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COMPARATIVE STUDIES OF ETHYLENE VINYL ACETATE FILMS WITH VARIOUS SILICATE NANOCOMPOSITES

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ABSTRACT

Ethylene vinyl acetate (EVA) a copolymer of polyethylene with 18% of VA are utilized in this study. Thin films of EVA with various silicates – MMT (Montmorillonite) and Sodium Silicate are cast by Solvent Evaporation technique at room temperature. Casted films are subjected to FTIR, Mechanical, Thermogravimetry(TGA) and SEM analysis. These studies are utilized to identify which is better-suited silicate among the two (MMT and Sodium Silicate) for the improvement of mechanical and thermal stability of EVA for engineering applications.

Keywords: EVA, MMT (Montmorillonite), Sodium Silicate, FTIR, Thermogravimetry, Thermal stability

INTRODUCTION

Polymers, an engrossing molecule in which chain and metameric motions are long-winded, bringing out an intricate mixture of characteristic properties.[1] Polymer thin-film techniques play a vital role in recent scientific developments: polymer glaze helps to preserve, decorate and protect core substances. Montmorillonite(MMT) enhances the char rigidity and thermal stability of the composite materials due to its unique heat and mass flow barrier properties.[2,3] In particular, the polymer clay nanocomposites have been gained considerable interest in the past decades due to their well-improved strength, firmness and barrier properties with minimum incorporation of organoclay, when compared to conventional filler, composites.[4-7] MMT is a phyllosilicate group of minerals that are formed when its water solution are precipitated as microscopic crystals, termed as clay. MMT is a smectite group of clay have an octahedral sheet of alumina sandwiched between two tetrahedral silica sheets. The particles of MMT are about 1 μm diameter, 0.96 nm of thickness and are normally plate-like structured, the individual clay particle structure can be viewed with magnification of about 25,000 times with the help of an electron microscope. Sodium Silicate is generally transparent, colorless solids or white powders, and are soluble in water in various amounts. Sodium silicate is a common name for a mixture of compounds, mainly metasilicate, also well known as liquid glass or water glass. Those are having a broad range of uses, likely in the articulation of cement, manufacturing of refractory ceramics, submissive fire protection, textile, and lumber processing and in the production of silica gel and adhesives. Sodium silicate solution or commonly known as water glass has been extensively used as a fire retardant and a glue of cellulose-based materials such as paper, plywood, cotton fabrics and cardboard.[8-11] A novel breed of composite materials called as polymer layered silicate composites[12] are rising as the most significant compound materials due to their superior mechanical[13,14] thermal[15] and fire retardant.[16,17]

EXPERIMENTAL

The host polymer EVA, Chloroform, as a solvent and Vinyl Acetate were procured from M/S. Scientific Chemical Suppliers, Chennai. Montmorillonite and Sodium silicate were purchased from M/S. Sigma

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Aldrich, USA. The pellets of EVA were soaked in chloroform for about 10 hours and is stirred at the temperature of 30-32ºC in a magnetic stirrer until to obtain a homogenous solution of it. EVA/MMT composite films are prepared by varying the concentration of both the polymer (93%) and MMT (7%) in wt/wt ratio. EVA/Sodium Silicate composite films were prepared by varying the concentration of both the polymer (93%) and Sodium Silicate (7%) in wt/wt ratio. The resultant films of 0.1 mm thickness and even textured are further used for characterization studies.

Characterization Studies

Spectral Studies

The spectral technique helps to record the spectra, having a large number of absorption band structure, helps to derive information about the corresponding structure of crystalline, organic, inorganic and polymeric matters. The IR radiation of absorption results ranges of bands in the substance molecule which may bend and stretch concerning with each other. The Perkin Elmer made FT-IR instrumentation is employed to observe IR spectra in absorption mode for EVA/MMT and EVA/ Sodium silicate composite films, in the region of 4000–450 cm^{-1} is covered by this instrument. Vibrational bands assignments are made. Functional groups are identified both in the polymer and silicate composite. Figure-1 shows the FTIR spectra of EVA, EVA/MMT, EVA/Sodium silicate films.

Mechanical Studies

Mechanical studies of EVA/MMT & EVA/Sodium Silicate films are measured with Instran Model5567 testing machine with a crosshead speed 10 mm/min. Sample of 5cm length and 1cm width of each film is subjected to testing and the values are observed. The stress-strain data are recorded for EVA/MMT films and EVA/Sodium Silicate films. Mechanical parameters –Tensile strength, Flexural Strength and Toughness are measured for both the films. Figure-2(a) shows stress-strain graph of EVA/ MMT film. Figure-2(b) shows a stress-strain graph of EVA/ Sodium Silicate film.

