A COMPARATIVE EVALUATION OF THE PROPERTIES OF EGGSHELL-POLYVINYL CHLORIDE FILMS OBTAINED BY SOLUTION CASTING AND CO-PRECIPITATION TECHNIQUES

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Abstract:
This paper investigates the impact of the production methods on the tensile and thermal characteristics of polyvinyl chloride composite films. Untreated and vinyltrimethoxysilane-treated eggshells at various concentrations were utilized as fillers. The films are obtained via solution casting and co-precipitation techniques, and their tensile strength, elongation at break, and Young's modulus were compared. The results indicate that the co-precipitation method ensures better dispersion of the filler in the polyvinyl chloride matrix, and films have almost twice as high values of tensile strength (up to 7.46 MPa) and Young's modulus (up to 59.27 MPa) compared to those produced via solution casting (4.11 MPa and 34.5 MPa, respectively). The treatment of eggshells with vinyltrimethoxysilane enhances interfacial adhesion and further improves these characteristics. It was found for film 1:2 - polyvinyl chloride (PVC): vinyltrimethoxysilane-treated eggshell (VTMS-ES), an increase of about 30°C in the initial temperature of thermal degradation and a 12% reduction in mass loss compared to the same composition with untreated eggshells.

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1. INTRODUCTION

Recent research has shown that the incorporation of natural waste [1-3] into composite materials can reduce waste and offer a sustainable alternative to traditional materials [4-6]. Thus, in addition to creating environmentally friendly and cost-effective products [7], it is an effective method to reduce ecological impact and provide substitutes for conventional fillers [8, 9].

Waste eggshells are abundant, biodegradable, and inexpensive [10]. Due to their specific structure and chemical composition, eggshells are promising fillers for polymeric materials, as they can increase strength, improve thermal insulation, and barrier properties [10, 11]. Existing scientific research confirms that these wastes can effectively modify the characteristics of various polymer systems [8, 12-14]. Their use is challenging due to the compatibility between eggshell powder and the polymer, as well as the uneven distribution of filler particles in the matrix, which significantly affects the mechanical properties of the composites and can lead to weak areas in the material [15, 16]. To improve the final characteristics of composites, researchers are trying different strategies, including using nanosized fillers, of nanosized fillers, modification of blending sequences, and surface modifications. Mohan and Kanny [17] and Murugan et al. [18] have used nanosized fillers, particles with high surface area, to enhance the mechanical properties of composites. Sharmeeni et al. [19] found that the sequence of blending significantly determines the structural integrity and property attributes of the composites. Owing to the hydrophobic nature of the matrix and hydrophilic nature of the fillers, other researchers have employed various binding agents [20] and surface modification procedures on the fillers to render them well distributed and compatible with the

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matrix [9, 12]. By modifying eggshells with pimelic acid, Lin et al. [21] promote dispersion and cross-linking in PP (polypropylene). This resulted in a 228% increase in impact strength, as well as significant improvements in the tensile and flexural properties of the resulting composite. In their study, Shah et al. [22] treated eggshell powder with 1-3 wt% stearic acid and then mixed it with synthetic epoxy resin. Researchers found that adding 2.5 wt% stearic acid to pure epoxy resin enhanced its tensile elongation property due to hydrogen bonds between the stearic acid-coated particles and the epoxy matrix. Murugan's study revealed that adding a silane coupling agent to eggshell filler enhanced adhesion and interfacial contact, enhancing the composite's tensile strength, Young's modulus, and thermal stability [12].

Based on the above discussion, it can be concluded that the interfacial interactions between the eggshell filler and the polyvinyl chloride (PVC) matrix significantly influence the properties of polymer composites. However, other factors, such as the production method, also considerably influence their properties. This study aims to compare the mechanical behavior of PVC composite films incorporating eggshell powder, obtained by two different techniques: solution casting and co-precipitation. The investigation focuses on the effects of the processing method on filler dispersion, interfacial adhesion, and tensile properties. To enable a systematic evaluation, composite films were produced at varying filler loadings using both untreated and silane-treated eggshells. Furthermore, the thermal stability of selected samples was assessed by examining the influence of surface modification and filler concentration on the composites' thermal behavior.

The novelty of this study is the direct comparison of two of the most commonly used methods for the preparation of composite films, including the influence of surface treatment on eggshell fillers. While previous studies have focused mainly on the modification or amount of fillers, this work demonstrates the relationship between the processing method and the filler treatment to determine both the mechanical and thermal properties of the resulting PVC composites. This approach distinguishes the study from existing works and provides valuable guidance for the design of polymer materials with optimized properties.

2. MATERIALS AND METHODS

The experimental part of this study was carried out in the laboratories of the Department of Material Science, Faculty of Technical Sciences, Burgas State University, Bulgaria

2.1. Materials

In this research, suspension polyvinyl chloride (PVC, grade K 67) supplied by Aqua Yantra Ltd. and waste eggshells from the local food industry were used to prepare polymer composite films. Cyclohexanone ($C_6H_{10}O$) with a purity of 97% and a molecular weight of 98.15 g/mol was used as the solvent. The surface treatment of the eggshells was carried out with vinyltrimethoxysilane (VTMS). Both reagents were products of Sigma-Aldrich.

2.2. Pretreatment of Waste Eggshells

The waste eggshells were washed with hot water without removing the membrane, followed by drying at 90°C until a consistent weight was achieved. Mechanical processing was performed, including crushing and grinding, as well as fractional analysis. A particle size of less than 0.315 µm was used for the experiment. The surface treatment of the eggshell powder was performed with a 0.003% 1:5 VTMS solution for 15 minutes at 23°C. The untreated eggshell powders were designated as ES, while the silane-treated powders were designated as VTMS-ES.

