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Abstract: Ethylene-vinyl alcohol copolymers (EVOH), with appropriate barriers and processability, can be chemically modified through vinyl alcohol units. Amides and polyamides based on condensation reactions of adipoyl chloride and hexamethylenediamine were grafted onto EVOH. Grafting was characterized by contact angle measurement, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), nuclear magnetic resonance spectroscopy (NMR) and scanning electron microscopy (SEM). Amide peaks at 3302 cm^{-1} corresponding to –NH bond stretching and the absorption of HN-CH_2 at 7.8 ppm, were observed from ATR-FTIR and NMR, respectively, as a result of grafting. SEM showed the formation of amide structures as bundles, agglomerates and needle-like particles. Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) showed considerable changes in onset of melt temperature, crystallinity and various transitions in grafted EVOH, showing an effective alteration in the physical properties compared with the virgin resin. Nylon grafted EVOH can be considered as a potential compatibilizer in polyethylene (PE)/polyamide blends via increasing interactions at the interface.

Keywords: compatibilizer; EVOH; grafting; modification; nylon-6,6.

1 Introduction

Ethylene-vinyl alcohol copolymers (EVOH) offer conjointly gas barrier properties from vinyl alcohol units and moisture resistance, mechanical and thermal properties and processability of the ethylenic units [1], two classes of specific characters which are not observed in polyvinyl alcohol and polyethylene (PE) alone. In addition to the barrier properties of EVOH, blending with other polymers, such as poly(vinyl chloride), poly(methyl methacrylate), polystyrene [2] and polyamide [3, 4] for various applications in molding film and fibers [5] has been reported.

In binary blends of polyamide and polyolefins, which have different properties such as polarity, compatibilization is necessary to improve the affinity toward obtaining blends with acceptable physical and mechanical properties. In this regard, chemical treatments of each polymer, or the use of a third polymer with affinity to both polymers, to reduce interfacial tension, have been considered. Grafting is a promising way to overcome problems encountered in polymer blends. Previously, it has been reported that grafting of nylon-6,6 onto glass and Kevlar fiber surfaces has produced better adhesion in composites of nylon-6,6/Kevlar and nylon-6,6 glass fiber composites [6–8]. EVOH having vinyl alcohol units can be used for grafting nylon chains through polycondensation reactions; then, by incorporation of grafted EVOH in polyolefin/nylon blends, improvement in compatibility and stability of the blends could be achieved. Miscibility of EVOH with polyamide has been studied and several reports on reactions based on existing -OH groups on EVOH, such as silanation by triethoxysilane [1], polycaprolactone grafting [9] and ethoxylation [10] and acid grafting EVOH through reaction with succinic anhydride [11] in nylon6/EVOH blends, have been issued. Furthermore, EVOH copolymers with two different vinyl alcohol compositions have been modified to produce glycopolymers containing aminosaccharide pendant groups [12]. Surface treatment of EVOH with plasma source ion implantation was carried out by Hong et al. [13]. Synthesis of sulfonated EVOH [14], EVOH-grafted-poly (3-hydroxybutyrate-co-hydroxyvalerate) copolymers [15], EVOH-graft-poly(ε-caprolactone) by reactive extrusion [16] and phosphorylcholine-modified poly(ethylene-co-vinyl alcohol) [17] has also been reported.

In this study, grafting of the nylon-6,6 structure onto EVOH as a new route to prepare a compatibilizing agent for olefin/polyamide blends was performed by a polycondensation reaction of adipoyl chloride and hexamethylenediamine, and its effects on physical and thermal properties of the resulting EVOH were investigated. Investigation of the performance of nylon grafted EVOH as a compatibilizer for PE/polyamide blends is continuing.

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2 Experimental

2.1 Materials

Adipoyl chloride and hexamethylenediamine from Aldrich (USA), triethylamine (TEA), dichloromethane (CH_2Cl_2), dimethylsulfoxide (DMSO) and methanol from Merck (Germany) were used. Ethylene-vinyl alcohol copolymer (EVOH, 44 mol% ethylene) was purchased from Aldrich (USA). Granules of EVOH were transformed into a powder by grinding using a lab grinder and a mesh size of 60–100 (150–250 microns) of the ground EVOH was used.