Thermo Gravimetric Studies

The thermal stability of EVA, EVA/MMT, and EVA/ Sodium Silicate films are investigated through TG analysis with the PerkinElmer/ Pyris made instrumentation at the temperature of 20 ºC/min and the weight loss of sample against the temperature in the range of 50-800ºC is observed under the atmosphere of N_2 gas. Figure-3 shows the thermogravimetric graph of EVA, EVA/ MMT, EVA/ Sodium Silicate films respectively. Degradation temperature is identified for all the films.

Morphological Studies

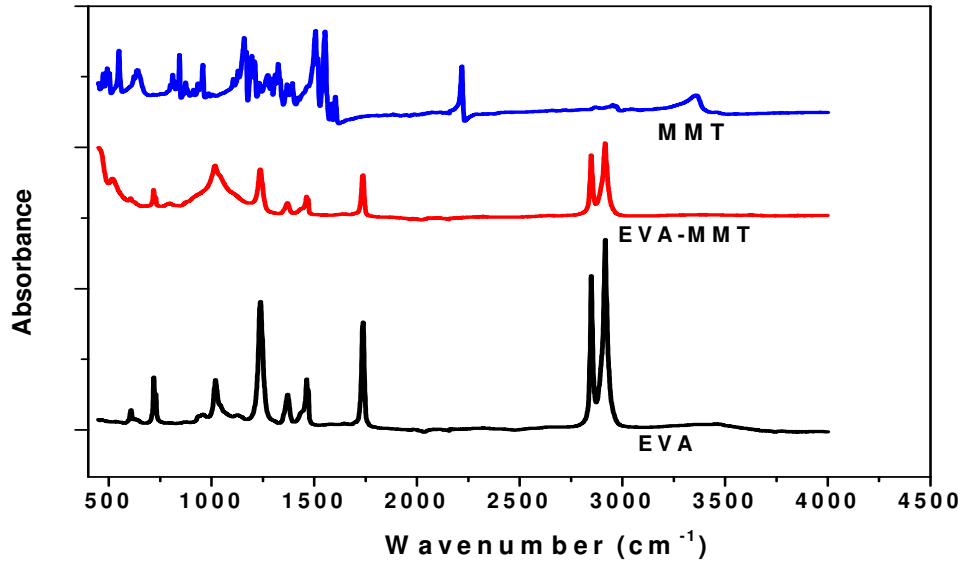
The morphology of EVA, EVA-MMT, EVA-SS composite films are characterized with a Scanning Electron Microscope (SEM, Phenom world pro) and are shown in fig.4a, 4b,4c with the magnification of 44K, 51K and 50K respectively.