2.3. Preparation of PVC-ES Films by Co-Precipitation and Solution Casting

For each polymer film, 5 g of PVC was dissolved in 40 ml of cyclohexanone and stirred at 40°C until the PVC was completely dissolved. Eggshell (ES) and VTMS-ES powders in a ratio of 1:0.3; 1:0.5; 1:1, and 1:2 by weight of polymer were added to each PVC solution in cyclohexanone and stirred again until completely homogenized. The prepared mixtures were cast into Petri dishes and dried at room temperature for 24 hours to remove most of the cyclohexanone. After that, the films prepared by solution casting were placed in a drying oven at 40°C, whereas those obtained by co-precipitation were co-precipitated in deionized water for 24 hours before being dried at 40°C. The films are labelled as 1:0.3 PVC:ES, 1:0.5 PVC:ES, 1:1 PVC:ES, 1:2 PVC:ES, 1:0.3 PVC:VTMS-ES, 1:0. PVC:VTMS-ES, 1:1 PVC:VTMS-ES, and 1:2 PVC:VTMS-ES,

respectively, according to the ratio of PVC to the content and type of eggshells used.

2.4. Tensile Properties of PVC Eggshell Composites

The tensile strength, elongation at break, and Young's modulus of pure PVC and composite films containing varying amounts of ES or VTMS-ES powders were tested using an Instron 4203 dynamometer at room temperature with a testing speed of 50 mm/min.

2.5. Thermal Analysis

TG-DTA analysis was performed using a Perkin Elmer Diamond TG/DTA thermal analyzer to investigate the thermal stability of PVC, PVC:ES, and PVC:VTMS-ES films in ratios of 1:1 and 1:2, obtained by the co-precipitation method. The analysis was conducted in a temperature range from 50°C to 800°C with a heating rate of 20°C/min under a nitrogen atmosphere (20 ml/min).

3. RESULTS AND DISCUSSION

The tensile behaviour of polyvinyl chloride (PVC) composite films was evaluated to compare the influence of two fabrication methods—solution casting and co-precipitation—on their mechanical performance. The analysis focused on three main parameters: tensile strength, elongation at break, and Young's modulus, as shown in Figs. 1-3. While filler loading, surface treatment, and composition impact mechanical properties, they are discussed here to explain the differences between the two preparation techniques.

The results presented in Fig. 1 demonstrate that the method of film preparation significantly influences tensile properties. Solution-cast PVC films showed a maximum tensile strength of 4.91 MPa for the pure polymer. As the amount of eggshell filler increased, the tensile strength consistently decreased—from 4.11 MPa at a 1:0.3 PVC:ES ratio to 1.78 MPa at 1:2. This decrease is attributed to the weak bonding between the polymer matrix and the rough texture of the eggshells, which creates stress concentration points [19, 23].

Adding VTMS-treated eggshells to solution-cast films mitigated this effect. At equivalent filler ratios, the VTMS-modified films exhibited higher tensile strength. For the 1:1 and 1:2 PVC:VTMS-ES films, strengths of 3.15 MPa and 2.49 MPa were achieved, respectively. These values show increases of about 20% and 40% compared to the untreated films, proving that the silane treatment helps improve the bond between the filler and the matrix [12].

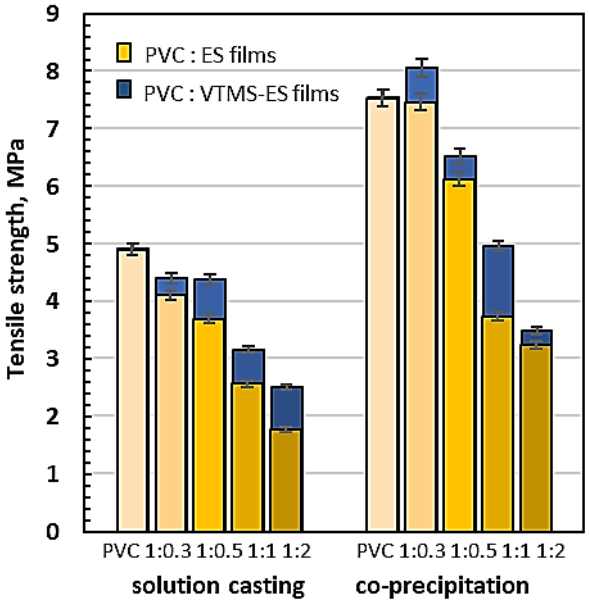

Fig. 1. Tensile strength of PVC composite films obtained by different techniques

The co-precipitation technique significantly enhanced the mechanical performance of all samples. At the same filler ratios, co-precipitated films exhibited much greater tensile strength, approximately double the values recorded for solution-cast counterparts. These improved characteristics can be attributed to better dispersion, afforded by the concurrent precipitation of both the polymer and the filler in a homogeneous solution, which facilitates intermolecular interactions and the uniform distribution of filler particles. This process effectively reduces filler agglomeration and the occurrence of stress concentration points, which are key factors that typically compromise mechanical strength [17, 23]. The highest tensile strength recorded for a composite film was 7.46 MPa for the 1:0.3 PVC:ES composition, only marginally (1%) lower than that of pure PVC (7.53 MPa). VTMS surface treatment on the eggshells further enhanced the effect of the co-precipitation technique on the tensile strength of composite films. The tensile strength of the 1:1 PVC:VTMS-ES film showed the most significant enhancement, with a 32% increase compared to the untreated version. Further enhancements of around 8%, 6%, and 7% were noted for the 1:0.3, 1:0.5, and 1:1.2 ratios, respectively.