2.2 Solution grafting of EVOH (EVOH-g-amide)

EVOH powder (10 g) was suspended in CH_2Cl_2 with stirring in a three necked flask equipped with a condenser and inlet N_2. According to the particle size and approximate depth of reaction on the surface of the particles, an approximate reacting mass of EVOH was estimated to be equal to 0.0015 mol vinyl alcohol in the copolymer. Therefore, 0.0015 mol TEA was first introduced in a flask containing suspended EVOH in CH_2Cl_2 and the solution of adipoyl chloride in CH_2Cl_2 was added to the EVOH suspension. Mixing was continued for 1 h, after which the suspension was filtered and the grafted EVOH was washed with CH_2Cl_2 several times to remove unreacted acid chloride, while keeping the grafted EVOH wet by CH_2Cl_2 to avoid acid chloride hydrolysis. Adequate washing was verified by adding a small portion of each wash to a diamine solution in CH_2Cl_2 and observing nylon formation as a white precipitate, due to the free acid chloride in the washed solution. Absence of any precipitation or color change indicated complete washing of grafted EVOH. Reacted EVOH was then transferred to a solution of 0.0015 mol hexamethylenediamine in CH_2Cl_2, with stirring for 1 h at room temperature, to produce amide linkage at the EVOH surface. The grafted EVOH sample was then washed several times with CH_2Cl_2 and methanol to remove unreacted diamine, until a neutral pH was attained, followed by vacuum drying at 40°C to a constant weight. This sample was abbreviated as EVOH-g-amide.

2.3 Interfacial grafting

Two series of reactions at ambient temperature and at 40°C were performed with the same stoichiometry of the reactants. For grafting at 40°C under N_2 atmosphere, the acid chloride reaction with EVOH was prolonged to 3 h. After the first step of acid chloride grafting, aqueous diamine solution was introduced into the reactor with stirring and interfacial polycondensation of nylon-6,6 took place at the CH_2Cl_2/water interface. After 1 h of stirring, the reaction mixture was filtered and washed with methanol until a neutral pH was obtained. The samples were abbreviated to EVOH-g-PA and EVOH-g-PA40; in the latter, 40 indicates the acid chloride reaction temperature.

2.4 Grafting onto EVOH film

In order to evaluate the chemistry of the different grafting reactions on EVOH, a very thin film of EVOH was prepared by casting from a dilute N-Methyl pyrrolidone (NMP) solution of EVOH and evaporating the solvent. It was then cut into three pieces. One and five pass procedures to produce EVOH-g-amide and EVOH-g-PA were performed on the two pieces of the films, including successive acid chloride/diamine treatment in each pass, with CH_2Cl_2 washing of the treated film after every acid or amine reaction, to remove all non-reacted monomers and a final washing with methanol and drying. These films and the neat EVOH film were used for attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM) experiments. The grafting reaction scheme is shown in Figure 1.

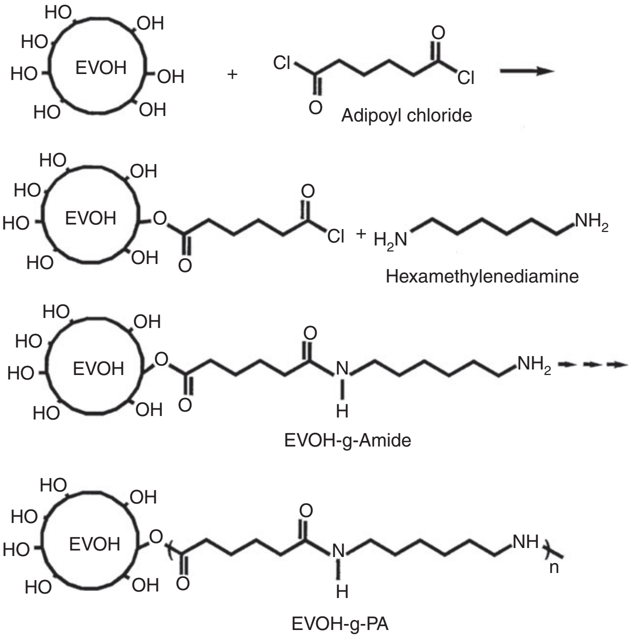

Figure 1 Scheme of amide and polyamide grafting onto ethylene-vinyl alcohol (EVOH).

