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EFFECT OF VINYLTRIMETHOXYSILANE SURFACE TREATMENT AND IMMERSION IN WATER ON THE TENSILE BEHAVIORS OF EGGSHELLS POLYVINYL CHLORIDE FILMS PREPARED BY SOLUTION CASTING

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Abstract. Films based on polyvinyl chloride and different ratios of untreated and silane-treated eggshell powders were obtained by solution casting. The samples were exposed to water for 25 days. The effect of the degree of filling and filler treatment on the behavior and tensile properties of the compositions was determined and compared to that of the materials before immersion.

Keywords: polyvinyl chloride, waste eggshells, treatment, solution casting, immersion in water, tensile properties.

1. Introduction

Polyvinyl chloride (PVC) is a well-known polymer that belongs to the group of amorphous thermoplastics, with wide use and application in various fields of industry.[1,2] It is produced in two main forms - unplasticized (rigid) and flexible PVC. Rigid PVC does not contain plasticizers and has a brittle structure. Therefore, various additives (*e.g.* stabilizers, antioxidants, lubricants, fillers, etc.) must be added to the materials based on it. Among the fillers used in the polymer industry, calcium carbonate products occupy the largest share in the production of PVC compositions.

In recent years, it has become necessary to use such waste as fillers, which can become an alternative source of raw materials and limit the depletion of non-renewable natural resources. One such secondary raw material resource that has a suitable composition and prospects is the use of bio-waste eggshells (BWE) in polymer matrices as a source of calcium carbonate.

Several publications have appeared on the reinforcement of compositions based on various polymers with eggshell waste.[3-9] In addition to the traditional methods of mixing PVC and ES[10-14], composites based on PVC with or without plasticizer can also be obtained by solution casting.[6,15-18] A review of the scientific literature showed that there are not many publications on the use of waste eggshells as a biofiller in the production of PVC-based materials.[10-14] For the most part, these studies consider the effect of ES particle size,[12] the degree of filling,[13,14] and the preparation and mixing methods[10,11] on the structure, tensile, and thermal properties of PVC-ES composites. An area where more investigation needs to be done and which has not been studied in detail is the behavior and performance of these materials after exposure to water.

On the other hand, eggshell powders usually agglomerate in the polyvinyl chloride matrix, making it difficult to disperse them. Therefore, it is necessary to modify[19-24] or use silane coupling agents[7] on the surface of ES particles to improve the interaction between ES and the polymer. In addition, silanes can reduce the hydrophilic properties of the filler, limit water absorption, and increase the efficiency of the polymer composites.[25]

The above considerations determined the aim of the present paper, namely, to prepare polyvinyl chloride films using silane-treated eggshells by solution casting and to investigate how the degree of filling and treatment of the filler affects the behavior and tensile properties of the composites after immersion in water.

2. Experimental

2.1. Materials

A suspension grade polyvinyl chloride (PVC) in the form of powder with K value 67, kindly supplied from Aqua Yantra Ltd, Bulgaria; vinyltrimethoxysilane (VTMS) and cyclohexanone, products of Sigma-Aldrich were used as received without any further purification.

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2.2. Preparation and surface treatment of the eggshells

The collected waste eggshells were washed with hot tap water without removing the membrane and left in the air for 24 hours. Then they were dried in an air oven at 90°C to constant weight. The dried eggshells were crushed mechanically and sieved. The selected fraction with a particle size smaller than 0.315μ m was stored in containers for further characterization and chemical treatment.[26]

50 g of thus prepared eggshell powders were soaked at room temperature for 15 min in a ratio of 1:5 in 0.003% VTMS solution. Before their characterization, they were filtered and dried. Raw eggshell powders were designated as ES and silane-treated powders as VTMS-ES.

2.3. Preparation of PVC-eggshell films by solution casting

For every polymer film, 5 g of PVC was mixed with 40 ml of cyclohexanone and stirred at a temperature of 40°C until PVC was completely dissolved. ES or VTMS-ES powders in proportion 1:0.3; 1:0.5; 1:1, and 1:2 (polymer to powders) were added to the solutions of PVC in cyclohexanone and stirred again until they were well homogenized. The prepared mixtures were cast into petri dishes and left to dry for 24 h at room temperature to remove most of the solvent. For further drying, the films were then placed in an oven at 40°C. Films obtained had a thickness of 0.7 to 1 mm.

