

Composites of polyvinylpyrrolidone and polystyrene with rice husk ash as a bio and silica-rich material: thermal characteristics and water vapor absorption ability

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Abstract

The rice husk ash (RHA), which is bio-based and rich in the amorphous silica, was separately composited with polystyrene (PS) and K30 grade of polyvinylpyrrolidone (PVP) through the solution casting procedure. This bio- and natural-originated material was obtained from thermal pyrolysis of the rice husk (RH) at an elevated temperature. PS used in this study, was prepared by suspension radical polymerization and then the average molecular weight and polydispersity index for the synthesized PS were obtained via gel permeation chromatography. The pure polymers and the prepared bio-composites were characterized using X-ray diffraction (XRD) analysis and Fourier transform infrared (FT-IR) spectroscopy. Also, the effects of RHA on the XRD and FT-IR results were also studied. The thermal properties of these composites verified via thermogravimetry (TGA) analysis and differential thermal analysis (DTA), showed the enhancing effect of this additive on the thermal stability of the polymer matrices. In other word, the degradation temperatures of the polymers were enhanced as well as the increase of the final residual chars after incorporating the additive to the polymers that can be due to its good interactions and compatibility with these polymer matrices. Owing to the solubility of polyvinylpyrrolidone in water, some studies were performed on the hydrophilicity (water vapor absorption) of PVP and its composite. But, polystyrene due to its non-polar nature, didn't show the detectable ability in the water vapor absorption, so its hydrophilic characteristics were not additionally investigated. The results showed that the PVP-RHA bio-composite has the more hydrophobicity than the pure polyvinylpyrrolidone, which can be important in its usages, especially in the medical/pharmaceutical fields. Generally, RHA exhibited the good interactions with both PVP (the water-soluble material) and PS (the hydrophobic material) that can be attributed to the high diversity in the RHA components with the different polarities. RHA contains carbonic material, metal oxides, silica, silanol groups, etc.

Keywords: polyvinylpyrrolidone, polystyrene, rice husk ash, composite, thermal and hydrophobic features

Kulcsszavak: polyvinilpirrolidon, polisztirol, rizshéj hamu, kompozit, termikus és hidrofób tulajdonságok

1. Introduction

Polymer composites are the multi-component materials that are synthesized with the aim of modifying properties of various polymers and achieving the new characteristics and products [1-5]. The issues that accompany crude oil-based materials have encouraged many researchers to turn to biomaterials for different applications such as polymer composites. Polymer bio-composites in which at least one component is bio origin, are environmentally friendly and have benefits, e.g. renewability, non-toxicity, abundance and good availability. Among the bio-originated materials for this purpose, the residual material resulted from the industry of rice cultivation and production (i.e., both the cultivation and the post-harvest periods) as agricultural wastes can be used as the cheap and high-quality bio-additive. In rice mill industry, during the processing of the harvested rice, the large quantities of rice husk are produced. This material is the substantial environmental residue that can

be converted into the proper materials with the high thermal stability, namely, rice husk ash by thermal decomposition protocol under the certain atmospheres and conditions [6-8].

Based on the review of the scientific literature, it was found that this bio-additive has been employed in many research studies. For example, rice husk ash has been exploited as the sustainable and the green biological waste for applications in renewable energy industries and building materials [6]. Also, in different cases, it has been studied as the convenient bio-sorbent for the removal of various pollutants such as toxic heavy metal ions from aqueous systems that the applicable results were obtained for the water treatment [9]. In addition to these examples, rice husk ash has been used in the structure of geopolymers to improve their desired traits [10]. Moreover, rice husk ash has been exploited as the suitable and inexpensive filler for the preparation of various polymeric composites [7, 8, 11 and 12], as well as its usages in highly efficient catalysts for using in organic chemical reactions [12-15].

Solution casting is the simple and the widely applied procedure in various research studies for the preparation of polymeric and other composites. For example, it has been employed to synthesize the efficient Nafion/mordenite composite membranes with the good permeability and the high uptake ability [16] and to prepare the superhydrophobic composite films [17].

Polystyrene which is soluble in non-polar solvents such as benzene and toluene, is the common polymer exploited in many usages and researches, e.g., the linear polystyrene films were synthesized via dissolving in the tetrahydrofuran/ethanol mixture and then evaporating with the aid of electricity for evaluating the effect of applied voltage on its characteristics [18]. Also, in another research work, a thin layer of polystyrene was created by casting the polystyrene solution in dimethylformamide under special conditions and then the light reflection features of the resulting films were studied [19].

