

# Effect of the Amino-carboxylate as Volatile Compatibilizer in EVA/clay Nanocomposites

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**Abstract.** The scope of this study involves the evaluation of the effect of amino-carboxylate (AC) compound on the structure, thermomechanical and rheological properties of EVA (19 wt. % vinyl acetate)-clay nanocomposites. Two commercial organoclays were pre-swollen in AC compound at 1, 2.5 and 5 wt. %, in a solvent free procedure. Later, a torque rheometer dispersed the organoclays/AC mixtures in EVA matrix. The X-ray diffraction (XRD) and Fourier transfer infrared (FTIR) spectroscopy carried out the volatilization and interaction of AC with the organoclays as well as the structure of nanocomposites. The shear flow in a parallel plate rheometer followed the change in the viscosity of the nanocomposites. These changes depended on the organoclay and the synergy between the organoclays and AC concentration. Thermal analysis was evaluated using a Thermogravimetric analysis (TGA) and Dynamic scanning calorimetry (DSC). The AC compound decreases the catalization effect of organoclay in the deacetylation reaction of EVA. Mechanical properties were also evaluated. The increase in the Young modulus and elongation (as measured via tensile testing), provided evidence of a good level of dispersion and surface interaction in the EVA/clay/AC nanocomposites. These results demonstrate the feasibility to use amine-carboxylate compounds as compatibilizer in polymer/clay nanocomposites to enhance their performance.

**Keywords:** vapor phase corrosion inhibitor, Amine carboxylate, EVA, clay, nanocomposite.

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## INTRODUCTION

Poly(ethylene-co-vinyl acetate), EVA, has been used widely in several applications [1] such as packing of food or parts, photovoltaic films, shoes industry, cable jacketing, drug carrier and electrical insulation due its low-cost and low-energy manufacturing. Most of these applications require a balance in the mechanical, thermal, dielectric or permeability properties.

In fact, to accomplish the referred balance of properties and meet the corresponding industrial requirements, researchers have studied certain issues for improving the use of EVA in several applications. Thus, authors have analyzed potential problems in food packing, [2] drug delivery [3] and corrosion in photovoltaic films [4] probably due to acid acetic formation during EVA degradation [5]. In terms of EVA/clay nanocomposite, several variables including different types of organoclays [6], acetate content in EVA [7], degradation of EVA-clay [8] or compatibilization [9] have been studied. The aim was to improve the dispersion of the organoclays and enhance physical-chemical properties. Nevertheless, there are unexplored issues in degradation and dispersion of the organoclays in EVA nanocomposites and their performance.

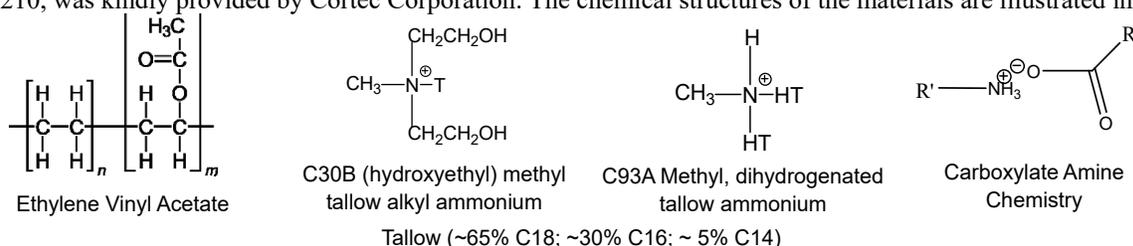
In this research, an Amino-carboxylate (AC) compound was incorporated in EVA/clay nanocomposite processing. These compounds are environmental friendly and have been used extensively as vapor phase corrosion inhibitor (VpCI) for industrial applications [10]. Amino and carboxylate ions dissociate and interact with anionic and cationic metal surfaces [11]. Therefore, AC can potentially interact with all organoclay surfaces. Besides, AC would promote a green nanocomposite processing approach, since it avoids the use of solvents, acids or high temperatures during the mixing procedures. This is relevant in terms of development a new kind of non-toxic and easy processing compatibilizer. For this reason, EVA/organoclay nanocomposites with different concentration of AC were studied to determine the AC ability to disperse the organoclays. The objective was to improve physical-chemical and processing properties for obtaining high performance applications of these nanocomposites.

