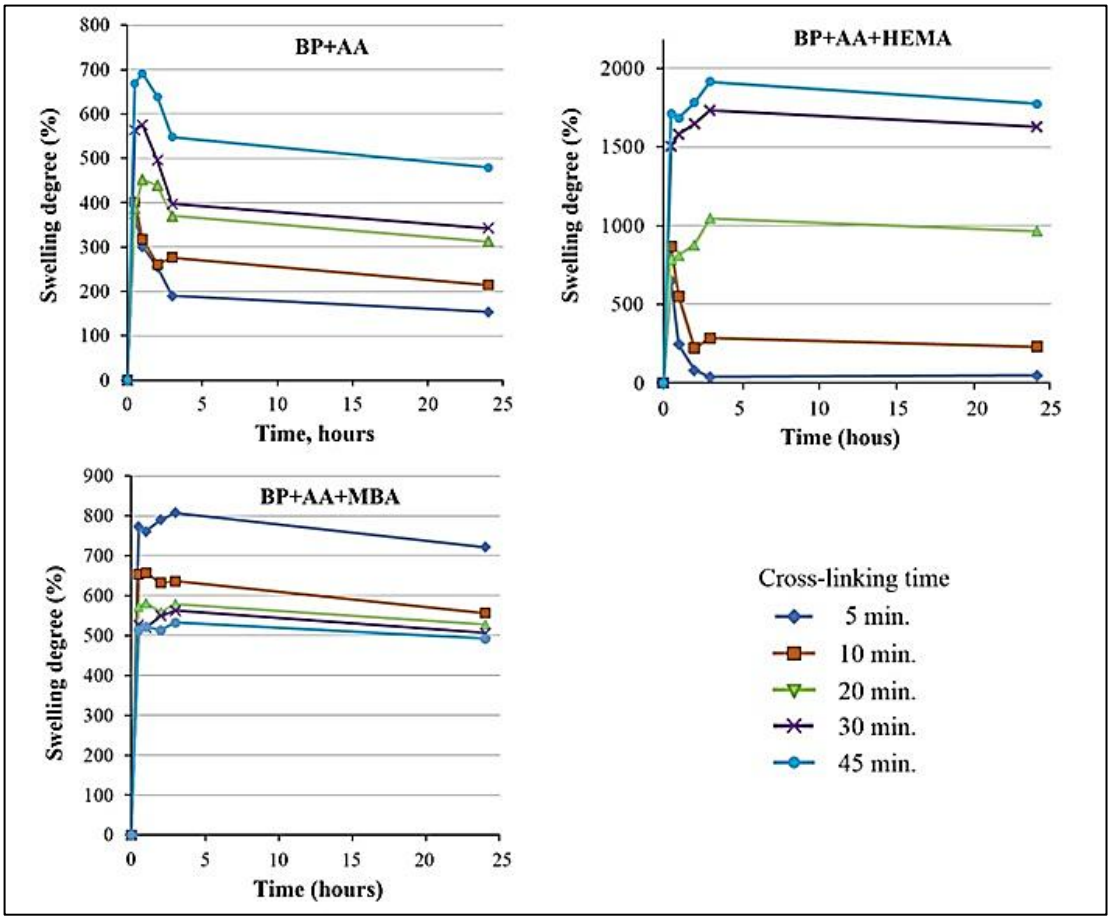


Fig. 3. Swelling kinetics of the photo-crosslinked PVA films

The observed increase in swelling degree over the UV-exposure time suggested that at short exposure time, the polymer network was insufficiently crosslinked and contained a large partition of sol-fraction. That resulted, on the one hand, in low swellability of weakly crosslinked films and, on the other hand, in losing a sol-fraction via its diffusion into the aqueous phase during longer immersion time of films in water. Thus, a significant UV-exposure time is necessary for the formation of a sustainable crosslinked polymer network for this formulation.