2.4. Characterization of PVC-eggshell films

2.4.1. Weight reduction

Pre-weighted PVC films containing different contents of untreated and silane-treated eggshell powders were placed in distilled water and kept at room temperature and atmospheric pressure. The weights of samples were measured after different periods, namely 1, 10, 15, and 25 days. The weight reduction in percentage due to immersion according to ASTM D570 was calculated by Eq. (1):[27]

$$\text{Weight reduction (\%)} = \frac{W_0 - W_t}{W_0} \cdot 100 \qquad (1)$$

where: W_0 and W_t are the weights of the specimens before and after immersion in water at a given immersion time t, respectively.

2.4.2. Thickness swelling

In this work, the determination of the thickness swelling in percentage was carried out according to ASTM D570 and calculated by Eq. (2):

$$\text{Thickness swelling (\%)} = \frac{d_t - d_0}{d_0} \cdot 100 \qquad (2)$$

where: d_0 is the initial thickness of specimens, measured to a precision of 0.0001 mm using a digital size gauge, and d_t is the thickness of the films after immersion in water at time t.

2.4.3. Tensile Properties

The tensile strength, elongation at break and *Young*'s modulus of PVC and its films with different ratios of ES or VTMS-ES powders before and after immersion for 25 days in water were conducted according to EN ISO 50527-1 at room temperature, crosshead speed – 50 mm/min on Instron 4203, England.

2.4.4. Shore hardness

The Shore hardness of the resulting PVC films was determined on an apparatus "Stendal", Germany scale A and ASTM D-2240.

3. Results and Discussion

To study how the degree of filling and treatment of the filler affects the behaviors of the obtained PVC films after immersion in distilled water for different periods, their weight reduction, thickness swelling, and Shore hardness were determined. The analysis of the films was supplemented by the measurement of their mechanical properties such as tensile strength, elongation at break, and Young`s modulus. The results for the determined tensile properties after exposure to water for 25 days were compared to those of the materials before immersion.

3.1. Weight reduction of PVC-eggshell films

Exposure of polymer composite products to atmospheric conditions or a humid environment can cause changes in their structure, composition, mechanical, and other properties. In addition, as a result of the action of water, materials swell/dissolve, soluble components are removed or defects are formed. This, in turn, leads to an increase or decrease in the weight of the samples, which can be expressed by their water absorption or weight reduction, respectively. The key here is the duration of immersion.[28]

Since the films obtained by solution casting showed a decrease in weight due to immersion, the weight reduction values were calculated for them. Figures 1 (a) and (b) represent the percentage of weight reduction of PVC films with different ratios of treated and untreated eggshell fillers after immersion in water for 1, 10, 15, and 25 days. As can be seen, the samples show similar weight reduction curves, and the weight reduction increases with immersion time. After only 1 day of immersion, the weight loss for the PVC materials with ES and VTMS-ES at a ratio of 1:0.3 was 0.19 (Fig. 1 a) and 0.16% (Fig. 1 b), respectively. With the increase in immersion time, the tendency to increase the weight reduction is preserved, and the greatest decrease in mass after immersion for 25 days is shown by the films with a ratio of PVC:ES = = 1:0.3, namely 0.47%.

We hypothesize that eggshell particles, which mainly contain $CaCO_3$ above 95%[29] do not affect lowering the mass of the films, due to their low solubility and low degree of water diffusion in them.[30] Moreover, a large part of the polymers are not permeable to water so immersion should not cause dissolution, deformation, or fragmentation of components.[28] The weight reduction observed for all films when immersed in water is probably due to the solvent used in the preparation of the PVC films. Cyclohexanone may interact with polyvinyl chloride to lock the movement of PVC chain segments, and this causes the retention of a significant amount of solvent in the samples. Although the cyclohexanone solution-cast films were subjected to drying at 40°C before testing, the cyclohexanone in the formed films evaporates slowly and there is likely to be residual solvent in them. When immersed in water, cyclohexanone does not form hydrogen bonds with water molecules. Because of the carbonyl group in its structure, it can form very weak dipole-dipole interactions with the water molecules due to which cyclohexanone is somewhat water-soluble (5–10 g/100 ml).[31] That is why we attribute the reason for the weight reduction of the PVC-eggshell samples to the removal of retained solvent with an increase in the duration of immersion in water.