## METHODS

### Materials

Ethylene vinyl acetate (EVA), Braskem 3019 PE, was kindly provided by Nutec America. The material has 18% vinyl

acetate content, melt flow of 2.5 gr/10 min as stated by the manufacturer. Two commercial organoclays, purchased from Southern Clay products, were: Cloisite 30B (C30B) and Cloisite 93A (C93A). The Amino-carboxylate (AC) compound, RM-210, was kindly provided by Cortec Corporation. The chemical structures of the materials are illustrated in Figure 1.



**FIGURE 1.** Chemical structures of materials used in this research.

## Preparation

For organoclay pre-swelling, AC was mixed with organoclays using a Flacktek DAC 400.1 FVZ speed-mixer operating at 2500 RPM for 1 minute, and then heated at 60°C during 10 min to induce AC volatilization. This procedure was repeated twice. For mixing composition of organoclays, AC parts were 5:1, 2:1 and 1:1, mixtures were kept in a dessicator for 24 hours until processing with EVA. For nanocomposite preparation, the mixtures EVA/Organoclay (5%wt)/AC (Content of AC: 1, 2.5 and 5% wt.) were melt mixing using Brabender Torque Rheometer at 60 r.p.m., from 90°C for 10 minutes to 80°C for 10 minutes. The transition time between both temperatures was about 10 minutes. The melted mixture was pressed in a compressing molding machine from 1000 psi to 3000 psi for about 95 °C for about 5 minutes, depending on the appropriate size and shape for further characterizations and evaluation.

## Characterization and Evaluation

X-ray diffraction patterns were obtained using a Phillips PANalytical XPert-Pro model diffractometer equipped with Cu K $\alpha$  ( $\lambda=1.54060$  Å) radiation operated at 45 kV and 40 mA with a 1/8 incident slit and 1/16" detector slit, scanning from 1° to 10° 2 $\theta$  with a 0.5° step size a 20 second count time per step. In the case of morphology of the nanocomposites, similar operating condition were used, except for the incident and detector slit 1/4" and 1/8", respectively. FTIR absorption spectra of 50  $\mu$ m films (32 scans) were analyzed in the mid-range using a Perkin Elmer FTIR Model 100. TGA characterization was performed using TA instrument model Q600 SDT. Approximately 10 mg of the sample was placed in alumina crucible and heated from room temperature to 600°C, at a heating rate of 10°C/min in nitrogen atmosphere. Glass transition,  $T_g$ , was obtained using DSC 200 operating from -50 °C to 110 °C at heating/cooling rate of 10°C/min. Viscosity measurements were accessed using a Malvern Kinexus Pro+ Rotational Rheometer at 100 °C. A parallel plate (20 mm /20 mm) arrangement with a 2.5 mm gap setting was used. Tensile tests were based on ASTM D 638. A samples Typo IV were performed at room temperature at a tensile rate 1.96 in/min using a Shimdazu AGS 10 N load frame.

## RESULTS AND DISCUSSION

Figure 2 illustrates the XRD patterns of organoclays/AC. The organoclays showed primary reflections at about 5° (~18 Å) and 3.54° (~25 Å) for C30B and C93A, respectively. The increase in the AC concentration in the organoclay mixture revealed different intercalation and dispersion behaviors. A well-defined peak at about 1.95° (~45 Å) was observed from lowest C93A:AC ratio in the case of C93A modification, while XRD patterns of C30B:AC ratios showed a broad shoulder reflection at same basal spacing. Carboxylate part and amino part developed polar and dispersive interactions with the surfactant and hydroxyl groups of the organoclays. Peaks at about 4.9° (~18 Å) and 6° (~14 Å) showed intercalations effects due to AC interaction via re-arrangements of the tallow and adsorption on organoclays surfaces. However, these peaks did not show the usual harmonic series peaks associated with the main reflection illustrated previously. Thus, mixed layering in clay occurred [12]. For the case of nanocomposites, EVA/C30B/AC also showed peaks at lower basal spacing due to regularly packed silica tatoids with collapse d-spacing of C30B, as reported in other EVA/clay studies [13]. It was also observed the presence of AC for the peak at about 8° (~11 Å) in its pure state. For the EVA/C93A, a peak of about 2.9° (~30 Å) was caused by intercalation from EVA into the galleries of C93A. Nevertheless, the XRD patterns of EVA/C93A/AC series showed an interlayer spacing collapse illustrated in the peak at about 6.8° (~13 Å). It seems that AC increases the polarity in the system. Hence, tertiary ammonium modifier from C93A is probably deprotonated by AC in the melted mixture EVA/AC. Similar deprotonation has also been observed with low molecular weight amines molecules [14].