Unlike polystyrene, polyvinylpyrrolidone is the water-soluble polymer that its composites are used in the bio-related fields, such as biomedicine. For instance, the films consisting of chitosan, polyvinylpyrrolidone and silver oxide nanoparticles were produced as the wound healing agents with the high antibacterial activity due to the presence of chitosan and silver oxide in their structure. Wound healing specifications of this substance was better than those of cotton, pure chitosan and other reported chitosan-based hemostatic dressings [20]. As well, polyvinylpyrrolidone/polyvinylbutyral composite has been applied as the stable binder for electrodes in supercapacitor structure that can be dispersed in aqueous electrolytes [21]. In another study, the palladium nanospheres stabilized on polyvinylpyrrolidone, were employed as the simple and new electrochemical sensor for amperometric detection of H_2O_2 [22].

It is expected that the rice husk ash can properly interact with both PS and PVP that are different together in polarity. This could be owing to the high diversity in the components present in RHA. This bio-material can react both chemically (e.g., by silanol groups (Si-O-H) with PVP) and physically (e.g., through the carbonic part of the bio-additive specially with PS that is the hydrophobic polymer) with these polymers. Van der Waals bondings are from the physical interactions that can be occurred between these polymers and the ash as an interfacial interplay.

It is noteworthy that after reviewing the literature, no article or the research work was reported on the thermal traits of RHA composites with polyvinylpyrrolidone and polystyrene. Based on the aforementioned ideas and the historical explanations, the main purpose of this paper was to prepare the PVP-RHA and PS-RHA composites by the solution casting technique and then to investigate the thermal properties of these materials. In addition, due to the importance of the polyvinylpyrrolidone hydrophilicity in some applications such as sutures, hemostatic materials (e.g., wound dressings) and other medical applications, the hydrophilicity of the PVP composite with RHA was also studied via evaluating the water vapor absorption by these composites.

2. Experimental

2.1 Materials

Polyvinylpyrrolidone (type K30) was purchased from Sobhan Pharmaceutical Company (Rasht, Iran). Polystyrene was synthesized by suspension polymerization method based on the published article [23]. The toluene sample used to dissolve polystyrene and to prepare the favorite solution of this polymer was produced by Merck chemical company. The rice husk studied in this study and its preparation procedure were the same ones as reported in [24]. Also, the rice husk ash was synthesized by pyrolysis of the prepared rice husk sample in a lab-scale furnace as previously reported [24].

2.2 Instrumentation

The process of sonication on the solutions was done using an ultrasonic bath (Sono Swiss, Sw3H, Switzerland). The gel permeation chromatography (GPC) was done via Knauer Instrument (Germany) for evaluating the average molecular weight and polydispersity index of the synthesized polystyrene. X-ray diffraction (XRD) measurements were performed on a Philips diffractometer (PW1840 made in Holland Netherlands) with Cu-K α radiation. The Bruker Alpha FT-IR spectrometer was used to record the Fourier transform infrared (FT-IR) spectra using KBr disks. Thermogravimetric (TGA) analysis and differential thermal analysis (DTA) for investigating the thermal behaviors of the prepared samples were performed under the nitrogen atmosphere via Perkin-Elmer thermoanalyzer apparatus at the heating rate of 20 °C/min in the temperature range of 40 - 800 °C. The transformation of the rice husk to the favorite ash was accomplished by using a Nabertherm furnace (made in Germany) adjustable up to the temperature of 3000 °C. The moisture content of RH was removed via heating protocol via a drying oven (FN500P, NÜVE, Turkey).

2.3 Synthesis of polystyrene

The polystyrene sample used in this paper was synthesized via the suspension polymerization of styrene as the olefin monomer and benzoyl peroxide as the initiator of radical polymerization in a three-neck balloon under a nitrogen atmosphere and the certain conditions on the basis of the reported procedure carried out by Slobodian et al. [23]. The three-neck balloon was equipped with a mechanical stirrer to properly agitate the polymerization medium during the polymerizing the styrene monomer.

2.4 Preparing the rice husk and the rice husk ash

The rice husk (RH) was obtained by using the steps of milling, washing with distilled water, drying, smashing and then sieving by a stainless-steel sieve (200 mesh size), respectively, as reported in the previous study [24]. The rice husk ash was produced by burning the finely powdered rice husk at elevated temperatures as in [24].