RESULT AND DISCUSSION

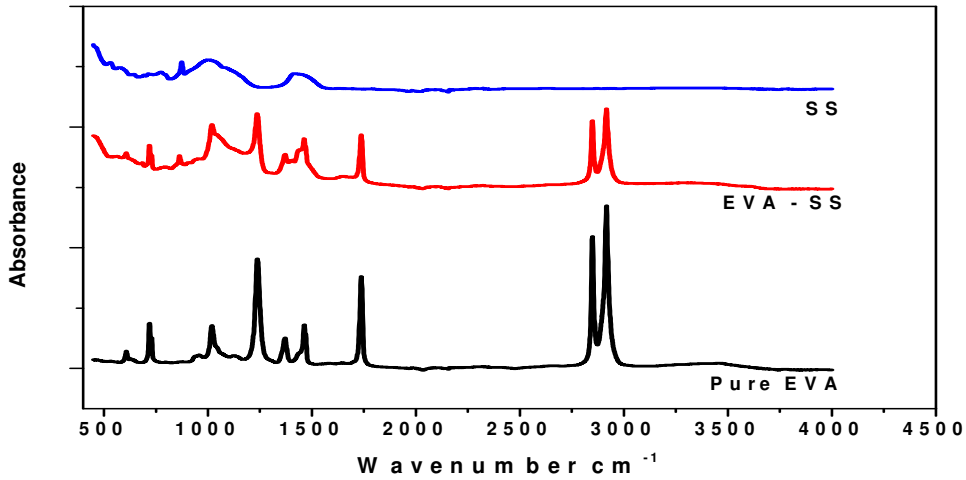
FTIR Analysis

Vibration band assignments are made as follows; O-H vibration occurs at 3100-3600cm^{-1}, C=O vibration occurs at 1739cm^{-1} C=C vibration occurs between 1600 and 1700 cm^{-1}, 1372 cm^{-1} corresponds toCH_3 stretching and C-O stretching occurs at 1237 cm^{-1} for EVA copolymer. The incorporation of MMT in the EVA/MMT composite film is established by peaks as Si-OH stretching corresponds to 3360 cm^{-1} appears at 3377 cm^{-1} in the composite film, OH stretching of 1637 cm^{-1} appears at 1645 cm^{-1} and wave numbers 1040 cm^{-1} , 526 cm^{-1} corresponds to Si-O stretching and Al-O deformation appears in the EVA-MMT nanocomposite film confirms the presence of Organoclay in the film of composite material. The shifting of some bands in the composite film confirms the existence of molecular interaction as compared to the spectra of pure MMT powder.[18] The presence of Sodium silicate (SS) in the film is also clear by the assignments of the functional groups of SS and EVA-SS nanocomposite films. For the EVA-SS films, apparent interaction among molecules could be observed with the shift in the Si-O(Na) asymmetric stretching, whose peak shifted from 1005 cm^{-1} in the SS powder to 1020 cm^{-1} in the film. Similarly IR vibrations correspond to (Na)O-Si-O(Na) stretching, (H)O-Si-O(H)δ_{as} appears at 874 cm^{-1}, 775 cm^{-1}

respectively. Hence the incorporation of MMT and SS in the EVA copolymer can be confirmed by identifying the functions groups corresponds to EVA,MMT and SS in the EVA-MMT, EVA-SS nanocomposite films.



(a) FTIR Spectra of EVA, EVA-MMT,MMT



(b) FTIR Spectra of EVA, EVA-SS,SS

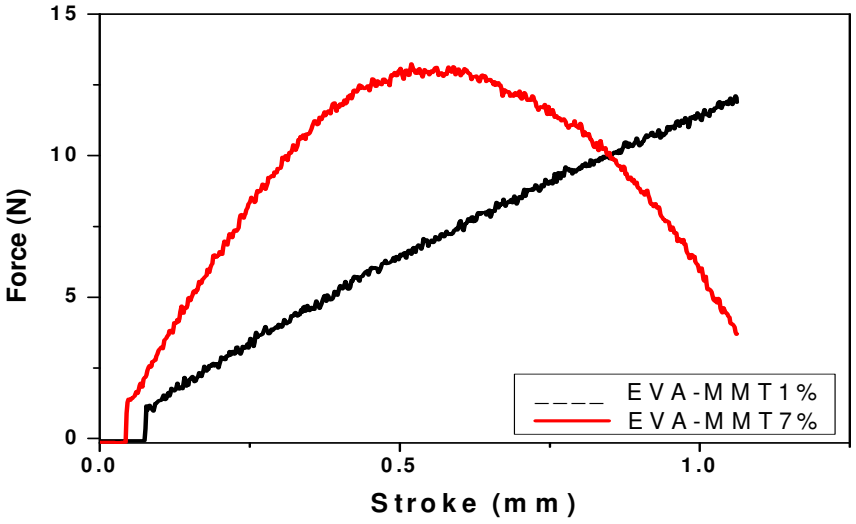
Fig.-1

Mechanical Analysis

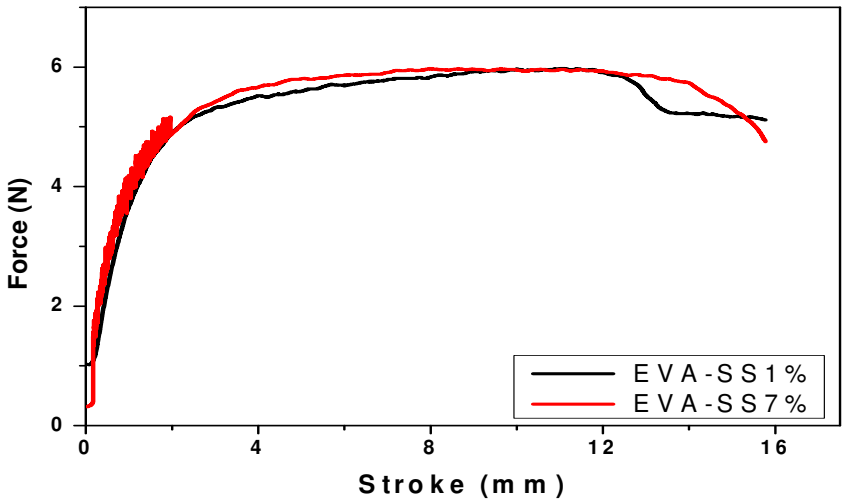
It is confirmed from the Table-1 that, as the percentage of nanocomposite materials increases the tensile strength also increases. Mechanical studies are used as a tool to identify the better silicate nanocomposite for EVA films. Better silicate nanocomposite for EVA is MMT since this film can withstand maximum force value (13.02N) before it fractures.