As presented in Fig. 2, for films prepared via solution casting, the PVC sample exhibited a high elongation break of 264.8%. The incorporation of

untreated eggshell filler caused a notable initial decrease in flexibility, with the 1:0.3 PVC:ES composition showing a reduction of approximately 16%, reaching 221.7%. Further increases in filler content to 1:0.5 and 1:1 ratios led to only slight additional reductions in elongation at break, with values of 217.6% and 212.1%, respectively. These results show that with increasing eggshell content, the flexibility of the composite films increases to a certain value, after which further increase in filler has minimal impact on the mechanical properties.

The PVC:VTMS-ES films obtained by solution casting demonstrate a similar trend. Surface treatment with VTMS significantly improved the tensile strength of the samples, but the elongation at break remained in the range of 247% to 199.1%. This confirms that the inclusion of solid filler particles reduces the mobility of the polymer chains in the composite films. The restricted deformation capability is a result of localized stiffening near the filler–matrix interface, where the stress is partially transferred through the rigid inclusions rather than the polymer matrix itself [24, 25].

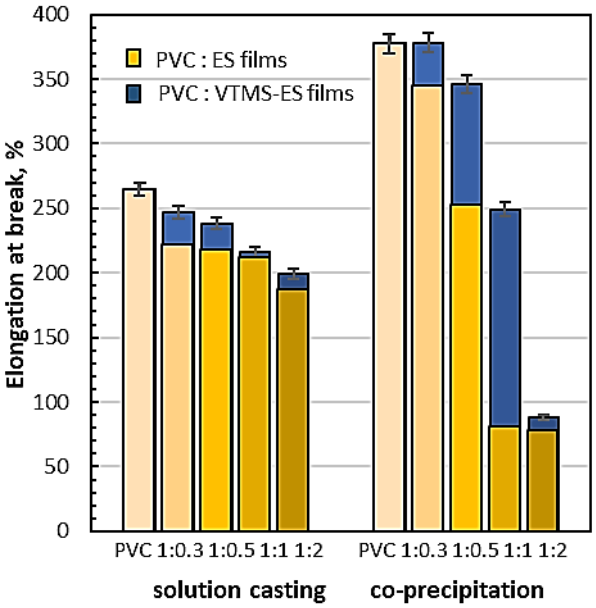

Fig. 2. Elongation at break of PVC composite films obtained by different techniques

Films prepared via the co-precipitation method exhibited markedly different behaviour. The pure PVC film demonstrated a higher baseline elongation at a break of 377.3%, indicating the superior flexibility of films obtained by this method. Although the inclusion of untreated eggshells reduced this value (344.8% for 1:0.3 PVC:ES and 77.9% for 1:2 PVC:ES), the drop was more gradual and followed a clearer trend. Fig. 2 revealed significant improvements in flexibility and in VTMS-ES composites. For instance, the 1:0.3 PVC:VTMS-ES film achieved an elongation break of 378%, which was nearly the same as that of pure PVC. Moreover, the 1:0.5 and 1:1 VTMS-treated films exhibited increases of 37% and 68%, respectively, over the same compositions with unmodified fillers.

These results clearly indicate that the co-precipitation method is superior to solution casting for producing flexible, stretchable composite films. The superior performance can be explained by the improved compatibility between filler and matrix, as well as by the more uniform dispersion of particles obtained through co-precipitation. This method creates stronger bonding at the interface, which helps preserve chain mobility and prevents local hardening. The lack of leftover solvent, which often remains in films prepared by solution casting, also adds to the improved mechanical strength of the co-precipitated materials [26].

As shown in Fig. 3, the Young's modulus increased after adding eggshell powder. This was expected, since the rigid mineral structure of the filler makes the films stiffer [18]. This reinforcing effect, however, was not uniform across all compositions and was significantly influenced by both filler treatment and the method of film fabrication. For films obtained by solution casting, the incorporation of untreated eggshells resulted in a progressive enhancement of Young's modulus with increasing filler concentration. Starting from 10.2 MPa for the PVC film, the modulus increased nearly threefold, reaching 35.7 MPa at the highest filler ratio of 1:2 PVC-ES. The increase is attributed not only to the stiffness of the filler itself but also to the restriction of polymer chain mobility caused by the introduction of rigid particles into the matrix. However, this improvement is partially mitigated by the limitations of the solution casting process, which often leads to inhomogeneous filler distribution, agglomeration, and weak interfacial bonding zones.

VTMS surface treatment of the filler proved to enhance filler–matrix compatibility, especially at higher loadings. For the 1:1 and 1:2 PVC:VTMS-ES films, Young's modulus increased by 27% and 12%, respectively.

The observed improvements are due to the formation of chemical bonds between the hydroxyl groups on the eggshell surface and the silane coupling agent, which helps create a stronger connection between the filler and the matrix. As a result, the reinforced interface exhibits improved resistance to external mechanical stresses. This interfacial reinforcement translates into greater

resistance to external mechanical stress [18]. However, with lower filler contents (1:0.3 and 1:0.5), the positive effect of VTMS treatment on Young's modulus was marginal. Increases of only 1% and 6% were observed, likely due to the insufficient filler quantity to significantly alter the stiffness of the overall matrix.