2.5 Determining the solid and moisture content of the rice husk

The weight difference of the sample before and after the drying process at 110 °C for 1 h, was used for evaluating the moisture content of RH. And then, the percentage of the moisture trapped in the RH samples was computed by Eq. (1) [24].

$$\text{Moisture content of RH (\%)} = \frac{\text{Initial weight} - \text{Final weight}}{\text{Initial weight}} \cdot 100 \quad (1)$$

To determine the solid residues of RH after pyrolysis, the given amount of the dried RH was put under the pyrolysis conditions at 600 °C for 1h and then the solid content of the RH sample after burning process was measured by Eq. (2) [24].

$$\text{RHA (\%)} = \frac{\text{Weight of dried RH} - \text{Weight of RHA}}{\text{Weight of dried RH}} \cdot 100 \quad (2)$$

The more detailed information about the protocols used to determine the solid and moisture content of RH, have been reported in [24].

2.6 Preparing the PVP and PS composites with RHA

The uniformly powdered and sieved ash was added to the solution of PVP in the acidic distilled water along with the simultaneous stirring with a magnetic stirrer. The resulting mixture was agitated with the magnetic stirrer for 24 hours and then was placed in an ultrasonic bath for 20 min in order to the better dispersion of RHA in the solution. Finally, the well-dispersed ash in the aqueous PVP solution was poured into a glass plate and posited under the drying condition at 60 °C to prepare the final PVP-RHA composite. To synthesize the polystyrene composite, the uniform polystyrene solution in the toluene solvent was obtained at the ambient temperature. Then, by using the mechanical and ultrasonic agitation methods, the rice husk ash was uniformly dispersed in the polystyrene solution. Afterward, by evaporating toluene and drying the sample, the PS-RHA composite was synthesized for employing in the various desirable analyses.

2.7 Water vapor absorption tests

A simple method was applied to investigate the hydrophilicity of the PVP samples. In this experiment, the certain amounts (initial weight) of the polyvinylpyrrolidone samples was placed on a Whatman paper for the certain period of time and then incubated in the cylindrical chamber with the dimensions similar to Fig. 1. The chamber was then sealed for a convenient time at 25 °C and the water vapor absorbed by the samples during the period of incubation was evaluated by weighing the sample via Eq. (3). At least 5 specimens of each sample were tested in this experiment and the average of the results was considered as the final result for the water vapor absorption of the sample. In all the hydrophilicity tests, the chamber contained 2 ml distilled water and the experiments were carried out in the ambient temperature and pressure.

$$\text{water vapor absorption (\%)} = \frac{\text{final weight} - \text{initial weight}}{\text{initial weight}} \cdot 100 \quad (3)$$

In addition, the photographic method was employed to determine the amount of water vapor absorption by taking a picture of the wetted paper beneath the sample and evaluating

the wetted area as the qualitative criterion of the absorbed water.

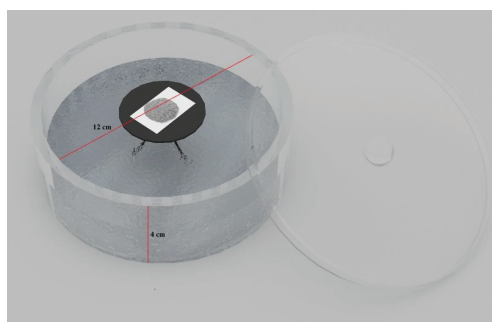


Fig. 1 The schematic representation of the chamber dimensions used in this study for testing the water vapor absorption by the PVP samples

1. ábra A PVP-minták vízgőzfelvételének vizsgálatához használt kamra méreteinek sematikus ábrázolása

3. Results and discussion

3.1 The compositions of RH and RHA

The main components of RH were observed to be silica, cellulose, lignin, hemicelluloses, soluble compounds and inorganic residue as reported in the previous study [24]. Moreover, the RHA composition was measured as L.O.I (12.70%), Al₂O₃ (0.25%), SiO₂ (80.82%), P₂O₅, (0.44%), SO₃ (0.39%), K₂O (1.25%), CaO (0.82%), Fe₂O₃ (0.38%), Cl (1.99%) and Na₂O (0.96%) by using X-ray fluorescence (XRF) analysis. The moisture content of the rice husk sample (8.2 ± 0.3 wt%) was found to be within the range of the reported values (8-15%). Also, the results exhibited that the RH weight loss during the pyrolysis process is 79.4 ± 1%, i.e., RH leaves 20.6 ± 1% of the solid residue (RHA) [24].

3.2 Gel permeation chromatography (GPC)

Gel permeation chromatography analysis was employed to determine the molecular weight and the molecular weight distribution (PDI) of the synthesized polystyrene. The results of this analysis were shown in Fig. 2 and Table 1. As can be seen from these data, the weight and number average molecular weight values are 33949 and 19905 g mol⁻¹, respectively. The amount of molecular weight distribution for this prepared polymer was similar to that of the commercial polystyrene as reported in the literature [25].