A similar situation was observed for the PVA composition, which was crosslinked by the photoinitiating mixture comprised of only BP and AA (Fig. 3). These films demonstrated an even lower swelling degree and a significant weight loss of the swollen films upon prolonged contact with water, indicating their insufficient crosslinking. As a result, such films were unable to maintain their shape and resist dissolution.

Regarding the PVA composition crosslinked by the system comprised of BP and AK with adding MBA (Fig. 3), these films exhibited the highest swelling degree at short exposure time, among all the studied samples, owing to the extremely high crosslinking degree achieved even at relatively short exposure time – 5 minutes (Fig. 2). On the contrary to other formulations, for this composition, a decrease in the swelling degree of

Journal of Chemistry and Technologies, 2026, *34*(2), 365-374

the films was observed with increasing UV exposure time. This phenomenon can be explained by increase in the crosslinking degree, which, in turn, reduced the internodal distance in the polymer network, making it more rigid and less prone to deformation and volume increase, thereby reducing the ability to absorb large amounts of water. It's worth noting that this photo-crosslinkable composition demonstrated remarkable stability, maintaining its shape even after 24 hours of immersion in water, although the dimensions changed owing to water uptake.

The swelling rate constant (K) and the equilibrium (i. e. maximum achievable) swelling degree (S_∞) of hydrogel films were estimated from the graphical dependencies of $t/W=f(t)$ and the results were summarized in Table 2.

The estimations were performed for the initial, rising stage of swelling in the interval time ranging from 0 to 30 minutes. It should be noted, that S_∞ is a theoretical value, which did not take into an account dissolution of sol fraction. That happened because swelling of polymer films is more rapid process as compared to dissolution of sol-fraction. Indeed, swelling occurred via diffusion of water molecules, which have a low size, into polymer network; while dissolving of sol-fraction was connected with diffusion of large polymer macromolecules from polymer network into aqueous phase. As can be seen from Table 2, the values of both the swelling rate constants and the equilibrium swelling degrees gradually increased with increasing irradiation time in the case of a crosslinking system consisting of BP and AA, as well as BP and AA with HEMA added. This increase in the both swelling parameters well correlated with accumulation of gel-fraction in polymer films crosslinked with these systems over irradiation time (see Fig. 2).

On the contrary, an opposite tend was observed in the case of films crosslinked in the presence of the system comprised of BP, AA and MBA. For this formulation, the equilibrium swelling degree and the maximum value of the swelling rate constant were reached at the shortest exposure time (5 min.).

Table 2

Effect of the composition and crosslinking time of polymer films on their swelling ability

No	Crosslinking system	UV exposure time (min)	Gel fraction (%)	Swelling degree after 24 hours' soaking (%)	K, (%•min^{-1})	S_∞, (%)
1.	BP + AA	5	1.20	154	$9.73\cdot10^{-4}$	401
		10	2.33	214	$9.80\cdot10^{-3}$	432
		20	6.10	313	$1.27\cdot10^{-3}$	484
		30	8.74	342	$1.56\cdot10^{-3}$	584
		45	11.09	479	$2.45\cdot10^{-3}$	682
2.	BP + AA + HEMA	5	9.79	115	$1.37\cdot10^{-3}$	675
		10	15.13	229	$1.77\cdot10^{-3}$	789
		20	23.10	1015	$1.87\cdot10^{-3}$	1046
		30	54.34	1629	$5.14\cdot10^{-3}$	1733
		45	71.97	1774	$8.63\cdot10^{-3}$	1920
3.	BP + AA + MBA	5	79.51	730	$3.41\cdot10^{-2}$	776
		10	80.06	556	$2.29\cdot10^{-2}$	655
		20	83.40	528	$2.21\cdot10^{-2}$	568
		30	83.65	506	$1.86\cdot10^{-2}$	527
		45	86.91	492	$1.40\cdot10^{-2}$	512

Increased irradiation time resulted in a gradual decrease in both these parameters. This phenomenon can be explained by an increase in the crosslink density of the polymer matrix, as previously mentioned; at the same time, only a slight increase in gel-fraction were achieved (see Fig. 2) at increased irradiation time. The similar results and conclusions were reflected in papers [30, 31], where authors observed a decrease in the swelling degree of polymers with increasing crosslinking content.