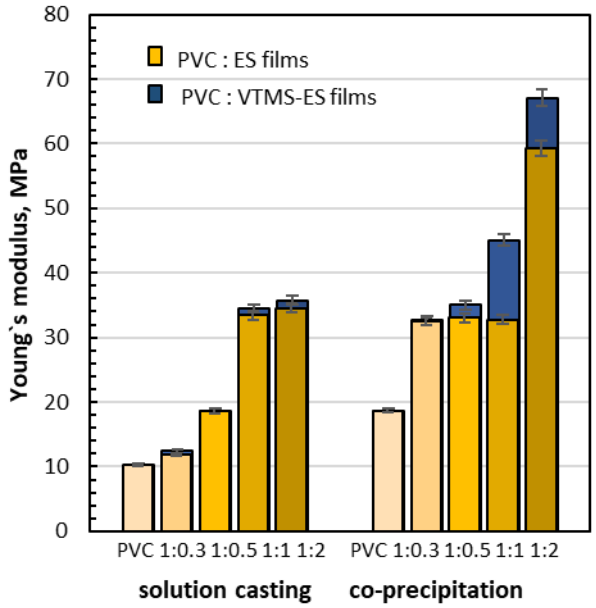

Fig. 3. Young's modulus of PVC composite films obtained by different techniques

The co-precipitation method resulted in a more significant and consistent enhancement in Young's modulus. Across all filler ratios, films prepared by this technique exhibited higher stiffness. This increase can be attributed to the better microstructural homogeneity offered by co-precipitation, which facilitates more uniform filler distribution and minimizes the formation of stress concentration sites. A maximum modulus value of 67.07 MPa was observed in the 1:2 PVC:VTMS-ES film, which is about twice as much as the values found in the same composition solution-cast samples (35.7 MPa). This pronounced enhancement underscores the significant influence of the processing method on the final mechanical performance of composite materials.

The presented results on the mechanical properties of PVC films are in accordance with the existing literature on polymer composites reinforced with bio-derived calcium carbonate fillers. Farahana et al. [27] reported a decrease in tensile strength with the addition of powdered eggshell filler due to filler-matrix incompatibility. Silane treatment increased the values, but they remained lower than those of the matrix. However, our results show a significantly stronger effect when co-precipitation is applied in addition to surface modification, reaching a tensile strength of 7.46 MPa and an elastic modulus of 59.27 MPa. Sharmeeni et al. [19] found elongation at break values of 210-230% for PVC composites with untreated eggshell filler, which was lower than the 378% achieved in the coprecipitated VTMS-modified composites. Lin et al. [21] achieved a 228% improvement in impact strength in polypropylene with pimelic acid-modified eggshell, consistent with reinforcement trends.

Fig. 4 shows the relative improvement in mechanical properties of the composite films prepared by the co-precipitation compared to the solution casting. All polymer films show significant improvements due to the method specificity and the filler characteristics. The PVC film shows 42.5% higher elongation at break, 53.5% higher tensile strength, and 83.4% increased Young's modulus. The PVC-ES composites show a significant increase in tensile strength (81.6%) and elongation (55.5%). However, the improvement in modulus is 71.7%, which is less than that of the PVC film. This proves the dual role of the filler, increasing the strength but at the same time partially compromising the stiffness of the film.

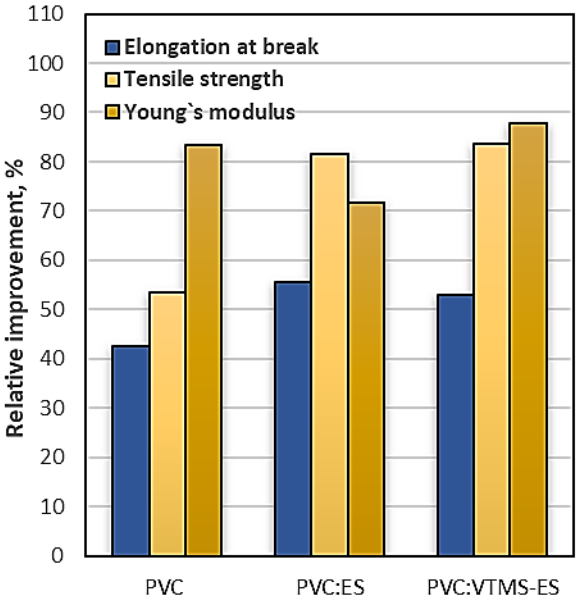

Fig. 4. Relative improvements in the mechanical properties of PVC composite films obtained by co-precipitation techniques

Most notably, VTMS-modified PVC-ES composites achieved peak values with 83.5% higher tensile strength, 87.9% greater Young's modulus, and elongation at break of 53.0%. The 30.1 % difference in tensile strength between PVC and

PVC-VTMS-ES films indicates: (*i*) improved dispersion eliminating stress concentrators through homogeneous co-precipitation, and (*ii*) silane-mediated covalent bonding allowing efficient stress transfer across the filler-matrix interface. It is important to note that the inverse relationship - where PVC-ES films show an 11.7% decrease relative to pure PVC, while PVC-VTMS-ES shows a 16.2% increase relative to PVC-ES - confirms the role of VTMS in overcoming interfacial incompatibilities.

The thermal behavior of PVC and its composites with untreated and vinyltrimethoxysilane-treated eggshell filler, prepared at 1:1 and 1:2 ratios (PVC: filler) via co-precipitation, was investigated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). From the TGA curves of the composite films presented in Figs. 5 and 6, it is evident that all samples revealed a minor mass loss of approximately 3% upon heating to 120°C. This initial weight loss is due to the evaporation of residual moisture and volatile components, including trace solvents retained from the film fabrication process, as well as adsorbed water present in the eggshell powder filler [28]. In the initial stage of thermal degradation, occurring within the temperature range of 220–350°C, the thermogravimetric (TG) curves of the composite films exhibit a comparable degradation profile. This stage is primarily attributed to the dehydrochlorination of polyvinyl chloride, during which hydrogen chloride (HCl) is released and conjugated polyene sequences are formed. The evolution of HCl promotes further degradation through an autocatalytic mechanism, thereby accelerating the decomposition of the polymer matrix [29]. Although the onset temperatures for degradation are similar across samples, the pure PVC film underwent a more significant mass compared to the reduced degradation observed in the PVC-ES (Fig. 5) and PVC:VTMS-ES composites (Fig. 6). A subsequent degradation stage is observed between 400 and 550 °C, which is associated with oxidative decomposition and the breakdown of the conjugated polyene structures formed during dehydrochlorination [30]. While pure PVC showed sustained mass loss beyond 550°C due to char oxidation, composites exhibited suppressed degradation in this range, indicating a stabilizing effect imparted by the eggshell filler. This enhanced stability is attributed to the filler's inherent thermal resistance and potential insulation properties [31, 32].