Characteristic	Amplitude
Weight Average Molecular Weight	33949 g mol ⁻¹
Number Average Molecular Weight	19905 g mol ⁻¹
Z Average Molecular Weight	56512 g mol ⁻¹
Z+1 Average Molecular Weight	84505 g mol ⁻¹
Peak Molecular Weight	22409 g mol ⁻¹
Polydispersity Index	1.705

Table 1 Average molecular weight and molecular weight distribution data for the synthesized polystyrene

1. táblázat A szintetizált polisztirol átlagos molekulatömege és molekulatömeg-eloszlása

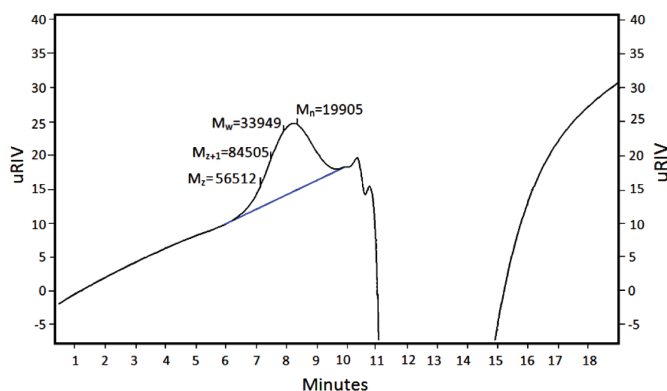


Fig. 2 GPC chromatogram for the synthesized polystyrene
2. ábra A szintetizált polisztirol GPC kromatogramja

3.3 X-ray diffraction (XRD)

Sample	Pos. [°2 θ .]	Height [cts]	FWHM [°2 θ .]	d [Å]	Rel. Int. [%]	Crystal size
PS	19.2	1084	1.3	4.6	100	1.2
	3.7	41.6	0.2	23.6	21.4	6.5
	5.3	34.8	0.2	16.56	17.9	7.9
PS-RHA	8.5	10.5	0.6	10.3	5.4	2.4
	11.1	8.6	2.5	7.9	4.4	0.6
	20.2	193	2.8	4.4	100	0.5
PVP	9.9	86.7	1.9	8.9	30.8	0.8
	23.0	281.0	1.0	3.9	100	1.5
	3.4	14.3	2.8	26.2	7.6	0.5
PVP-RHA	9.9	86.2	2.5	8.9	45.9	0.6
	11.6	111.7	1.2	7.6	59.4	1.2
	23.5	188	0.3	3.7	100	4.4

Table 2 Characteristics of the peaks observed in the XRD patterns
2. táblázat Az XRD mintákban megfigyelt csúcsok jellemzői

The crystallinity degree of the polymer composites as an essential factor determining the physical and mechanical differences between the composites and the parent polymers, was qualitatively investigated by XRD analysis. Fig. 3 shows the XRD patterns of polystyrene, polyvinylpyrrolidone and their composites with the rice husk ash. The large and relatively narrow peak of polystyrene at 2θ around 20 indicate the semi-crystalline nature of polystyrene [26, 27] while the peaks of polyvinylpyrrolidone located at 2θ of 10 and 23 indicate the amorphous morphology for PVP [28]. It is obvious that the molecular arrangement and interactions between the composite components are of the main factors controlling the polymer crystallinity. According to Table 2, upon incorporating the filler to the polymer mortices, the polystyrene peak at 2θ of 19.2 was shifted to 20.2 and also d parameter accordance with this peak was decreased from 4.6 Å to 4.4 Å while its FWHM (full width at half maximum) was enhanced from 1.3° to 2.8°. the examples of peaks shift for PVP were 23.0° to 23.5°, 3.9 Å to 3.7 Å and 1° to 0.3° for 2θ , d-spacing and FWHM, respectively. These studies exhibited that upon adding the ash to these polymeric materials, FWHM and thereby the crystal size values of the samples are also changed, indicating the effect of RHA on the morphology of these polymers. It is noteworthy that, the intensity of the composite peaks was

also significantly decreased as compared to the pure polymers. Moreover, the appearance of the new peaks in the patterns of the composites, exhibits the creation of the new crystalline area in the composites (Table 2). These changes occurred in the XRD patterns of PVP and PS after incorporating RHA into the polymer matrices, indicate the effective interfacial interplays between RHA and the polymers.