The effect of both the crosslinking formulation and crosslinking degree (in term of gel-fraction) on the maximal swelling degree of the crosslinked PVA films is clearly seen in Fig. 4.

Journal of Chemistry and Technologies, 2026, *34*(2), 365-374

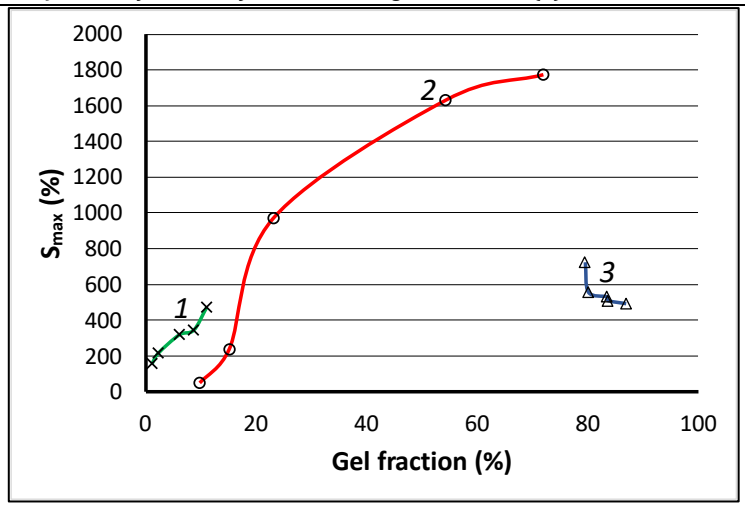


Fig. 4. Effect of the gel-fraction content on the maximum swelling degree (S_{max}) of PVA films crosslinked by the systems: 1 – BP + AA; 2 – BP + AA + HEMA; 3 – BP + AA + MBA

Compositions with BP + AA and BP + AA + MBA systems provided low intervals of variation in the swelling degrees of crosslinked PVA films (Fig. 4, curves 1 and 3). In the first case, the obtained films were not completely crosslinked at any irradiation time; this was the reason for their low swellability and significant weight loss when immersed in water. On the contrary, in the latter case, films were over-crosslinked; this resulted in the formation of a rigid polymer network structure, characterized by less free volume, as well as reduced water absorbed by the PVA film, and finally lower swellability.

In the case of BP + AA + HEMA (Fig. 4, curves 2), both the crosslinking degree and the swelling degree can be varied in wide ranges. The swelling degree rose by an order of magnitude when the gel-fraction content increased from 10 to 80%. This composition demonstrated the highest values of swelling degrees. The reason for such behaviour was probably the formation of a polymer network with quite large, elastic, hydrophilic cells and an optimal crosslinking density. An enhanced hydrophilicity of this polymer network was achieved due to the presence of –OH functionality in the HEMA molecules involved in building interchain bridges.

Study of physico-mechanical properties of the photo-crosslinked PVA films

Besides the swelling properties of photo-crosslinked PVA films, their physico-mechanical properties are of high importance for evaluating the possibilities of their use in certain applications, such as coatings, packaging materials, medical uses, and optoelectronics, etc. In this connection, a study of the effect of the film composition and photo-crosslinking time on the physico-mechanical properties of crosslinked PVA films was carried out, the results of which were summarized in Table 3.