Fig. 5 compares the thermogravimetric behavior of neat PVC with PVC:ES composites containing untreated eggshell at filler loadings of 1:1 and 1:2.

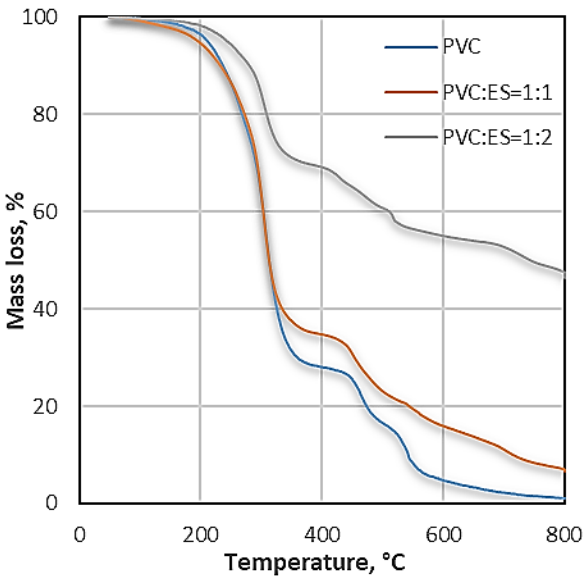

Fig. 5. TG curves of PVC and PVC:ES films

At the lower filler ratio, the composite exhibits a marginally reduced thermal stability, manifested as a slight shift of the degradation onset to lower temperatures. This effect likely arises from residual organic membrane residues within the eggshell powder, which catalyzes chain scission during early stages of heating [33]. By contrast, increasing the eggshell content to a 1:2 ratio significantly retards the onset of dehydrochlorination and yields a more gradual weight loss profile. The char yield at 800 °C increases markedly from 1 % for PVC to 8 % and 48 % for the 1:1 and 1:2 PVC:ES films, respectively. This improvement is attributed to the multifunctional role of biogenic $CaCO_3$ in the eggshell filler. During the thermal degradation of PVC, HCl is released, which can be neutralized by $CaCO_3$ from eggshells, yielding $CaCl_2$, CO_2, and H_2O, and thus reducing autocatalytic breakdown [33]. In addition, the solid porous structure of eggshell particles acts as a barrier to heat and radicals, delaying decomposition and encouraging char formation. Their porosity also traps volatile products, lowering the degradation of volatile products and enhancing flame-retardant performance [34].

VTMS surface treatment significantly improved thermal stability. PVC:VTMS-ES composites showed an about 30°C increase in the onset temperature of the primary degradation stage compared to untreated counterparts. The 1:2 PVC:VTMS-ES film exhibited only 29% mass loss during this stage, representing an approximately 12% improvement over the untreated 1:2 PVC:ES (Fig. 6). In

comparison, Murugan et al. [18] reported only a 15°C increase in decomposition temperature and a negligible decrease in mass loss when using untreated eggshell fillers. This further highlights the importance of surface treatments and forming the siloxane (Si-O-Si) linkages between hydrolyzed VTMS silanols and functional groups on both $CaCO_3$ and PVC [35]. These covalent bonds improve filler-matrix adhesion, restrict polymer chain mobility, hinder volatile diffusion (e.g., HCl), and promote char retention. The silane layer also acts as a protective thermal barrier, increasing degradation activation energy and improving overall thermal resistance [35]. While final char yield remained $CaCO_3$ dependent, VTMS modification significantly altered degradation kinetics and shielding behavior

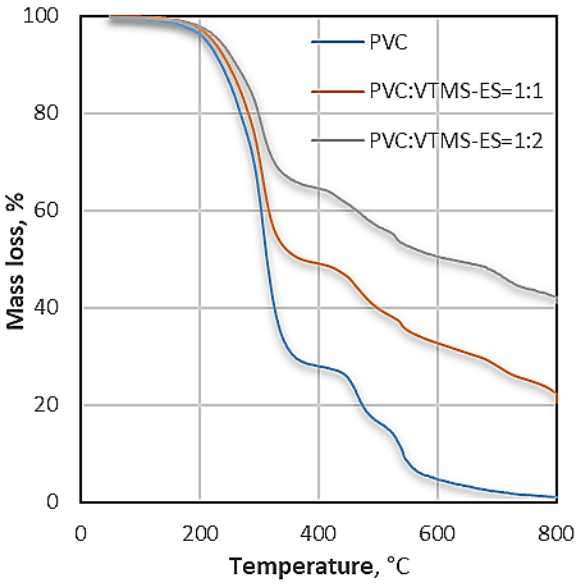

Fig. 6. TG curves of PVC and PVC:VTMS-ES films

The DTA profiles presented in Figs. 7 and 8 reveal the dynamics of the thermochemical processes accompanying the thermal decomposition of PVC and its composites with untreated and VTMS-treated eggshell fillers. Notably, the exothermic peak around 500°C exhibits marked differences between pure PVC and PVC:ES composites (Fig. 7). The 1:2 PVC:ES film displays a markedly intensified exothermic peak compared to PVC film, indicating additional heat-releasing reactions. This is attributed to the dual contribution of the biogenic calcium carbonate in neutralizing the evolved hydrogen chloride and the porous microstructure of the eggshell particles, which effectively retain volatile degradation products. These volatiles undergo secondary oxidation within the composite matrix, thereby prolonging heat release and amplifying the thermal response [36].