With an increase in the content of fillers in PVC-based films, the percentage of weight reduction decreases, and the use of vinyltrimethoxysilane in the treatment of eggshell surfaces resulted in smaller values of the weight reduction (Fig. 1 b). The reason for this difference is that the coupling agent used lowers the Brunauer-Emmett-Teller surface area and pore volume of ES[25], which makes it difficult to absorb water and thus reduces the weight reduction of the PVC:VTMS-ES films. For example, the calculated value of weight loss after 25 days is smallest for the films with silane-treated filler at a ratio 1:2 – 0.03%. In comparison, this value for the films with the same amount of untreated ES and the same immersion time is 0.08%.

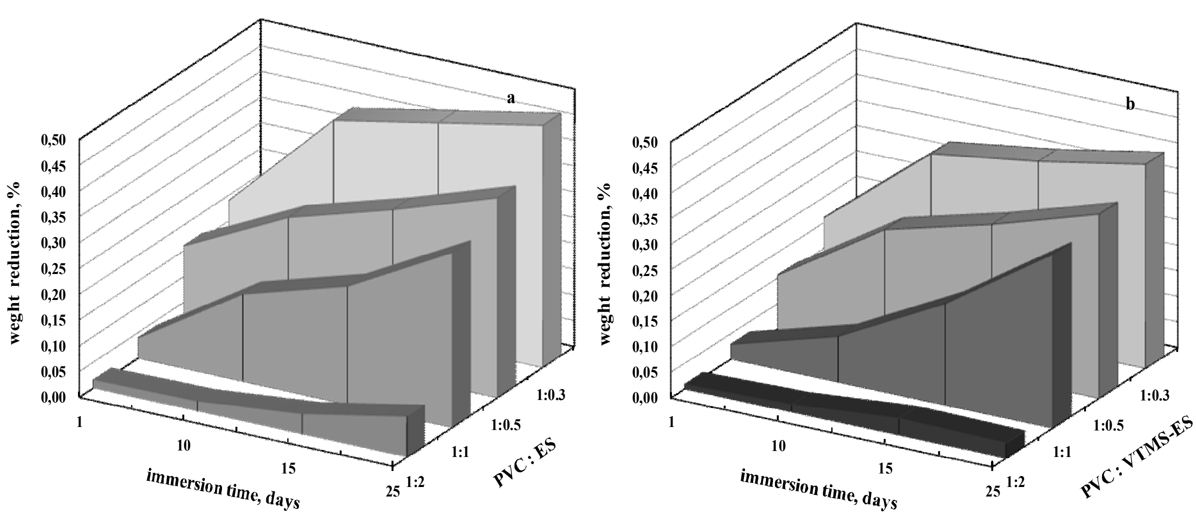

Fig. 1. Weight reduction of PVC films with different ratios of untreated (a) and silane-treated (b) eggshell fillers after immersion in water

3.2. Thickness swelling and Hardness by Shore of PVC-eggshell films

Table presents the thickness swelling and hardness by Shore of PVC films with different ratios of untreated and silane-treated eggshell fillers after immersion in water for 25 days. After exposure to water, all materials showed minus thickness swelling values. There are two most likely reasons for this. The first, as discussed above, is the possibility of removing residual solvents in PVC films. The second reason is the possibility of forming a transparent layer on the surface of the films.[32] Depending on the time of immersion in water, this layer is washed away[32] and thus the samples lose their initial thickness.