2.5 Instrumental analysis

ATR-FTIR spectroscopy was performed on EVOH film samples and spectra were recorded on an EQUINOX 35 FTIR spectrometer. The spectra were taken over the spectral range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Contact angle measurements were performed using a G10 KRUSS device. An average angle of five points of a drop of water on each EVOH film sample is considered as the average contact angle. Dynamic mechanical thermal analysis (DMTA) was performed on compression molded EVOH and grafted samples of 5 cm length, 0.5 cm width and 0.1 cm thickness prepared at 220°C under a pressure of 25 MPa using a PL-DMTA instrument. The dual cantilever bending mode was used in a temperature range from ambient temperature to 200°C. The heating rate and frequency were 5°C/min and 1 Hz, respectively. Differential scanning calorimetry (DSC) was performed with a differential scanning calorimeter from Polymer Laboratories (PL-DSC) to measure the glass transition temperature (T_g) and melting temperature (T_m) of all EVOH samples. The samples were weighed and heated from ambient temperature to 300°C, at a heating rate of 10°C/min under nitrogen atmosphere. The first heating thermograms were recorded. Nuclear magnetic resonance spectroscopy (NMR) (HNMR and ^{13}CNMR) was performed on EVOH solutions in DMSO using a Bruker 400 MHz Avance NMR spectroscope. A Vega Tescan SEM was employed to examine the surface and cross section of modified and neat EVOH films. Film cross sections were prepared by cryofracturing following more than 20 min of exposure to liquid nitrogen. Films were coated with gold and representative images were captured.

3 Results and discussion

3.1 ATR-FTIR spectroscopy

Figure 2 illustrates the ATR spectra of EVOH and grafted EVOH in one pass and five pass procedures. As can be seen clearly from Figure 2, the area under peak at 3346 cm^{-1} corresponding to –OH bond stretching of vinyl alcohol units decreased considerably with increase in the pass number, from one pass to five passes, and a new peak at 3302 cm^{-1} corresponding to -NH bond stretching appeared, which indicates –OH consumption and polyamide grafting onto the film surface. Amide I and amide II peaks of nylon-6,6 at 1610 cm^{-1} and 1540 cm^{-1} [18] appeared with grafting, which were not seen in EVOH neat resin. In-plane bending of the O-H bond at 1660 cm^{-1} in the EVOH copolymer was shifted to a lower wavenumber and amide I appeared in combination with –OH absorption, while the height of the peak increased. This can be attributed to loosening of the hydrogen bonding among OH groups after reactions during one or five pass grafting procedures. The FTIR results indicated that grafting of nylon-6,6 onto the EVOH surface had occurred.

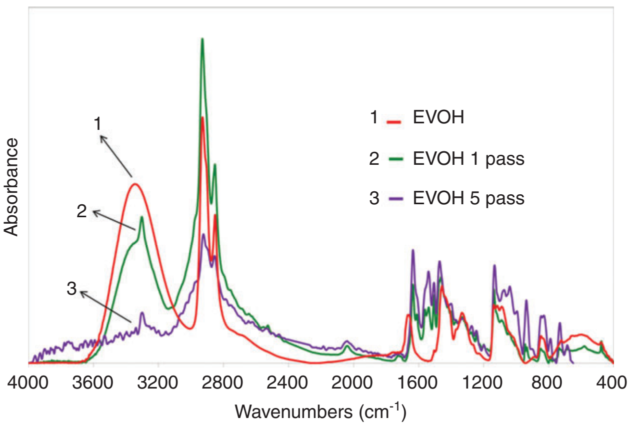

Figure 2 Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) spectra of ethylene-vinyl alcohol copolymer (EVOH) with various pass numbers.

3.2 SEM micrographs

SEM micrographs of surface and cross sections of neat and grafted EVOH films are presented in Figures 3 and 4, respectively. It can be seen from Figure 3A to D, that the smooth and clear surface of virgin EVOH becomes relatively strained after the one pass procedure and then the grafted amide units appear successively by increasing the pass number, initially as bright spots on the surface, which grow and form bundles, agglomerates and needle-like particles of amide units. These grafted amide structures, as schematized in Figure 1, are synthesized from the reaction of adipoyl chloride primarily with hydroxyl groups of vinyl alcohol units on the EVOH surface and a subsequent reaction of grafted acid chloride with the diamine. The growth of the amide structures, therefore, is proportional to the passage number in acid chloride and diamine solutions and eventually could reach oligomeric and polymeric natures, with an adequate number of passages. The cross sections of neat and treated EVOH films are shown in Figure 4A–D. As can be seen from Figure 4B, after grafting through the first pass procedure, the amide structure appeared on the surface, while a diffusion of reactions beneath the surface, up to two microns, could be observed, which shows the