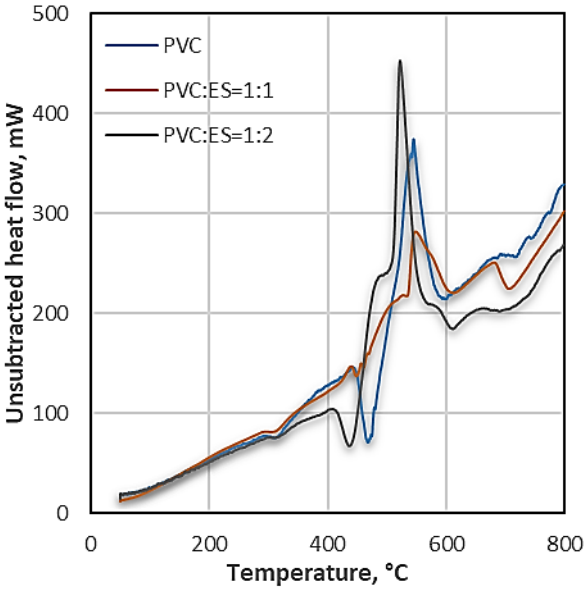

Fig. 7. DTA curves of PVC and PVC:ES films

The reduced peak intensity in the 1:1 PVC:ES film may be explained by an insufficient concentration of the active mineral component to drive significant heat-generating reactions during this stage of thermal decomposition. Despite its presence, the calcium carbonate in this composition does not reach the concentration required for efficient interaction with the liberated HCl. Simultaneously, the presence of organic residues from the eggshell membrane catalyzes premature chain scission within the polymer matrix. This leads to fragmentation of the structure before a stable carbon skeleton can form, thereby limiting the subsequent formation and effective oxidation of carbonaceous residues. Consequently, this attenuates the exothermic response in the high-temperature region.

Films containing VTMS-ES filler demonstrate a different thermal behavior. For both 1:1 and 1:2 PVC:VTMS-ES ratios, the exothermic peak associated with the oxidative degradation of char residues remains nearly unchanged in terms of temperature, intensity, and profile compared to pure PVC. This indicates that surface saturation of the filler with silanol groups is achieved at the 1:1 ratio, enabling sufficient interfacial bonding and matrix stabilization. Increasing the content of modified eggshells to a 1:2 ratio does not induce further changes in the thermochemical response, indicating that the role of the inorganic filler in this temperature range is secondary to that of the PVC matrix.

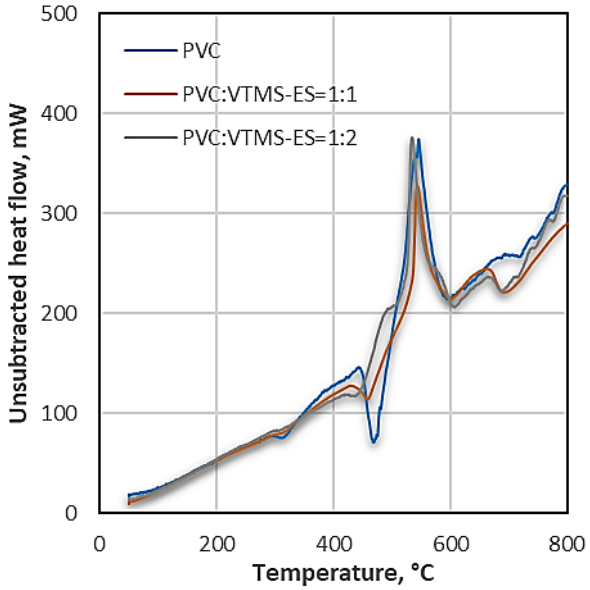

Fig. 8. DTA curves of PVC and PVC:VTMS-ES films

These observations align with previous studies. Murugan et al. [18] reported that while increasing the concentration of finely dispersed eggshell filler enhances thermal resistance and char yield, this effect plateaus beyond a certain loading, indicating thermodynamic saturation. Similarly, Sharmeeni et al. [19] emphasized that thermal degradation in PVC-ESP composites is primarily governed by the matrix–filler compatibility. Although surface modification improves the interfacial interactions and thermal stability, it does not fundamentally alter the decomposition mechanism of the polymer matrix.

4. CONCLUSION

In this study, PVC composite films were effectively produced by solution casting and co-precipitation methods. The comparative analysis demonstrates that co-precipitation leads to better filler dispersion and a more homogeneous microstructure, effectively eliminating issues related to residual solvent typical of solution-cast films. This led to a significant improvement in mechanical properties for all obtained films, with the PVC film reporting 42.5% higher elongation at break, 53.5% higher tensile strength, and 83.4% higher Young's modulus, while for the PVC-ES composite, the increase reached 81.6% for tensile strength and 55.5% for elongation at break The PVC:VTMS-ES composite films showed the most improvement, with 83.5% higher tensile strength, 87.9% higher Young's modulus, and 53.0% higher elongation at break. The better thermal stability of the composites, especially when VTMS-treated eggshells are used, is due to stronger interactions between the filler and the polymer matrix and stable siloxane bonds.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