Table 3

Dependence of the physicomechanical properties of polymer films on composition and crosslinking time

No	Crosslinking system	Photo-crosslinking duration, min.	Breaking strength, MPa	Elongation at break, %	Relative hardness*, RU
1.	–	0	18.5	176	0.11
2.	BP + AA	5	21.5	162	0.15
		10	26.1	119	0.21
		20	26.9	8.3	0.26
		30	31.6	7.1	0.27
		45	37.3	8.4	0.32
3.	BP + AA + HEMA	5	31.6	31	0.26
		10	44.5	11	0.41
		20	50.6	9.1	0.49
		30	55.5	8.4	0.56
		45	60.4	9.8	0.58
4.	BP + AA + MBA	5	48.4	6.4	0.59
		10	51.3	5.7	0.64
		20	52.1	5.9	0.64
		30	53.0	5.0	0.64
		45	59.4	4.0	0.69

* – the hardness of the polymer film relative to the hardness of the glass plate, which was taken as 1.00 RU

As follows from the analysis of the data presented in Table 3, both breaking strength and surface hardness were increased, while elongation at break was decreased for all of the PVA films crosslinked at any photo-crosslinking time, compared with the virgin PVA film. The longer photo-crosslinking time, the higher strength and hardness, and the lower elongation of films, indicating that they became stiffer as the gel-fraction increased.

The composition with BP + AA exhibited a higher relative elongation and the lowest strength and hardness among all other crosslinked PVA films, indicating a small number of crosslinks in the polymer structure. Conversely, the second and third compositions (with added HEMA or MBA) exhibited lower elongation values with higher breaking strength owing to a more extensively crosslinked structure. In all cases, a consistent trend was observed toward increasing tensile strength and decreasing elongation with longer photo-crosslinking times, obviously caused by enhanced stiffness of the polymer film owing to an increase in the number of crosslinks in the polymer matrix.

Comparing the last two compositions, it can be concluded that the addition of MBA increased the film's hardness and made it more rigid. Indeed, films obtained with the added MBA had about twice lower elongation values then those obtained with the added HEMA at the comparable crosslinking degrees (content of gel-fraction). Thus, the addition of HEMA contributed to the formation of a more elastic polymer network, which resulted in these films exhibiting a swelling degree several times higher than that of the other two formulations (Table 2 and Fig. 4).

Conclusions

Polymer hydrogel compositions based on PVA, a photoinitiator and functional acrylic monomers were developed; the crosslinking of these compositions under the influence of UV irradiation was investigated; and the influence of formulation and UV crosslinking conditions on their properties was determined. The addition of a small amount of functional monomer, such as HEMA or MBA, significantly altered the properties of photo-crosslinked PVA compositions. Strong, quickly crosslinkable and highly crosslinked polymer films were obtained by introducing MBA into the composition. Introducing HEMA endowed the films with the highest water-absorbability reaching about 1700 %, while their crosslinking required longer UV-irradiation. Such materials can find application as membranes for nanofiltration, as well as in medicine.

References

[1] Finch, C. A. (Ed.). (1992). *Polyvinyl Alcohol - Developments* (2nd ed.). Wiley.

[2] Sanjib, S., Subhankar, P., Sarathi, K. (2021). Crosslinked poly (vinyl alcohol): Structural, optical and mechanical properties. *Surfaces and Interfaces, 25*, 101198. https://doi.org/10.1016/j.surfin.2021.101198.

[3] Bercea. M. (2024) Recent Advances in Poly(vinyl alcohol)-Based Hydrogels. *Polymers*, 16(14), 2021. DOI: 10.3390/polym16142021.

[4] Xiaoxu, L., Zhong, H.-J., Ding, H., Yu, B., Ma, X., Liu, X., Chong, C.-M., He J. (2024). Polyvinyl Alcohol (PVA)-Based Hydrogels: Recent Progress in Fabrication, Properties, and Multifunctional Applications. *Polymers*, *16*(19), 2755. doi: 10.3390/polym16192755.

[5] Khan, M. M. R., Rumon, M. H. (2025) Synthesis of PVA-Based Hydrogels for Biomedical Applications: Recent Trends and Advances. *Gels*, 11(2), 88. DOI 10.3390/gels11020088.

[6] Vatanpour, V., Teber, O. O., Mehrabi, M., Koyuncu, I. (2023) Polyvinyl alcohol-based separation membranes: a comprehensive review on fabrication techniques, applications and future prospective. *Materials. Today Chemistry*, 28, 101381. doi: 10.1016/j.mtchem.2023.101381.

