Synthesis of a New Compatibilisant Agent PVC-g-MA and Its Use in the PVC/Alfa Composites

Dalila Hammiche, Amar Boukerrou, Hocine Djidjelli, Meriama Beztout, Salem Krim

Laboratoire des Matériaux Organiques, Département de Génie des Procédés, Université Abderrahmane MIRA, Route de Targa-Ouzemmour, Béjaïa 06000, Algerie

Received 4 May 2011; accepted 4 August 2011 DOI 10.1002/app.35422 Published online 30 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The main objective of this research was to synthesize a new compatibilisant agent (PVC-*g*-MA), which was grafted from the maleic anhydride on the PVC chains. The presence of maleic anhydride grafting on PVC was made evident by infrared analysis. PVC-*g*-MA was used like compatibilisant to solve the problem of the incompatibility between the hydrophobic polymeric matrix (PVC) and hydrophilic fiber (alfa). Composites samples were prepared with different alfa fiber loading (10, 20, and 30 wt %) and incorporating PVC-*g*-MA (1, 3, and 5 wt %) or PP-*g*-MA (3 wt %). The tensile properties, the thermal stability and the morphology of the composites were investigated. The result indicated that the PVC-*g*-MA increased the interfacial adhesion between the fibers and

INTRODUCTION

In the recent years, great attention has been dedicated to the exploitation of natural fibers as reinforcement for plastics, replacing glass fibers, and other synthetic materials.¹ This occurs not only due to environmental concerns but also for providing a unique combination of high performance, great versatility, and processing advantages at favourable cost.

Advantages of natural fibers have encouraged their application in polymer composites. Relating to this, many researchers reported the incorporation of various natural fibers in thermoplastics composites.² The main problem in natural fibers filled thermoplastics composites is the incompatibility of hydrophilic natural fibers and hydrophobic polymer matrix, which yields composites of poor interfacial adhesion.

Several methods of improving adhesion in natural fiber/polymer composites have been described in the literature. Some methods were based on fiber modification (physical or chemical) and others were based on the addition of a coupling agent for interfacial adhesion improvement.³

the polymer matrix and this effect was better than that obtained for the maleated-polypropylene-coupled composites. Microstructure analysis of the fractured surfaces of MAPP modified composites confirmed improved interfacial bonding. The addition of alfa and PVC-g-MA increased the thermal stability of the composites. The temperature of degradation of the polymer matrix increased about 16° C in comparison to the noncoupled composite, indicating that PVC-g-MA improved the thermal stability of the polymer. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4352–4361, 2012

Key words: composites; compatibilization; polyvinylchloride; mechanical properties; thermal properties

It reported that small amounts of PP modified with maleic anhydride added to the composites significantly increased the mechanical properties. After this treatment, the surface energy of cellulose fibers were increased to a level much closer to the surface energy of the matrix.⁴ The coupling agent more often used was a polypropylene grafted with maleic anhydride.¹ Interactions between the anhydride groups of maleated coupling agents and the hydroxyl groups of natural fibers can overcome the incompatibility problem and increase tensile and fiexural strengths of natural fiber thermoplastic composites.⁵ The hydrophilicity of natural fibers generates high moisture absorption and weak adhesion to hydrophobic matrix.⁶

Lu et al.⁷ found that maleation significantly influenced thermal and dynamic mechanical properties of resultant wood-PVC composites. Experimental results indicated that storage modulus (E) and complex modulus (E^*) increased with increase of maleated polypropylene (PP-g-MA) retention, but leveled off or decreased at high PP-g-MA retention. Compared with wood, PVC and untreated composites, maleated wood-PVC composites had significant shifts in most dynamic mechanical analysis, thermogravimetric analysis (TGA), and differential scanning calorimetry spectra due to chemical coupling by PP-g-MA at the interface.

Mishra et al.⁸ reported that maleic anhydride treatment reduced the water absorption to a great

Correspondence to: D. Hammiche (dalila040774@yahoo.fr).

Journal of Applied Polymer Science, Vol. 124, 4352–4361 (2012) © 2011 Wiley Periodicals, Inc.

extent in banana, hemp, and sisal fiber-reinforced novolac composites. Mechanical properties like Young's modulus, fiexural modulus, hardness, and impact strength of plant fiber-reinforced composites increased after maleic anhydride treatment.