REFERENCES

[1] S. Sunardi, D. Ariawan, E. Surojo, A. Prabowo, H. Akbar, B. Cao, H. Carvalho, Assessment of eggshell-based material as a green-composite filler: Project milestones and future potential as an engineering material. *Journal of the Mechanical Behavior of Materials*, 32(1), 2023: 20220269. https://doi.org/10.1515/jmbm-2022-0269

[2] A. Feng, G. Wu, Y. Wang, C. Pan, Synthesis, Preparation and Mechanical Property of Wood Fiber-Reinforced Poly (vinyl chloride) Composites. *Journal of Nanoscience and Nanotechnology,* 17(6), 2017: 3859–3863. https://doi.org/10.1166/jnn.2017.13987

[3] B. Dan-asabe, Thermo-mechanical characterization of banana particulate reinforced PVC composite as piping material. *Journal of King Saud University-Engineering Sciences,* 30(4), 2018: 296–304. https://doi.org/10.1016/j.jksues.2016.11.001

[4] A. Sujin Jose, A. Athijayamani, S.P. Jani, A review on the mechanical properties of bio waste particulate reinforced polymer composites. *Materials Today: Proceedings,* 37, 2021: 1757–1760. https://doi.org/10.1016/j.matpr.2020.07.360

[5] F.C. Cabrera, Eco-friendly polymer composites: A review of suitable methods for waste management. *Polymer Composites,* 42(6), 2021: 2653–2677. https://doi.org/10.1002/pc.26033

[6] S. Chandra Dubey, V. Mishra, A. Sharma, A review on polymer composite with waste material as reinforcement. *Materials Today: Proceedings,* 47, 2021: 2846–2851. https://doi.org/10.1016/j.matpr.2021.03.611

[7] S. Owuamanam, D. Cree, Progress of Bio-Calcium Carbonate Waste Eggshell and Seashell Fillers in Polymer Composites: A Review. *Journal of Composites Science,* 4(2),

2020: 70.
https://doi.org/10.3390/jcs4020070

[8] A.G. Supri, H. Ismail, S. Shuhadah, Effect of Polyethylene-Grafted Maleic Anhydride (PE-g-MAH) on Properties of Low Density Polyethylene/Eggshell Powder (LDPE/ESP) Composites. *Polymer-Plastics Technology and Engineering,* 49(4), 2010: 347–353. https://doi.org/10.1080/03602550903414035

[9] R. Dweiri, Processing and Characterization of Surface Treated Chicken Eggshell and Calcium Carbonate Particles Filled High-Density Polyethylene Composites. *Materials Research*, 24(3), 2021: e20210078 https://doi.org/10.1590/1980-5373-mr-2021-0078

[10] R.K. Chandrappa, S.S. Kamath, The Egg shell as a filler in composite materials-a review. *Journal of Mechanical and Energy Engineering,* 4(4), 2021: 335–340. https://doi.org/10.30464/jmee.2020.4.4.335

[11] S. Kowshik, S. Sharma, S. Rao, M. Shettar, P. Hiremath, Mechanical Properties of Post-Cured Eggshell-Filled Glass-Fibre-Reinforced Polymer Composites. *Journal of Composites Science*, 7(2), 2023: 49. https://doi.org/10.3390/jcs7020049

[12] S. Murugan, Y. Munusamy, M. Muniandy, H. Ismail, Development of HDPE-modified eggshell composite. *Polymer Composites,* 39(5), 2016: 1630–1637. https://doi.org/10.1002/pc.24108

[13] H. Wu, D. Xiao, J. Lu, T. Li, C. Jiao, S. Li, P. Lu, Z. Zhang, Z. Preparation and Properties of Biocomposite Films Based on Poly (vinyl alcohol) Incorporated with Eggshell Powder as a Biological Filler. *Journal of Polymers and the Environment,* 28, 2020: 2020–2028. https://doi.org/10.1007/s10924-020-01747-2

[14] C. Pavon, M. Aldas, M. Samper, D. Motoc, S. Ferrandiz, J. López-Martínez, Mechanical, Dynamic-Mechanical, Thermal and Decomposition Behavior of 3D-Printed PLA Reinforced with $CaCO_3$ Fillers from Natural Resources. *Polymers,* 14(13), 2022: 2646. https://doi.org/10.3390/polym14132646

[15] Y.-T Zheng, D.-R. Cao, D.-S. Wang, J.-J Chen, Study on the interface modification of bagasse fibre and the mechanical properties of its composite with PVC. *Composites Part A: Applied Science and Manufacturing*, 38(1), 2007: 20–25. https://doi.org/10.1016/j.compositesa.2006.01.023

[16] V. Vandeginste, Food waste eggshell valorization through development of new composites: A review. *Sustainable Materials and Technologies*, 29, 2021: e00317. https://doi.org/10.1016/j.susmat.2021.e00317

[17] T.P. Mohan, K. Kanny, Thermal, mechanical and physical properties of nanoegg shell particle-filled epoxy nanocomposites. *Journal of Composite Materials,* 52(29), 2018: 3989–4000. https://doi.org/10.1177/0021998318773445

[18] S. Murugan, Y. Munusamy, H. Ismail, Effects of chicken eggshell filler size on the processing, mechanical and thermal properties of PVC matrix composite. *Plastics, Rubber and Composites,* 46(1), 2017: 42–51. https://doi.org/10.1080/14658011.2016.1260217

[19] M. Sharmeeni, Y. Munusamy, H. Ismail, The effect of blending sequence on the structure and properties of poly (vinyl chloride)/chicken eggshell powder composites. *Journal of Vinyl and Additive Technology,* 23(4), 2015: 298–304. https://doi.org/10.1002/vnl.21503