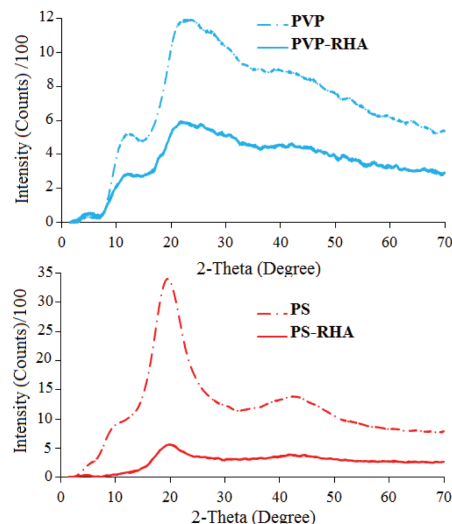


Fig. 3 XRD patterns of the samples
3. ábra A minták XRD eredményei

3.4 FT-IR spectroscopy

FT-IR analysis was performed to investigate the effect of the silica-rich rice husk ash on the polystyrene and polyvinylpyrrolidone vibrational bands. The recorded FT-IR spectra of PS, PS-RHA, PVP and PVP-RHA can be observed in Fig. 4. In the case of polystyrene, the important peaks were occurred at around 3070-3000 cm^{-1} (the C-H stretching modes for the benzenoid ring), 2850-2920 cm^{-1} (the stretching modes of the saturated C-H bands) and 1596 cm^{-1} (assigned to the aromatic C=C bonds) [29]. The weak peaks at 1660 to 2000 cm^{-1} were attributed to the C-H bending mode of benzenoid rings while the ones at 1446 and 1490 cm^{-1} were related to the stretching vibration mode of the benzenoid rings framework. The bands appearing at around 757 and 695 cm^{-1} were also attributed to the C-H bending vibration mode of the benzenoid ring [30]. The peak at 3442 cm^{-1} could be related to the stretching vibration of O-H band due to the very small amounts of the absorbed water in the composite or to the peak overtone at 1721 cm^{-1} . It should be noted that the peak located at 3442 cm^{-1} was shifted to 3425 cm^{-1} wave number, which is the noticeable shift and can be due to the interactions and bonds between the silica-contained bio-additive and polystyrene structure. In other word, these interactions have been able to weaken the strength of these bonds thereby shift their stretching vibrations to the lower wave numbers as well as the significant decrement in their intensities.

In the case of polyvinylpyrrolidone, the C=O and C-N stretching modes were appeared at about 1654 and 1285 cm^{-1} , respectively. The results showed that the N and O atoms in PVP form the chemical bonds with SiO_2 existed in the rice husk ash,

which influenced on the coupling effect between C–O and C–N bonds [30–32]. The bands at 1014, 1222 and 1431 cm^{-1} were assigned to the CH_2 rocking, twisting and scissoring vibrations [26]. In addition, the wide band at 3452 cm^{-1} assigned to the O–H stretching vibration modes of the water molecules absorbed by the hydrophilic polymer, was observably shifted to 3428 cm^{-1} while the band at 2142 cm^{-1} was objectively shifted to 2131 cm^{-1} wavenumber [32]. As well as these observable shifts to the lower wavenumbers, their intensities were also noticeably reduced. Additionally, a weak peak appearing at about 460 cm^{-1} could be due to the deformation of the Si–O bonds present in the RHA structure [33].

All these remarkable change in the peak wavenumbers and their intensities are the strong reasons for the presence of the good interactions between the components within the composites that have been able to cause such extensive and observable changes in most of the FT-IR peaks of these polymers. It is worthy of note that the RHA sample led to the similar effects on the FT-IR and XRD patterns of linear low density and high density polyethylenes [34].

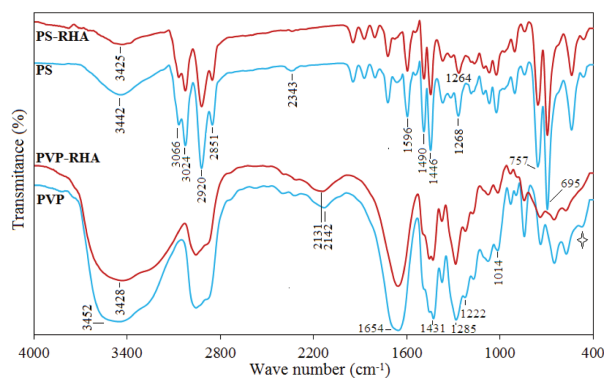


Fig. 4 IR spectra for the polymers and their composites
4. ábra A polimerek és kompozitjaik IR-spektrumai

3.5 Thermal properties

The thermal analysis is one of the most conventional and applicable experiments for studying polymeric materials. This analysis is very important because of the necessary to improve the thermal stability of materials for various type of applications, especially when the material is subjected to the condition with the high temperatures, e.g., especial applications in aerospace and defense industries.

TGA/DTG and DTA analyses revealed that the thermal features of PS and PVP can be improved by incorporating the rice husk ash to them that is detailed explained in the following sections.