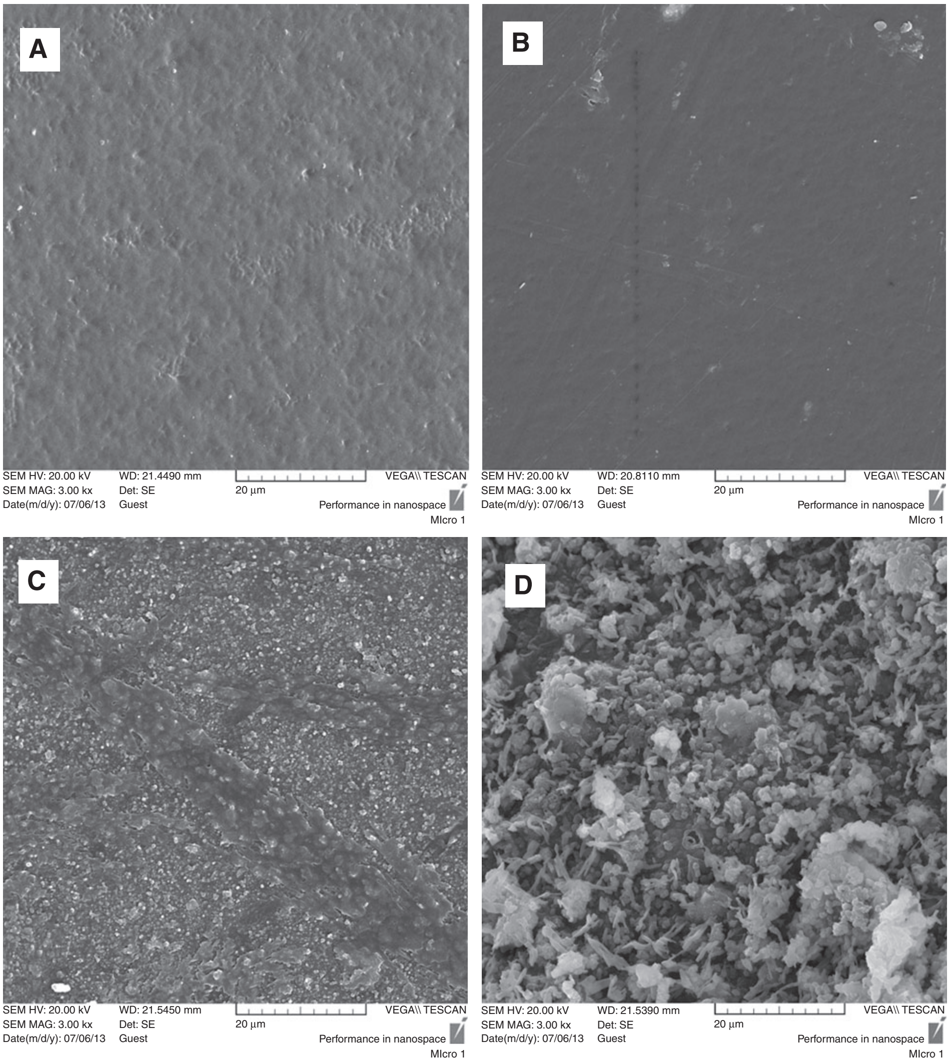

Figure 3 Scanning electron microscopy (SEM) micrographs of representative surface regions in neat and grafted ethylene-vinyl alcohol copolymer (EVOH) films. EVOH (A), EVOH 1 pass (B), EVOH 3 pass (C), EVOH 5 pass (D).

effectiveness of the treatments. As the reaction proceeds, the mass of amide structures grows and forms different topographies, which are presented in Figure 3.

3.3 HNMR and ^{13}CNMR investigation

HNMR spectra of neat EVOH and grafted samples were obtained from their solutions in DMSO-d$_6$. Figure 5 shows the spectra of EVOH, EVOH-g-amide and EVOH-g-amide five pass. Characteristic peaks in the EVOH copolymer shown in Figure 5 consist of broad peaks of methylene proton resonances from 1.25 to 1.44 ppm, methine proton resonance of vinyl alcohol units from 3.38 to 3.92 and hydroxyl protons from 4 to 4.50 ppm [19]. With the grafting process, as shown in Figure 1, OH groups react with acid chloride, followed by a reaction of the free acid chlorides moiety of grafted adipoyl chloride with diamine, and therefore, an amide linkage is formed. By repeating this process, nylon-6,6 can be synthesized on the EVOH surface. Figure 5 also shows grafted EVOH with one pass grafting and the same copolymer exposed to five passes of grafting. As can be seen in Figure 5, with increasing the number of passes, new peaks appear, indicating that a new structure is being introduced into the EVOH copolymer. After one pass, absorptions at 3.1 and 3.3 ppm, which are related to methylene protons of $-\mathrm{NH}\text{-}\mathrm{C}H_2(H)$, appeared [20]. In the five pass HNMR spectrum, a peak at 2.7 ppm for the methylene proton of $\mathrm{O{=}C\text{-}C}H_2$ is produced and peaks at 3.1 ppm and 3.3 ppm are present as a shoulder with DMSO and water absorptions. Furthermore, the absorption of the methine proton of HC-OH in the EVOH