Logical to the calculated weight reduction, the thickness swelling of PVC films with the smallest weight loss showed low thickness swelling. The use of VTMS-ES decreases the thickness swelling of the samples compared to the same samples containing untreated eggshells (from –0.24 to –0.30%). The decrease in swelling thickness for the treated eggshell samples is explained by the fact that silane treatment can reduce the hydrophilicity of the filler. This is because silanes are converted to dimers in an aqueous medium or oligomers by the condensation of silanol[33] and can therefore exhibit a water-repellent effect. The determined thickness swelling of the films with 1:0.3 silane-treated filler is the highest one (–0.08%). As the PVC:VTMS-ES ratio increases to 1:2, it decreases and reaches –0.29%.

As can be seen from the same Table, the films with a treated filler have a higher hardness than those containing untreated filler. After immersion in water for 25 days and the addition of VTMS-ES, the hardness by Shore increases, reaching 80 – 82 for the PVC films at a ratio of 1:1 and 1:2. The determined hardness of PVC-ES films is lower, being in the range of 65 – 75 for all compositions, regardless of the proportion of the filler used. The differences in the hardness by Shore observed can be attributed to the silane treatment of ES which probably improves the compatibility with the PVC matrix and positively affects the hardness.

Table. Thickness swelling and hardness by Shore of PVC films with different ratios of untreated and silane-treated eggshell fillers after immersion in water for 25 days

Parameter	PVC : untreated ES				PVC : treated ES			
	1:0.3	1:0.5	1:1	1:2	1:0.3	1:0.5	1:1	1:2
Thickness swelling, %	–0.24	–0.25	–0.27	–0.30	–0.08	–0.19	–0.21	–0.29
Hardness by Shore	65	72	75	75	75	77	80	82

3.3. Tensile properties of PVC-ES composite films

The tensile properties of PVC, PVC:ES and PVC:VTMS-ES films before and after immersion for 25 days are summarized in Figs. 2–4. As can be seen for all PVC-based films containing untreated filler before immersion, a decrease in tensile strength (Fig. 2) is registered, which suggests reduced compatibility and weak adhesion between the hydrophobic polymer and hydrophilic waste eggshells. The above is the reason why the tensile properties of films without coupling agent decreased as the content of fillers increased in the films.

For the composite films containing silane-treated ES, the tensile strength before immersion decreases more smoothly (from 4.386 to 2.493 MPa), compared to the films with the same content of untreated ES (from 4.109 to 1.781 MPa). The observed decrease is about 2 and 2.7 times the tensile strength of the PVC matrix, respectively. Since the films prepared contain no added plasticizer, the change in strength properties is likely due to the influence of residual solvent. On the other hand, the decrease in strength with increasing the content of ES up to a ratio of 1:2 is expected due to incompatibility, and the greater the amount of ES, the greater the probability that the eggshell particles would agglomerate. A decrease in strength after the addition of waste eggshells has also been found by other authors.[7,12] The use of a silane coupling agent increases the tensile strength compared to the films with untreated ES before immersion in water. The reason for this is that the use of vinyltrimethoxysilane as a coupling agent promotes better adhesion between the inorganic eggshells and organic PVC matrix.

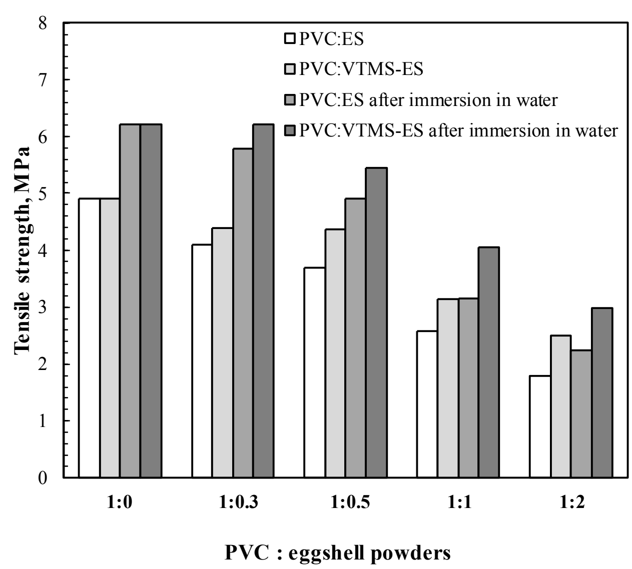

Fig. 2. Dependence of the tensile strength of PVC films with different ratios of untreated and silane-treated eggshell fillers before and after immersion in water