[7] Visakh, P. M., Nazarenko, O. B. (Eds.). (2023). *Polyvinyl Alcohol-Based Biocomposites and Bionanocomposites*. Scrivener Publishing LLC. https://doi.org/10.1002/9781119593218.

[8] Kumar, N., Gusain, R., Pandey, S., Ray, S. S. (2022) Hydrogel Nanocomposite Adsorbents and Photocatalysts for Sustainable Water Purification. *Advanced Materials Interfaces, 10*(2), 2201375. doi: 10.1002/admi.202201375.

[9] Berdiev, U., Khudaykulov, I., Iskandarov, S., Amirova, A., Ashurov, K. (2025) Influence of SiO_2 Nanoparticles on the Characteristics of a Polyvinyl Alcohol-Based Proton Exchange Composite Membrane. *East European Journal of Physics*, *12*(1), 265–271. doi: 10.26565/2312-4334-2025-1-30.

[10] Jailani, A., Hidzer, M. H., Firdaus, A. H. M., Sapuan, S. M., Zainudin, E. S., Atiqah, A., Jaafar, W. M. W., Suryanegara, L. (2026) Enhancing polyvinyl alcohol (PVA) nanocomposites: Key properties, applications and challenges in advanced engineering. *Defence Technology*, *55*(1) 11–29. doi: 10.1016/j.dt.2025.05.020.

[11] Elbakyan, L., Zaporotskova, I., Hayrapetyan, D. (2024) Nanocomposite Material Based on Polyvinyl Alcohol Modified with Carbon Nanotubes: Mechanism of Formation and Electronic Energy Structure. *J. Compos. Sci*., *8*(2), 54. doi: 10.3390/jcs8020054.

[12] Papapetros, K., Mathioudakis, G. N., Vroulias, D., Koutroumanis, N., Voyiatzis, G. A., Andrikopoulo, K. S. (2025) Structure-Properties Correlations of PVA-Cellulose Based Nanocomposite Films for Food Packaging Applications. *Polymers, 17*(14), 1911. doi: 10.3390/polym17141911.

[13] Tokarev, V. S., Korbutyak, D. V., Shevchuk, O. M., Bukartyk, N. M. (2025). Synthesis of multi-layered nanocomposite polymer films with embedded nanocrystals of PbS. *XX International Freik Conference Physics and Technology of Thin Films and Nanosystems. Materials*, Ivano-Frankivsk, Ukraine, 28.

[14] Wang, M., Bai, J., Shao, K., Tang, W., Zhao, X., Lin, D., Huang, S., Chen, C., Ding, Z., Ye, J. (2021) Poly(vinyl alcohol) Hydrogels: The Old and New Functional Materials. *Int. J. Polym. Sci*., *2021*(1), 2225426. doi: 10.1155/2021/2225426.

[15] Shim, S.-Y., Kim, J.-M. (2001) Alcohol-Assisted Photocrosslinking of Poly(vinyl alcohol) for Water-Soluble Photoresists. *Bull. Korean Chem. Soc.*, *22*(10), 1120–1122.

[16] Yuan, H., Liu, K., Luo, W., Wang, Z., Yan, C., Hu, J., Wang, X., Liu, G., Xu, Z., Lu, Z. (2024) Tartaric Acid Cross-Linking Polyvinyl Alcohol as Degradable Separators for Rechargeable Lithium Ion Batteries. *ChemSusChem*, 17(19), e202400359. DOI: 10.1002/cssc.202400359.

[17] Zhang, Z., Wang, S., Lucia, L. A., Abidi, N. (2024) Processing physically crosslinked polyvinyl alcohol. *Polymer*, *307*, 127313. doi: 10.1016/j.polymer.2024.127313.

[18] Serdiuk, V., Shevchuk, O., Tetiana, K., Bukartyk, N., Tokarev, V. (2023) Synthesis of reactive copolymers with peroxide functionality for cross-linking water-soluble polymers. *J. Appl. Polymer Sci*., *140*(1), e53254. DOI: 10.1002/app.53254.