Table-1: Variation of Mechanical Parameter Values for Different Silicate Nanocomposite Films.

S. No	% of Silicates	Tensile Strength N/mm^2		Flexural Strength N/mm^2		Toughness N/mm^2	
		EVA/MMT	EVA/SS	EVA/MMT	EVA/SS	EVA/MMT	EVA/SS
1	7%	13.02	5.979	4.158	4.784	4.365	5.023
2	1%	11.98	5.860	11.753	5.130	12.341	5.386



(a) Stress-Strain graph of EVA/ MMT film.



(b) Stress-Strain Graph of EVA/ SS Film
Fig.-2

Thermal Analysis

The thermal stability of the composite materials has been analyzed by thermogravimetric analysis under N_2 atmosphere. The Fig.-3 shows the TGA curves of EVA, EVA/MMT, EVA/SS nanocomposite films respectively at different conditions. Initially from room temperature to 150°C is ascribed to the removal of moisture and the tangled residue from the chain of polymer. The thermal degradation of EVA transpired in two successive stages as shown in Fig.-3a. The first stage of degradation between 300 and 380°C represents the deacylation of vinyl acetate group of EVA with the exclusion of acetic acid. The second stage between 380 and 450°C corresponds to the further deprivation of vinyl polyethylene chains formed in the earlier stage. At the second stage there is a rapid weight loss with increase of temperature in all the samples as in Fig.-3a. In the intercalated nanocomposites, the silicate layers with high aspect ratio which acquire barrier property efficiently block the degradation of EVA chain located in interlayer spacing.[19]

The introduction of sodium silicate(SS) in EVA shifting the first stage degradation temperature from the range of 300°C to beyond 400°C and the second stage to beyond 500°C as in fig.3(c). Increase in the

percentage of sodium silicate in EVA composite film increases the degradation temperature to the higher range. The introduction of MMT in EVA shifting the onset degradation temperature to the range higher than that of Pure EVA as in Fig.-3b. This behavior confirms the increased thermal stability of nanocomposites and also the residual weight of nanocomposite with greater MMT percentage as7% is much higher than that of pure polymer film. While comparing EVA/MMT and EVA/SS composite films, EVA with 1% of SS results higher the onset temperature and residual weight than that of films with 1% MMT. But better thermal stability occurs with higher percentage of MMT as7%, which results the residual weight of 57.45% much greater than that of composite film with 7% of SS, showing the increase of thermal steadiness of nanocomposite as the result of retardation effect of organoclay platelets on the decomposition of the polymer.[20]