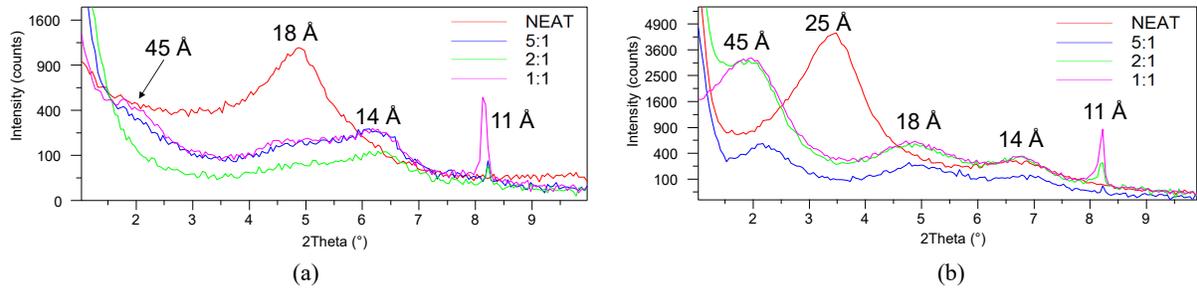


FIGURE 2. X-ray of Cloisite 30B (a) and Cloisite 93A (b) a different organoclay: AC ratio.

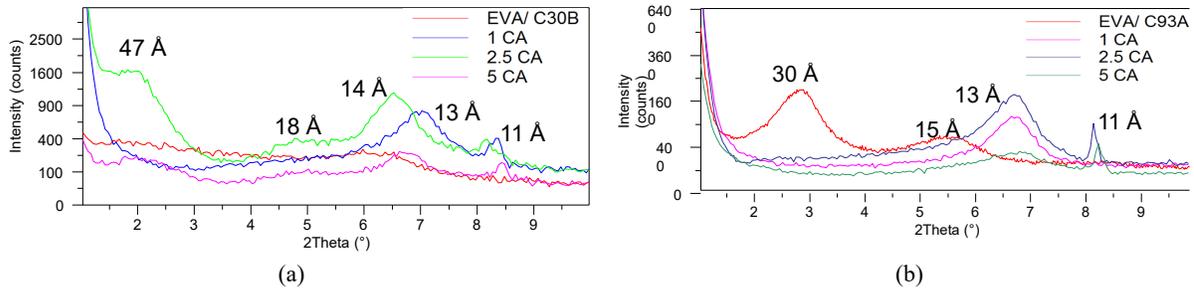


FIGURE 3. X-ray of EVA/organoclay/Clay with Cloisite 30B (a) and Cloisite 93A (c) different %weight AC concentrations.

Figure 4 shows the FTIR spectrum of AC, EVA and EVA/Clay and the addition of 5 wt. % AC. Asymmetric  $\text{COO}^-$  stretching frequency was found at  $1548 \text{ cm}^{-1}$ , while those corresponding to symmetric  $\text{COO}^-$  stretching were found at  $1364 \text{ cm}^{-1}$  and  $1338 \text{ cm}^{-1}$  as a result of carboxylate ion from AC [15,16]. A peak at about  $1555 \text{ cm}^{-1}$  due to antisymmetric  $\text{COO}^-$  stretching mode from carboxylate ion of AC was only observed in EVA/C93A/5AC. It was also noted in other AC concentrations incorporated in EVA/C93A, but not noticed in EVA/C30B/AC. This peak confirmed the interaction of carboxylate ion in the nanocomposite. A peak at about  $3190 \text{ cm}^{-1}$  resulted from NH stretching vibration of the amine ion from AC. Moreover, it was observed a shoulder at about  $3170 \text{ cm}^{-1}$  due to amine ion interaction of AC in nanocomposites for both clays. The other peaks of AC were overlapped with EVA. However, the peaks at about  $1236 \text{ cm}^{-1}$  assigned to C-O-C stretching vibration and those at about  $1740 \text{ cm}^{-1}$  due to C=O stretching vibration of EVA [17], shifted to shorter wave number for about  $25 \text{ cm}^{-1}$  and  $17 \text{ cm}^{-1}$ , respectively as polarity increased with the addition of AC in all nanocomposites. However, it might also be the consequence of the interaction of AC, acetate groups with hydroxyl and ammonium functional groups in the C30B and C93A. It is well known that the high sensibility of C-O-C and C=O stretching vibration changes in the surrounding polarity is generally transformed into infrared band shifts [18].