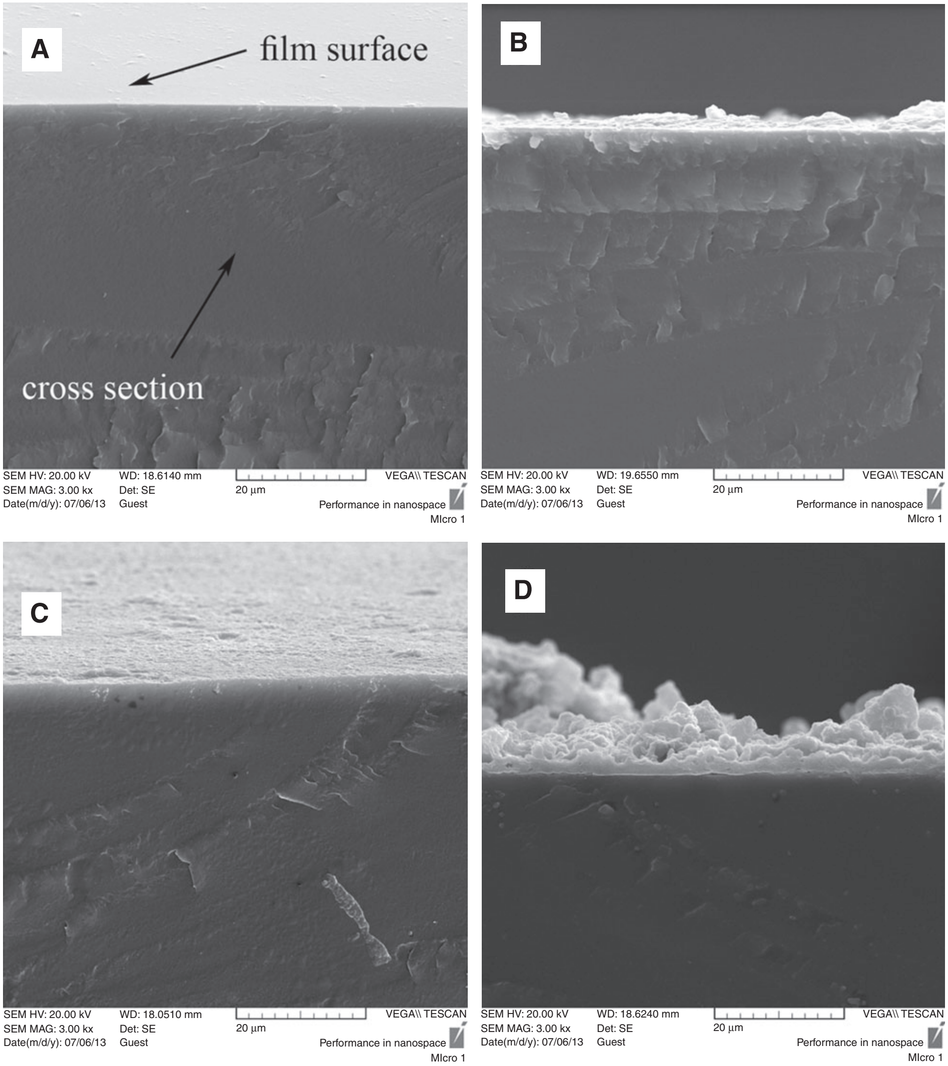

Figure 4 Scanning electron microscopy (SEM) micrographs of representative cross sections in neat and grafted ethylene-vinyl alcohol copolymer (EVOH) films. EVOH (A), EVOH 1 pass (B), EVOH 3 pass (C), EVOH 5 pass (D).

copolymer decreased and transformed to a shoulder at 3.78 ppm. Similarly, the peak area of OH protons of vinyl alcohol units diminished considerably and absorptions of *H*N-CH_2 also appeared at 7.8 ppm, which is a further indication of the success of the grafting. Further evidence of grafting with increase in the passage number is the change in EVOH solubility, such that DMSO-d_6 cannot easily dissolve the grafted samples.