It was found that the PVC matrix, including all samples (after immersion), regardless of the filler used, had higher strength values compared to the same samples before immersion in water. The tensile strength of the initial polymer, for example, increases from 4.909 to 6.218 MPa. The increase in the tensile strength may be due to the removal of cyclohexanone from the samples after immersing them in water for 25 days. Similar to films before immersion, increasing the amount of fillers used lowers the tensile strength, and after immersion in water the observed trend is maintained. PVC films with VTMS-ES possess higher tensile strength at all filler contents compared to untreated PVC-ES films – Fig. 2. At a ratio of 1:0.3 VTMS-ES, the tensile strength of the films after 25 days of soaking time has values as the PVC matrix (6.218 MPa). This means that VTMS is suitable for improving the compatibility between polyvinyl chloride and eggshell powders. After this ratio, the change in strength for the composite films containing silane-treated ES is in the range from 5.450 to 2.981 MPa, while for the films with the same content of untreated ES (from 4.916 to 2.250 MPa).

From the following Fig. 3, it can be seen that the elongation at break decreases with an increase in the ratio of the content of ES or VTMS-ES to that of the polymer for both of the films before and after immersion in water. For the PVC:ES samples before immersion, the elongation decreases from 264.8 (for the pure PVC) to 187.1%. The decrease is slightly smoother for the PVC:VTMS-ES samples. At a ratio of 1:0.3 (PVC:VTMS-ES), the influence of the silane treatment was negligible on the investigated parameter – 247.0%. Further increasing the filler content to PVC:VTMS-ES = 1:2 further decreased the elongation at break, reaching 199.1%. Adding waste eggshell fillers to a PVC matrix reduces the flexibility of the polymer chain. As a result, the elasticity of the films decreases, the stiffness increases (see Table), and therefore the elongation at break decreases.[7,27,34]

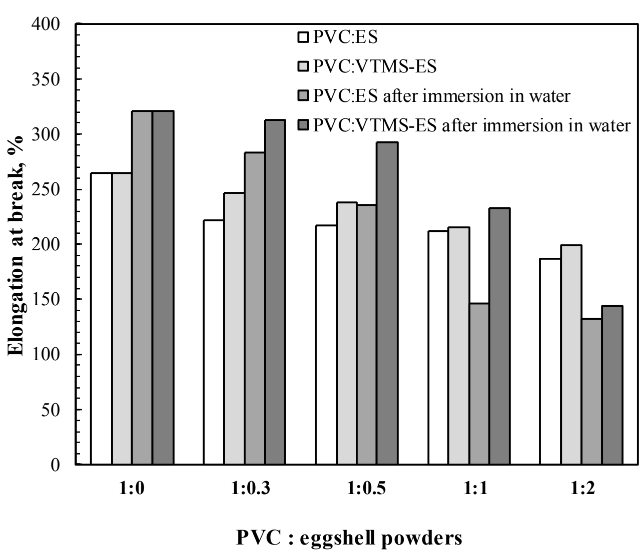

Fig. 3. Dependence of the elongation at break of PVC films with different ratios of untreated and silane-treated eggshell fillers before and after immersion in water

Here, as was the case for tensile strength, the PVC matrix showed higher values of elongation at break after 25 days of immersion time in water, from 264.8 (before immersion) to 321.5%. When using large amounts of untreated and treated eggshells (1:2), the measured elongation of the films after 25 days further decreased. For the mentioned films, it is even less than that of the films before soaking and is 132.5 and 143.5%, respectively. As was assumed above, the differences in the determined values of the elongation at break of the films after soaking are probably due to the removal of the retained solvent from the polymer films. After removing the cyclohexanone from the films, they become less ductile and more rigid. The obtained results are in good agreement with the determined higher Shore hardness – Table.