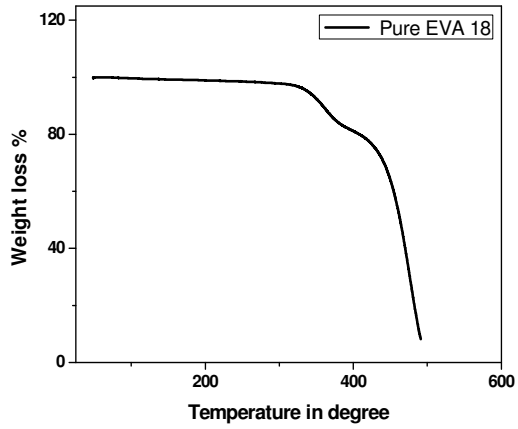


Fig.-(a): TGA Curve of EVA

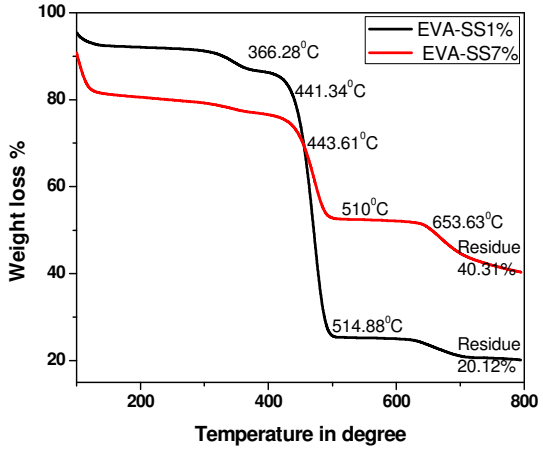


Fig.-(c): TGA Curve of EVA/SS

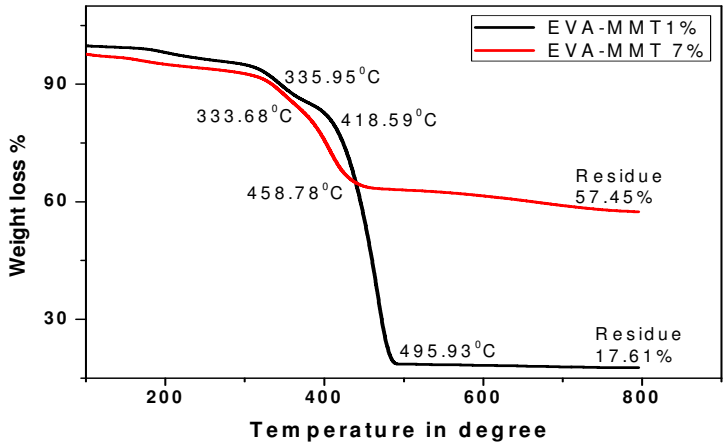


Fig.-(b): TGA Curve of EVA/MMT
Fig.-3

SEM Analysis

The SEM micrographs in Fig.-4 reveal the difference in surface morphology between the pure EVA (Fig.-4a) and EVA/MMT(Fig.-4b) EVA/SS(Fig.-4c) nanocomposite films. Images with the magnification of about 44K, 51K and 50K for EVA, EVA-MMT and EVA-SS thin films are shown in above Fig.-4(a), 4(b) and 4(c) respectively. It is noted that the films are smooth and well defined spherical crystallites with grain size < 1µm. All three samples almost exhibit a smooth surface. Among all the three samples EVA with MMT shows even textured morphology and it can be understood that the smaller degree of degradation

that took place in the meticulous composite was the result of the well dispersed and exfoliated organo-MMT. However with the increase of nanofiller concentration, the degradation kinetics also get increased as a result of poor nanofiller dispersion and exfoliation characteristics. Due to its more severe degradation the EVA nanocomposite with higher percentage of MMT shows the roughest surface morphology.[21]

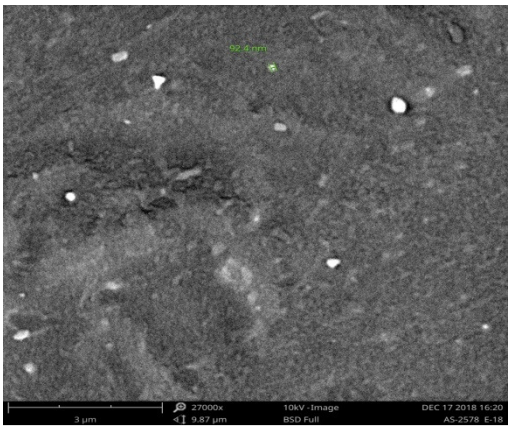


Fig.-(a): SEM Micrograph of EVA

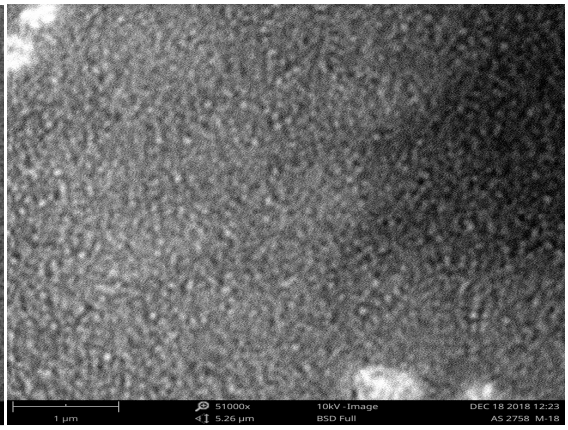


Fig.-(b): SEM Micrograph of EVA/MMT

Fig.-(c): SEM Micrograph of EVA –SS

Fig.-4

CONCLUSION

FTIR studies are used to identify functional groups. Mechanical studies are used to identify the better silicate for EVA. For the same force applied on composite films, better silicate composite is MMT since the tensile strength value is more than Sodium Silicate. Thermogravimetry analysis is used to identify eco-friendly silicate composite for EVA for engineering applications**.** Thermogravimetry analysis confirms eco-friendly silicate composite for EVA is MMT.SEM studies reveal that EVA nanocomposite with higher percentage of MMT shows the roughest surface morphology.

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