Figure 6 shows the ^{13}CNMR spectra of EVOH before and after grafting. In ^{13}CNMR spectra of EVOH, two regions of absorption, up to 50 ppm relating to all methylene carbons -***C***H_2-(*C*) and 60–80 ppm corresponding to all methine carbons ***C***H-OH, are present. With one and five pass procedures, all absorptions are shifted upfield by an extent of 4.5 ppm. Peaks with maximums at 26.8 ppm, 30.55 ppm and 34.5 ppm shifted to 22.1 ppm, 25.8 ppm and

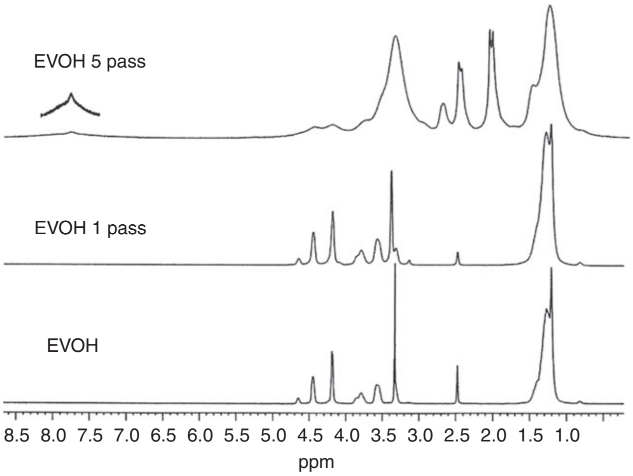

Figure 5 Nuclear magnetic resonance (HNMR) spectra of ethylene-vinyl alcohol (EVOH) with various pass numbers.

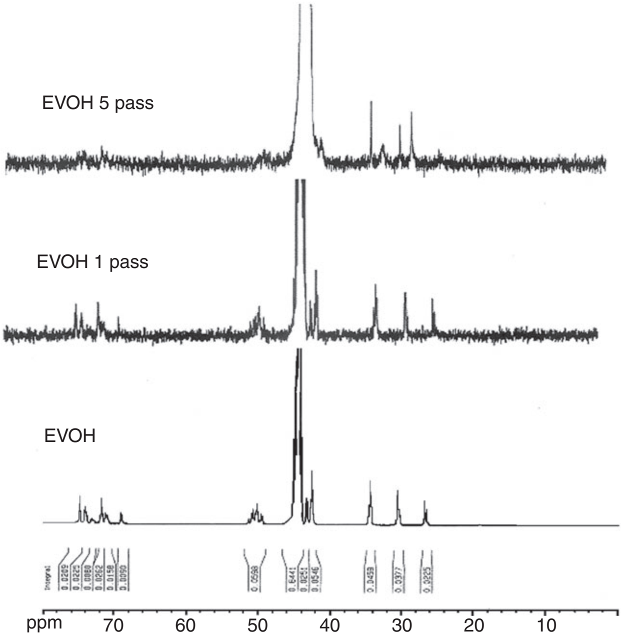

Figure 6 Nuclear magnetic resonance (^{13}CNMR) spectra of ethylene-vinyl alcohol (EVOH) with various pass numbers.

29.74 ppm, respectively. At the same time, new peaks at 27.31 and 31.17 ppm corresponding to NH-CH_2-CH_2-$\boldsymbol{C}H_2$ and NH-$\boldsymbol{C}H_2$-CH_2, respectively, of the nylon structure, appeared in the spectrum of the five pass sample. Furthermore, with increases in the passage number from one to five pass, the region of 42–44 ppm assigned for methylenes between VOH units decreases and weakens considerably in five pass samples, accompanied with shifting of all absorptions upfield. Moreover, the ratio of the methine carbons area to the methylene area decreases with passage number, which is an indication of the capability of the grafted nylon structure to introduce six methylene groups on each pass into the EVOH chains. The following equation [19], was used to quantify this change and the results are shown in Table 1:

$$(VOH)=2A_{65\text{-}80}/(A_{65\text{-}80}+A_{20\text{-}52}) \quad (1)$$

Table 1 Nuclear magnetic resonance (^{13}CNMR) results for peak area variation of methylene and methine carbons of ethylene-vinyl alcohol copolymer (EVOH) with various treatments.