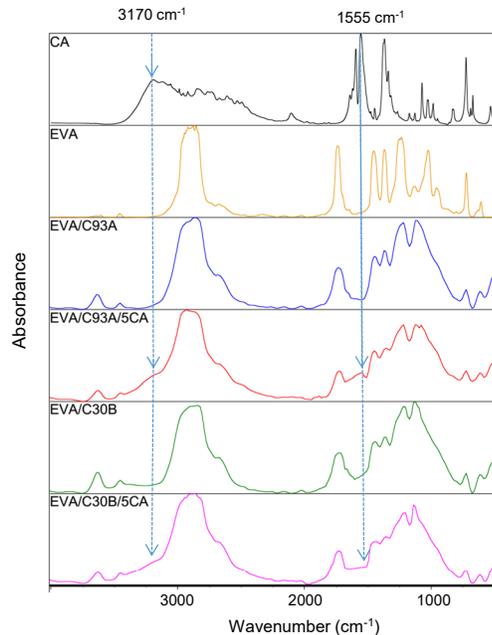
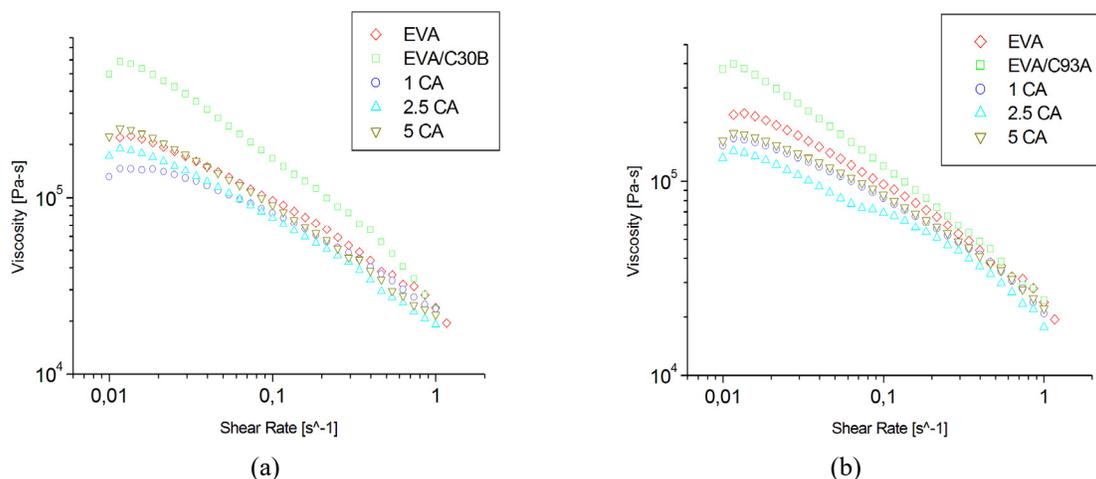


FIGURE 4. FTIR spectrum of AC, EVA and EVA nanocomposites including 5 wt. % of AC.