[20] A.A. Hassen, M. Dizbay-Onat, D. Bansal, T. Bayush, U. Vaidya, Utilization of Chicken Eggshell Waste as a Bio-Filler for Thermoplastic Polymers: Thermal and Mechanical Characterization of Polypropylene Filled with Naturally Derived $CaCO_3$. *Polymers and Polymer Composites*, 23(9), 2015: 653–662. https://doi.org/10.1177/096739111502300908

[21] Z. Lin, Z. Zhang, K. Mai, Preparation and properties of eggshell/β-polypropylene bio-composites. *Journal of Applied Polymer Science,* 125(1), 2011: 61–66. https://doi.org/10.1002/app.34670

[22] A.H. Shah, Y. Zhang, X. Xu, A. Dayo, X Li, S. Wang, W. Liu, Reinforcement of Stearic Acid Treated Egg Shell Particles in Epoxy Thermosets: Structural, Thermal, and Mechanical Characterization. *Materials*, 11(10), 2018: 1872. https://doi.org/10.3390/ma11101872

[23] V. Vandeginste, D. Madhav, Interface Modification and Characterization of PVC Based Composites and Nanocomposites. In: H, A., Sabu, T. (eds) Poly (Vinyl Chloride) Based Composites and Nanocomposites. Engineering Materials. *Springer*, Cham. 2023: 55-86. https://doi.org/10.1007/978-3-031-45375-5_3

[24] A.T. Abbas, A.J. Al-Obaidi, S.J. Ahmed, Synthesis and study of the mechanical properties of biodegradable polyvinyl alcohol/eggshell composites. *Journal of Engineering Science and Technology*, 16(4), 2021: 3084–3093.

[25] N.F. Alias, H. Ismail, H. Effects of Partial Replacement of Eggshell Powder by Halloysite Nanotubes on the Properties of Polyvinyl Alcohol Composites. *IOP Conference Series: Materials Science and Engineering*, 374, 2018: 012032. https://doi.org/10.1088/1757-899x/374/1/012032

[26] S.-S. Kim, M.S. Park, O. Jeon, C.Y. Choi, B.-S. Kim, Poly(lactide-co-glycolide)/hydroxyapatite composite scaffolds for bone tissue engineering. *Biomaterials*, 27(8), 2006: 1399–1409. https://doi.org/10.1016/j.biomaterials.2005.08.016

[27] R.N. Farahana, A.G. Supri, P.L. Teh, Tensile and Water Absorption Properties of Eggshell Powder Filled Recycled High-Density Polyethylene/Ethylene Vinyl Acetate Composites: Effect of 3-Aminopropyltriethoxysilane. *Journal of Advanced Research in Materials Science,* 5(1), 2015: 1-9.

[28] B.A. Oredokun-Lache, E.B. Ibrahim, A.G. Oluwafemi, G.O. Erifeta, S.J. Josiah, O.M. Oluba, A circular economical application of eggshell waste as a bio-filler in the fabrication of gum Arabic composite film. *Food Science and Preservation*, 31(3), 2024: 394-407. https://doi.org/10.11002/fsp.2024.31.3.394

[29] J. Tomaszewska, T. Sterzyński, A. Woźniak-Braszak, M. Banaszak, Review of Recent Developments of Glass Transition in PVC Nanocomposites. *Polymers,* 13(24), 2021: 4336. https://doi.org/10.3390/polym13244336

[30] Z. Wang, R. Wei, X. Wang, J. He, J. Wang, Pyrolysis and Combustion of Polyvinyl Chloride (PVC) Sheath for New and Aged Cables via Thermogravimetric Analysis-Fourier Transform Infrared (TG-FTIR) and Calorimeter. *Materials*, 11(10), 2018: 1997. https://doi.org/10.3390/ma11101997

[31] M. Baláž, E.V. Boldyreva, D. Rybin, S. Pavlović, D. Rodríguez-Padrón, T. Mudrinić, R. Luque, State-of-the-Art of Eggshell Waste in Materials Science: Recent Advances in Catalysis, Pharmaceutical Applications, and Mechanochemistry. *Frontiers in Bioengineering and Biotechnology,* 8, 2021: 12567. https://doi.org/10.3389/fbioe.2020.612567

[32] P. Liu, M. Zhao, J. Guo, Thermal Stabilities of Poly (Vinyl Chloride)/Calcium Carbonate (PVC/$CaCO_3$) Composites. *Journal of Macromolecular Science, Part B*, 45(6), 2006: 1135–1140. https://doi.org/10.1080/00222340600962650

[33] L. Khachatryan, M.-x. Xu, A.-j. Wu, M. Pechagin, R. Asatryan, Thermal degradation behavior and kinetic analysis of polyvinyl chloride. *Journal of Analytical and Applied Pyrolysis*, 121, 2016: 75-63. https://doi.org/10.1016/j.jaap.2016.07.004

[34] X. Fu, L. Bao, J. Lei, J. Wang, Thermal stability and flame retardancy of PVC composites reinforced with surface-modified biofillers. *Journal of Vinyl and Additive Technology*, 22(4), 2015: 452-459. https://doi.org/10.1002/vnl.21465

[35] J.K. Lee, J.H. Lee, K.H. Lee, B.S. Jin, Phase separation and crystallization behavior in extruded polypropylene/ethylene–propylene rubber blends. *Journal of Applied Polymer Science*, 81(3), 2001: 695-700. https://doi.org/10.1002/app.1486

[36] K. Skórczewska, K. Lewandowski, P. Szewczykowski, S. Wilczewski, J. Szulc, P. Stopa, P. Nowakowska, Waste Eggshells as a Natural Filler for the Poly(Vinyl Chloride) Composites. *Polymers*, 14(20), 2022: 4372. https://doi.org/10.3390/polym14204372