On the basis of Fig. 5 (a), the initial weight losses equal 5% and 8% were appeared in the temperature range of 40–150 $^{\circ}\text{C}$ for PVP-RHA and PVP, respectively that is attributed to the elimination of the absorbed water. The peak starting at 350 $^{\circ}\text{C}$ and ending at around 500 $^{\circ}\text{C}$ is related to the decomposition temperature of PVP while the final weight loss starting at 500 $^{\circ}\text{C}$ is related to the combustion of organic residuals in the matrix [28]. As can be seen, the onset and offset temperatures of PVP degradation step have not significantly changed. However, in the temperature range of 450–600 $^{\circ}\text{C}$, PVP-RHA exhibited

1–8.3% final char content more than that of PVP confirming the stabilizing effect of RHA on PVP. Additionally, no weight loss was observed above 675 $^{\circ}\text{C}$ for PVP-RHA and 710 $^{\circ}\text{C}$ for PVP which indicates the completion of the sample pyrolysis at these temperatures. This difference in the decomposition completion between two samples also implies the higher thermal stability of the composite as compared to pure PVP.

In the case of polystyrene (Fig. 5 (b)), it can be seen that polystyrene also decomposes in one step and its main degradation range is from 350 $^{\circ}\text{C}$ to about 450 $^{\circ}\text{C}$ that is consistent with the data reported in the literature [35]. As the stabilizing effect of silica on PS has been reported in literature [36], here, also the silica contained RHA enhanced the temperature in which polystyrene starts the degradation to the higher temperatures as compared to the pure polymer (Fig. 5(b)). Moreover, the composite has exhibited the higher residual char compared to the pure polystyrene indicating the stabilizing effect of the filler on the thermal stability of the polystyrene.

All the observed improvements in the degradation temperature and the higher residual char of the polymers at the elevated temperatures, can be attributed to the effective interfacial interactions between the polymers and RHA. Moreover, the ash undoubtedly has the high thermal stability that can lead to the enhancing influence on the thermal behavior of PS and PVP.

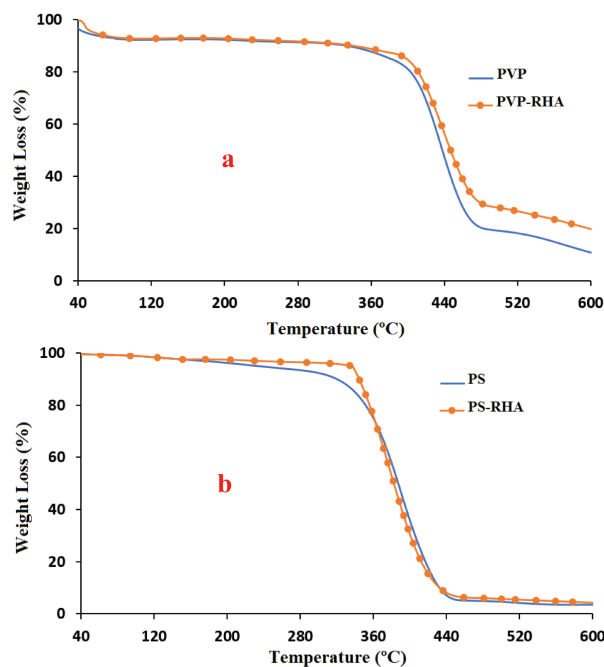


Fig. 5 TGA results of (a) PVP, PVP-RHA and (b) PS, PS-RHA
5. ábra TGA eredmények a) PVP, PVP-RHA és b) PS, PS-RHA

The results of DTA have been summarized in Fig. 6. The endothermic peak appeared at about 100 $^{\circ}\text{C}$, was related to the polyvinylpyrrolidone glass transition temperature (T_g) parameter. The broad endothermic peak at around 350 $^{\circ}\text{C}$, is assigned to the thermal decomposition of the PVP samples according to the main thermal weight losses in TGA of PVP samples. The exothermic peaks at about 450 $^{\circ}\text{C}$, are related to the thermal pyrolysis of the remaining residual organic

compounds. Also, the number of peaks observed for the pure polymer was greater than that of the composite (Fig. 6), i.e., the mechanism of the PVP thermal degradation is different from that of PVP-RHA. It can be seen that the surface area under DTA curve of PVP-RHA composite is lower than that of the pure PVP that shows the less absorbed thermal energy by the composite compared to the parent PVP (Table 3). This can be due to the fewer thermal events (such as degradation and other thermally events or changes) in this sample and also to the stabilizing effect of RHA on the PVP thermal traits.