Figure 5 shows the flow curves of EVA/C30B series (a) and EVA/C93A series including 1, 2.5 and 5 wt. % AC. The presence of the both organoclays increased the viscosity at low shear rates due to dispersion and interaction of the organoclays surfaces and EVA matrix. The presence of 1 and 2.5 wt. % AC in EVA/C30B decreased its viscosity compared to EVA at lower shear rates. Nevertheless, its viscosity was slightly greater than EVA at 5wt% AC. Moreover, the AC decreased the viscosity in all EVA/C93A nanocomposites at lower and higher shear rates. The deprotonation of C93A surfactant decreased the interaction of this organoclay and EVA matrix. Also, the flow curves were close to EVA. Therefore, flow curves revealed a Newtonian behavior at low shear rates due to dispersion, interaction effects and power law behavior at high shear rates as a result of alignment of clay parallel to the flow, as reported [19]. Thus, AC can potentially improve the processing behavior in EVA/organooclays nanocomposites.



**FIGURE 5.** Flow curves of EVA/C30B (a) and EVA/C93A nanocomposites including 1, 2.5 and 5 wt. % AC.

Table (1) illustrates the thermal and mechanical properties of these materials. The addition of both organoclays improved considerably the Young modulus (>70%) compared to EVA matrix. As demonstrated previously, platelet strongly interacted with soft EVA matrix. Then, the presence of rigid clay particles increased the rigidity of the system. Elongation at 10 Kg<sub>f</sub> decreased considerably in EVA/C30B nanocomposite, due to the strong interaction of the hydroxyl groups from either clay or surfactant to polar groups of EVA. AC decreased the Young Modulus compared to EVA/Clays, but it was greater compared to EVA matrix. AC improved the elongation related to EVA nanocomposites. Moreover, there is a progressive increase either in elastic modulus or in elongation as Clay: AC ratios increased in the system.

In terms of thermal stability, there are two states of degradation. The first occurred as a result of de-acetylation. The second was due to a break-down of carbon in EVA backbone [8]. It is possible that hydroxyl groups of the C30B or ammonium group in C93A and acetate of EVA interacted with AC compounds. Consequently, scission of the acetate group was vanished from EVA. The weight loss temperature at 5% of EVA/clay/AC was similar to EVA, particularly at lowest Clay:AC ratio. In the second step, there was also an increase in the weight loss temperature at 30% related to EVA nanocomposites. This might result from a previous interaction of AC with unsaturated chains or previous formation of carbon-carbon double bonds in EVA backbone. There were slight changes in EVA T<sub>g</sub> values from -1 to -3 °C. This could probably occur due to AC plastification effect on EVA polymer. These results indicated that AC can improve the thermal stability compared to EVA/Clay nanocomposites.

**Table (1).** Mechanical and Thermal properties of EVA nanocomposites systems.

	Young Modulus (MPa)	Elongation, % @ 10 kgf	T <sub>g</sub> (°C)	Weight Loss temperature at 5% (°C)	Weight Loss temperature at 30% (°C)
EVA	25.0 ± 0.2	343.2 ± 4.5	-29	340	453
EVA/C93A	43.6 ± 2.3	240.0 ± 16.7	-29	316	439
1 AC	33.4 ± 1.6	291.9 ± 15.3	-30	337	442
2.5 AC	35.7 ± 2.2	293.8 ± 17.9	-30	333	450
5 AC	41.4 ± 0.8	197.6 ± 4.2	-30	296	448
EVA/C30B	45.8 ± 1.1	46.5 ± 7.2	-28	314	439
1 AC	34.7 ± 1.1	263.7 ± 15.0	-31	332	448
2.5 AC	34.9 ± 1.2	278.1 ± 17.5	-30	326	452
5 AC	36.0 ± 1.5	307.2 ± 5.3	-31	173	433

## CONCLUSIONS

In this work, the effects of an amino-carboxylate compound in the morphology, thermal and mechanical properties of EVA/Clay nanocomposites have been investigated. XRD showed that AC enhanced the intercalated structure in both organoclays and EVA nanocomposite. C-O-C and C=O stretching vibration in FTIR showed AC, EVA and Clay interactions and also the presence of AC after processing. The change in viscosity at low and high shear rate depended on the organoclay and the synergy between the organoclays and AC concentration. It was observed improved thermal and mechanical properties in EVA/Clay/AC compared to the neat nanocomposite. AC showed a potential material for replacing conventional, functionalized or reactive compatibilizer for EVA nanocomposite applications. In addition, it promoted the green processing nanocomposite approach. Further studies will have to develop potential applications of these findings in protection packing for some applications such as photovoltaic or electronic encapsulation.

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