Sample	$A_{20\text{-}52}$	$A_{65\text{-}80}$	$2A_{65\text{-}80}/(A_{40\text{-}80}+A_{20\text{-}52})$
EVOH	0.246	0.102	0.588
EVOH-g-amide	0.131	0.046	0.522
EVOH-g-PA	0.033	0.007	0.356

3.4 Solubility test

All grafted EVOH powder samples were submitted to the solubility test. For EVOH-g-amide and EVOH-g-PA, complete solution in DMSO or NMP at 80°C was obtained, although it took a greater time when compared with untreated EVOH; for EVOH-g-PA40, some insoluble precipitate materials were observed. This could be attributed to the possible surface crosslinking of EVOH by diacid chloride at a higher reaction temperature.

3.5 Contact angle measurement

One of the most sensitive methods to changes on surface physicochemical properties is the contact angle measurement technique. The effect of treatment of EVOH film with plasma has been reported before [21]. In this study, the contact angles of water droplets with the surface of EVOH and grafted EVOH films were examined and the results are presented in Figure 7. In the first approach, it can be seen that with grafting reactions, the contact angle increases for all types of modifications. This means that the surface of EVOH is changed to a more hydrophobic character with grafting. From the grafting scheme in Figure 1, it can be seen that the polar –OH groups are being consumed during the reaction and replaced with nonpolar methylene groups of amide structure. Consequently, the contact angle is increased by amide grafting onto the EVOH surface. The highest contact angle is obtained for EVOH-g-PA40, which was attributed to partial crosslinking of surface O-H groups by adipoyl chloride during the first step of the reaction and less amide grafting.

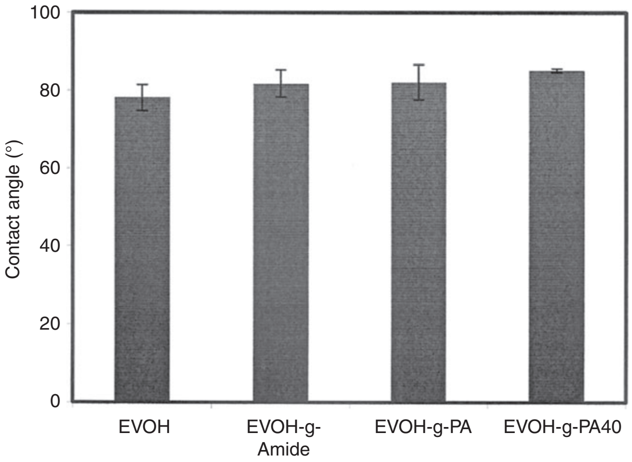

Figure 7 Variation of contact angle of ethylene-vinyl alcohol copolymer (EVOH) with various treatments.

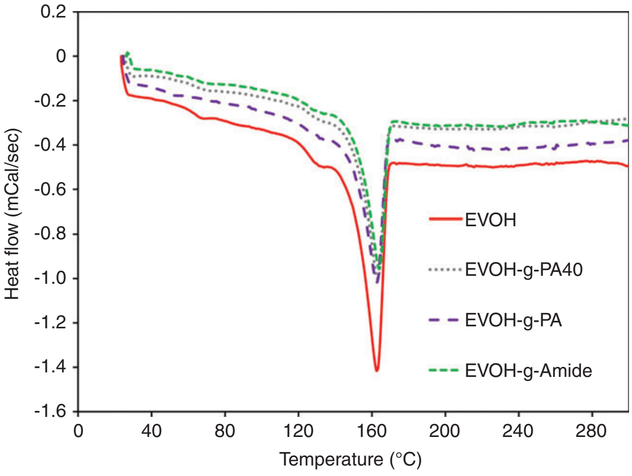

Figure 8 Differential scanning calorimetry (DSC) thermograms of ethylene-vinyl alcohol copolymer (EVOH) with various treatments.

3.6 DSC of EVOH samples

Dry samples were analyzed by DSC. Figure 8 shows the thermograms of EVOH samples and the results obtained are presented in Table 2. The common trend was maintaining the T_m of EVOH copolymers, which hardly varied with grafting, while a relatively considerable increase in the starting point for the melting of crystals (T_{onset}) and a significant decrease in ΔH were observed. Since the extent of grafting was low due to the surface treatment, T_m was not affected considerably. By contrast, T_{onset} was shifted to higher values up to 3°C. Since OH groups were involved in the grafting and amide structures are being introduced into the EVOH copolymer, new structures and interactions are developed which need higher energy to overcome the latter and start melting these modified structures. The most important feature of grafting is the reduction of ΔH of the treated EVOH copolymers. The highest decrease corresponds to EVOH-g-amide, which shows the highest increase in T_{onset} when compared with the two other methods. In fact, grafting decreases the crystallinity, due to consuming hydroxyl groups of vinyl alcohol units which form crystalline domains and modify the ordered structure to a less ordered one, through spacing -CH_2- groups in the grafted amides. At the same time, polar interactions between grafted amides themselves and with vinyl alcohol units are responsible for a higher T_{onset}.