In the case of PS samples, similar to PVP, the endothermic peak related to the T_g transition has appeared at 100 °C while the exothermic peak according to the decomposition of PS has occurred at the lower temperatures (around 300 °C) as compared to the PVP samples. Similarly, incorporating RHA to polystyrene affects the thermal stability of this polymer that led to the lower energy absorption (the surface area under the sample curve) during the temperature elevation from the ambient temperature to ~750 °C (see Table 3).

The same reasons mentioned in the TGA section (the improved interfacial polymer/RHA interactions and the high thermal stability of RHA) can be employed for explaining the improving effects of RHA on the DTA results.

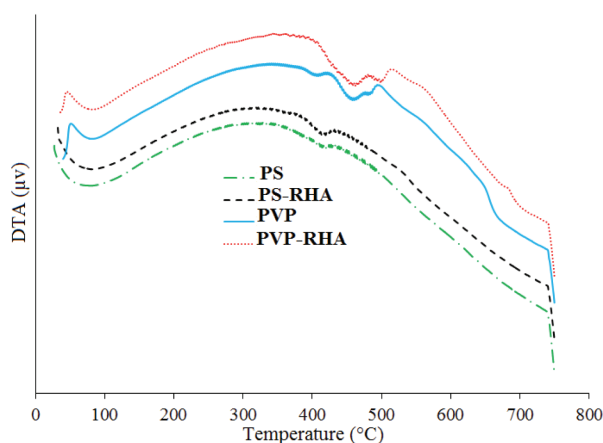


Fig. 6 Results of DTA analysis for the prepared samples
6. ábra Az előállított minták DTA-elemzésének eredményei

Sample	Surface area under the curves (µV °C) in the range of 100-600 °C
PS	4515
PS-RHA	4036
PVP	4750
PVP-RHA	4325

Table 3 Comparison of the thermal energy absorbed by the samples
3. táblázat A minták által elnyelt hőenergia összehasonlítása

3.6 Hydrophilicity study of polyvinylpyrrolidone and its composite

It is clear that polyvinylpyrrolidone is the very hydrophilic and water-soluble polymer. In contact with moisture, this polymer absorbs the water molecules and its shape is converted from the powdery morphology to the lumpy/aggregated morphology. Maybe, for this reason, it has been employed in the hydrophilic drugs as the hydrogel [37]. Decreasing the

PVP hydrophilicity could be the interesting aim for some usages of this polymer. For instance, the amount of water vapor absorbed by PVP-contained drugs has been previously studied [38]. Also, in other work the water vapor absorbed by PVP samples have been investigated that water vapor absorption was increased upon enhancing the relative humidity [39].

Here, the experimental results showed that the incorporation of the SiO₂-contained ash reduces the hydrophilicity of polyvinylpyrrolidone, according to which the water vapor absorption of polyvinylpyrrolidone composite was less than that of the pure PVP. This conclusion can be applicable/useful for the polyvinylpyrrolidone usages specially in some bio-applications that require the more hydrophobicity.

Also, the effect of the incubation time on the water vapor absorption was measured for the same amount (0.01 g) of the absorbent samples. The changes observed in the absorption values upon increasing the time can be seen in Fig. 7. Regardless of the difference in the amount of the water absorbed by the polymeric materials, the rate of water uptake by the samples was decreased after about 3 hours and reached its highest value after about 24 hours (Fig. 7).

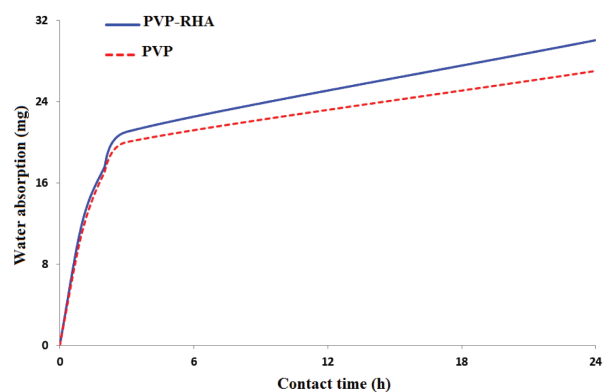


Fig. 7 Effect of the contact time (incubation time) on the water vapor absorption results

7. ábra A kontaktidő (inkubációs idő) hatása a vízgőz abszorpciójára

In other investigation, the effect of the initial weight (mass) of the absorbent on the water absorption parameter by the samples was evaluated and it was found that the water vapor absorption values of the samples increase upon increasing the amount of PVP and its composite. The trend of these changes (i.e., the changes occurred in the curve slope) can be seen in Fig. 8. This observation may be due to the fact that increasing the amount of absorbent leads to the increase of the number of water-absorbing sites at the sample surface.