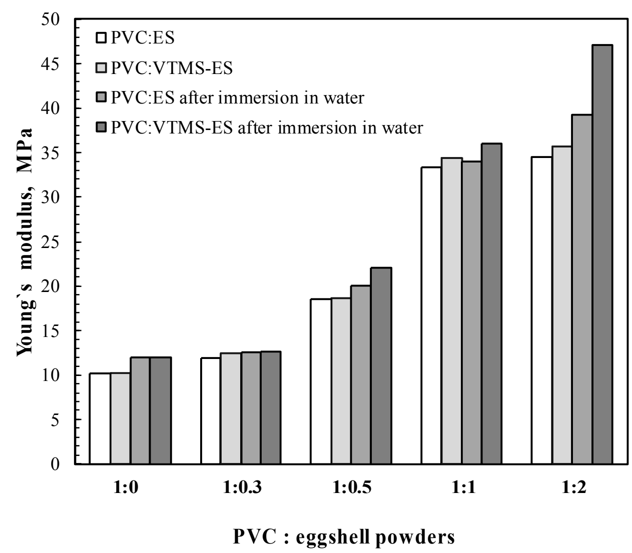

Fig. 4. Dependence of the *Young*'s modulus of PVC films with different ratios of untreated and silane-treated eggshell fillers before and after immersion in water

From Fig. 4 it can be seen that *Young*'s modulus values of the PCV films with untreated and silane-treated eggshell powders prepared by solution casting have values higher than that of the PVC matrix. As the filler content increases, the modulus also increases. The improvement of modulus is accompanied by a decrease in tensile strength (Fig. 2) and indicates that the films become stiffer at higher filler contents – Table. Due to better interfacial adhesion between the PVC polymer chain and silane-treated eggshell particles, it can be concluded that the films containing treated ES filler exhibit higher modulus compared to films with untreated ES at all filler loadings after immersion. The optimum *Young* modulus of 47.07 MPa is achieved for PVC:VTMS-ES = 1:2.

4. Conclusions

Films based on polyvinyl chloride and untreated or silane-treated eggshell powders were obtained by solution casting. The samples with different ratios of fillers (1:0.3, 1:0.5, 1:1, and 1:2 by weight of polymer) were immersed in water for 25 days. It was found that samples with untreated eggshells have a higher weight reduction than those treated with silane at the same degree of filling and immersion times in water. Films with a ratio of 1:0.3 untreated eggshells after immersion for 25 days show the greatest weight reduction of 0.47%, and the smallest weight reduction of 0.03% was observed for the films with the silane-treated filler at a ratio of 1:2. After exposure to water, all materials showed minus thickness swelling values. The addition of fillers leads to a decrease in the values of the tensile strength and elongation at break, and an improvement in the modulus of polymer films, both before and after immersion. The results obtained clearly show the influence of silane surface treatment of filler and immersion in water on the tensile properties of samples.

It is a challenge to the authors in further research to follow the influence of (i) the use of other coupling agents for ES surface modification, (ii) the surface treatment of the PVC matrix, (iii) the particle size of the secondary phase, (iv) the addition of heat stabilizers, plasticizers or other additives and/or (v) the pure PVC is replaced with recycled or a combination of fresh and recycled polymer. It would be useful to subject the method of obtaining the compositions to a systematic study. It is possible that the optimization of the processing method will reveal the potential of ES and have a positive influence on the properties investigated in this work.

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ВПЛИВ ОБРОБКИ ПОВЕРХНІ ВІНІЛТРИМЕТОКСИСИЛАНОМ І ЗАНУРЕННЯ У ВОДУ НА ХАРАКТЕРИСТИКИ РОЗТЯГУВАННЯ ПЛІВОК ПОЛІВІНІЛХЛОРИДУ З ЯЄЧНОЮ ШКАРАЛУПОЮ, ОТРИМАНИХ МЕТОДОМ ЛИТТЯ З РОЗЧИНУ

Анотація. *Плівки на основі полівінілхлориду та порошків необробленої й обробленої силаном яєчної шкаралупи в різних співвідношеннях були отримані методом лиття з розчину. Зразки витримували у воді протягом 25 діб. Визначено вплив ступеня наповнення й обробки наповнювача на поведінку і властивості композицій при розтягуванні та порівняно їх із матеріалами до занурення.*

Ключові слова: *полівінілхлорид, відходи яєчної шкаралупи, обробка, лиття з розчину, занурення у воду, міцність на розрив.*