Table 2 Various transition temperatures for ethylene-vinyl alcohol copolymer (EVOH) with different treatments obtained by dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC).

Sample	T_g (°C)[a]	T_{onset} (°C)[a]	T_m (°C)[b]	ΔH mcal/mg[b]
EVOH	67.6	145.8	163.3	17.0
EVOH-g-amide	70.3	148.6	164.1	11.4
EVOH-g-PA	70.6	146.5	162.7	12.8
EVOH-g-PA40	70.5	148.1	163.8	13.2

[a] Results from DMTA.

[b] Results from DSC.

3.7 DMTA

The DMTA behaviors of the EVOH samples are presented in Figure 9. EVOH shows three molecular relaxation processes above 0°C, which upon treatments, vary in different samples [21]. The beta relaxation which appears at 66.5°C for neat EVOH resin corresponds to the T_g. Upon heating, this transition shifts to higher temperatures, reaching 70.6°C; this means that higher interactions between grafted amide structures themselves and with EVOH chains were produced which restrict chain movements. The alpha relaxation, which is attributed to molecular motions in the crystalline phase, appears at 117°C for neat resin. For grafted EVOH samples, significant increases in transitions for α relaxation are obtained, indicating that in the crystalline phase with the same analogy, grafted amide structures give rise to the higher interaction between EVOH crystallites, so that the slippage between them is reduced [21]. The highest increase is obtained in the EVOH-g-amide grafting mode. Furthermore, for two other modes of grafting, EVOH-g-PA and EVOH-g-PA40, T_α is also increased considerably, indicating that regardless of the grafting type, amide grafting onto the EVOH chains is responsible for the observed changes in the different transition temperatures. The third transition is related

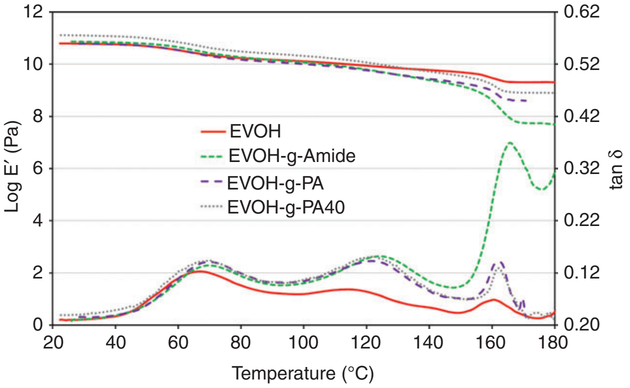

Figure 9 Elastic modulus E′ and tan δ as a function of temperature from ethylene-vinyl alcohol copolymer (EVOH) with various treatments.

to T_m, or the terminal region of the EVOH samples. This transition is comparable with the onset of the melting curve, as seen in DSC analysis which is shown in Figure 8. Once again, it can be seen from the tanδ peaks in Figure 9 that grafting increases the transition temperature T_m and the highest change is observed for EVOH-g-amide samples, which is the same trend as seen for T_α transition. This could be attributed to flexible longer polyamide chains, which are probably produced during EVOH-g-PA and EVOH-g-PA40, compared with amide units formed during the EVOH-g-amide procedure.

4 Conclusions

Amides and polyamides based on the nylon-6,6 structure were successfully grafted onto an EVOH copolymer via a condensation reaction of adipoyl chloride and hexamethylenediamine. FTIR and NMR spectroscopy confirmed the grafting reaction. Grafting created a number of nonpolar methylene carbons of the nylon-6,6 structure attached to the surface, causing an increase in contact angles of the grafted samples. SEM showed the formation of amide structures as bundles, agglomerates and needle-like particles due to the grafting reaction. Thermal behavior of grafted EVOH based on DSC and DMTA measurements revealed that grafting decreased the crystallinity of the treated samples, while simultaneously increasing their T_g and α relaxation of crystalline phase. A EVOH copolymer modified in this manner may have compatibilization characteristics in PE/polyamide blends; this is the subject of a forthcoming paper.

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