[19] Nguyen, K. T., West, J. L. (2002) Photopolymerizable hydrogels for tissue engineering applications. *Biomaterials*, *23*, 4307–4314. doi: 10.1016/S0142-9612(02)00175-8.

[20] Schmedlen, R. H., Masters, K. S., West, J. L. (2002) Photocrosslinkable polyvinyl alcohol hydrogels that can be modified with cell adhesion peptides for use in tissue engineering. *Biomaterials*, *23*(22), 4325–4332. doi: 10.1016/S0142-9612(02)00177-1.

[21] Goldvaser, M., Epstein, E., Rosen, O., Jayson, A., Natan, N., Ben-Shalom, T., Saphier, S., Katalan, S., Shoseyov, O. (2022) Poly(vinyl alcohol)-methacrylate with CRGD peptide: A photocurable biocompatible hydrogel. *J. Tissue Eng. Regen. Med.*, *16*(2), 140–150. doi: 10.1002/term.3265.

[22] Fouassier, J. P., Lalevée, J. (2012) *Photoinitiators for Polymer Synthesis: Scope, Reactivity and Efficiency*. Wiley-VCH, Weinheim.

[23] Katime, I., Mendizabal, E. (2010) Swelling Properties of New Hydrogels Based on the Dimethyl Amino Ethyl Acrylate Methyl Chloride Quaternary Salt with Acrylic Acid and 2-Methylene Butane-1,4-Dioic Acid Monomers in Aqueous Solutions. *Mater. Sci. & Appl*., *1*(03), 162–167. doi: 10.4236/msa.2010.13026.

[24] Zawadzka, O., Gnatowski, P., Piłat, E., Kucińska-Lipka, J. (2025) Investigation on the swelling kinetics of gelatin based hydrogels. *Chem. Chem. Technol*., *19*(2), 259–269. doi:10.23939/chcht19.02.259.

[25] ISO EN ISO 1522: 2022; Paints and Varnishes – Pendulum Damping Test. International Organization for Standardization: Geneva, Switzerland.

[26] ISO 527-1:2022 Plastics – Determination of tensile properties – Part 1: General principles. International Organization for Standardization: Geneva, Switzerland.

[27] Rånby, B., Yang, W., Tretinnikov, O., Tokarev, V., Xu, Y. H. (2001) Lamination of polymer films by bulk surface photografting process and properties. *Chinese J. Polym. Sci. (English Edition)*, *19*(2), 123–127.

[28] Aldebasi, S. M., Tar, H., Alnafisah, A. S., Salmi-Mani, H., Kouki, N., Alminderej, F. M., Lalevée, J. (2023) Surface Modification of PP and PBT Nonwoven Membranes for Enhanced Efficiency in Photocatalytic MB Dye Removal and Antibacterial Activity. *Polymers*, *15*(16), 3378. doi: 10.3390/polym15163378.

[29] Wang, Z., Cui, F., Sui, Y., Yan, J. (2023) Radical chemistry in polymer science: an overview and recent advances. *Beilstein J. Org. Chem*., *19*(1), 1580–1603. doi: 10.3762/bjoc.19.116.

[30] Hoti, G., Caldera, F., Cecone, C., Pedrazzo, A. R., Anceschi, A., Appleton, S. L., Monfared, Y. K., Trotta, F. (2021) Effect of the Cross-Linking Density on the Swelling and Rheological Behavior of Ester-Bridged β-Cyclodextrin Nanosponges. *Materials (Basel)*, 14(3), 478. doi: 10.3390/ma14030478.

[31] Iliasov, L., Shibaev, A., Panova, I., Kushchev, P., Philippova, O., Yaroslavov, A. (2023) Weakly Cross-Linked Anionic Copolymers: Kinetics of Swelling and Water-Retaining Properties of Hydrogels. *Polymers*, *15*(15), 3244. doi: 10.3390/polym15153244.