Other experiment was comparison of the wetted area of the paper beneath the samples after hydrophilicity tests by incubation of the samples in the chamber. Comparing the circular wetted area can be the qualitative presentation of the amount of water absorbed by the PVP sample from the chamber environment (Fig. 9). This moist circular area around the sample on the paper is due to the water vapor trapped by the samples and then transferred to the paper below it. As can be seen in Fig. 9, the prepared composite exhibited the lower wetted area as compared to PVP due to its lower tendency for absorbing the water molecules than the pure polyvinylpyrrolidone.

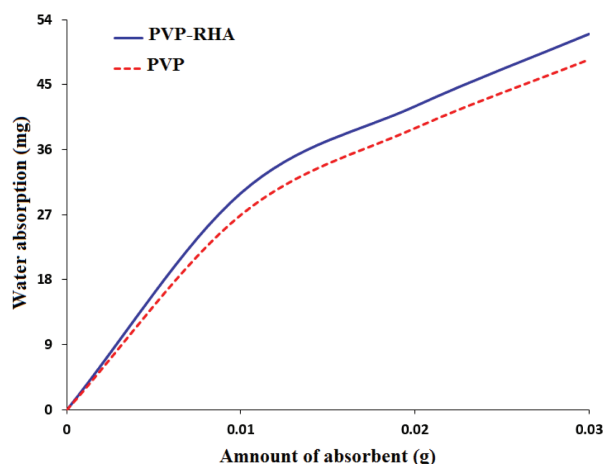


Fig. 8 Effect of the initial mass of the absorbent samples on the water vapor absorption results

8. ábra Az abszorbens minták kezdeti tömegének hatása a vízgőz abszorpciójára

A reasonable explanation for reducing the hydrophilicity of this polymer composite with RHA is the relatively strong bonds of polyvinylpyrrolidone with the bio-additives that are strong enough to reduce the dissolution of the composite in water. As shown in Fig. 9, the wetting area is uniform for polyvinylpyrrolidone because polyvinylpyrrolidone completely dissolves in water and uniformly penetrates into the paper. However, the image taken for the composite was seen as an irregular pattern due to the additive existence in its composition. The circles drawn on the papers after the test, are the areas in which water and the soluble polyvinylpyrrolidone have penetrated within the paper matrix, and the remaining dark stain from the composite can be related to the insoluble solid particles.

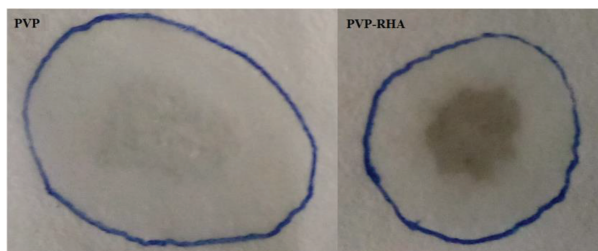


Fig. 9 The typical images taken from the wetted areas of the papers located beneath PVP and PVP-RHA, after the water vapor absorption test

9. ábra A PVP és PVP-RHA alatt található papírok nedvesített területeiről készült tipikus képek a vízgőzfelvétel vizsgálat után

4. Conclusion

In summary, this study showed that the rice husk ash can affect the XRD patterns of PS and PVP in the form of 2θ and intensity of the XRD peaks. Also, the FT-IR peak locations and intensities were also exhibited the changes after adding this bio-additive to the aforementioned polymers. Moreover, RHA led to enhancing the degradation temperature and the final residual solids (i.e., the thermal stability) of these polymers as observed in the TGA analysis. The DTA observations revealed the ~8.9% and ~10% decreases in the amount of the heat absorbed by PVP-RHA and PS-RHA, respectively during the elevation of temperature from ambient temperature

to ~600 °C as compared to the parent samples. Moreover, after incorporating the rice husk ash to the PVP matrix, the degradation behavior and mechanism (the number of the peaks appeared in the DTA analysis) of this polymer was also changed. These observations can be attributed to the chemical structure of this bio-additive that contains more than 80% silica and the small proportions of metallic elements, and to its high thermal stability. Additionally, the water vapor absorption procedures exhibited the increasing effect of the rice husk ash on the PVP hydrophobicity after compositing it with this polymer matrix, which can be useful results for the bio-applications of this polymer. The fact that RHA have been capable to properly interact with both the hydrophilic PVP and the hydrophobic PS and to change their characteristics, could be ascribed to the high variety in the components of RHA. On the other word, this bio-material can react both chemically (e.g., via -Si-O-H groups with PVP) and physically (e.g., via the carbonic part specially with the nonpolar/hydrophobic PS as the interfacial interactions) with the polymers.

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