In this work, we studied the suitability of using PVC modified with maleic anhydride (PVC-g-MA) as coupling agent for PVC/Alfa composites. Much research has been performed on the natural fiber composites but few work reported in the literature on the alfa fiber (esparto) and their used in the reinforcement of the composite based PVC. The results were compared with those obtained for similar composites coupled with PP modified with maleic anhydride (PP-g-MA). A system loading and coupling agent type and concentration was undertaken to obtain optimum mechanical strength. The thermal stability of the composites was analyzed employing TGA/DTG, whereas the fiber-matrix morphology was studied through scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

All the PVC/alfa formulations used in this work were based on PVC type SE-1200 provided by CABEL "Cablerie Electrique" located in Algiers (Algeria). The polymer has the following physical characteristics: K_{wert} (parameter that characterizes the viscosity of a material), 70.2–72.0; powder density, 0.521. The additives used in the preparation of the various formulations were dioctyl phthalate as a plasticizer, a thermal stabilizer system based on Ca/ Zn, and stearic acid as a lubricant. The alfa used as reinforcing filler was collected at M'Sila in Algeria and its average particle size is around 125 µm. The chemical constituents of alfa are listed in Table I. Maleic anhydride (MA, 99.5%) and benzoyl peroxide (BPO). PP-g-MA (1.71% of maleic anhydride) was synthesized at the laboratory of organic materials, University A. Mira of Bejaia, Algeria.

Synthesis of the coupling agent (PVC-g-MA)

The grafted PVC was synthesized in a solution state. In the typical solution-grafting process, 10 g of dried PVC were dissolved in 150 mL xylene at 140°C under a nitrogen atmosphere. After complete dissolution of the PVC, maleic anhydride (2 g) and the free radical initiator BPO (0.02 g) were added. The reaction was allowed to proceed for 1 h under continuous stirring to complete the graft copolymerization. The graft copolymer solution was precipitated by adding distilled water at room temperature. After thoroughly washing with distilled water, the graft

TABLE I Proportions of the Principal Components of Alfa Fiber

Component	Proportion (%)
Cellulose	45.00
Hemicellulose	20.94
Lignin	29.80
Others	04.26

copolymer was transferred to an oven at 50°C for 24 h to remove any trace of residual solvent and maleic anhydride.

Determination of the MA content

The quantity of MA grafted onto the PVC was determined by titration of acid groups derived from the anhydride functions. After dissolution of 1.0 g of PVC-g-MA in 100 mL of xylene at boiling temperature, 0.2 mL of water was added to hydrolyze anhydride functions into carboxylic acid functions. Then the solution was refiuxed for 2.0 h to complete the hydrolysis. The carboxylic acid concentration was determined by titration with 0.025N potassium hydroxide in methanol/benzyl alcohol 1/9 (v/v). The indicator used was a solution of 1% phenolphthalein in methanol. The graft copolymer (PVC-g-MA) was completely soluble in xylene at refiux conditions. Furthermore, precipitation was not observed during titration. The carboxylic acid concentration was converted to the MA content as follows:

$$\mathrm{MA}(\mathrm{wt\%}) = \frac{V_{\mathrm{KOH}} \times N_{\mathrm{KOH}} \times 98}{2p} \times 100,$$

where N_{KOH} is the concentration (mol/L) of potassium hydroxide dissolved in methanol/benzyl alcohol. V_{KOH} is the volume of the KOH. P is the weight (g) of the PVC-g-MA sample.

Preparation of the composites

PVC powder and the various additives were placed in a high-speed twin steel-wall mixer and processed at a speed of 3000 rpm at 70°C, below the glass transition temperature of PVC. The different PVC formulations obtained were used to prepare films by the calendering process at 140°C with a residence time of 8 min. Alfa and PVC were compounded in a tworoll mill. The temperature of the two rolls was maintained at 140°C. After the addition of the matrix and also in the presence of the PVC-g-MA or PP-g-MA compatibilizers according to Table II, the fiber was added as soon as the polymer had reached a steady plastifying state, which needed about 3 min. After mixing for 3-4 min, the resulting mixture was compression-molded. All of the samples were performed

4353

TABLE II	
Formulation Codes of PVC/Alfa Composites	Used

Constituent		Formulations			
Alfa(%)		0	10	20	30
PVC		100	100	100	100
Dioctyl phthalate Ca/Zn		30	30	30	30
, , , , , , , , , , , , , , , , , , ,		4	4	4	4
Stearic acid		0.5	0.5	0.5	0.5
PVC-g-MA	0%	F1	F2	F3	F4
	1%	-	F5	F6	F7
	3%	-	F8	F9	F10
	5%	-	F11	F12	F13
PP-g-MA	3%	-	F14	F15	F16

in a preheated press at 170°C under a pressure of 250 KN for 5 min, and following by cooling to room temperature. The 2 mm thick plates obtained were then removed to be used in various characterizations. The preparation of composites was carried out in the laboratory of CABEL "Cablerie Electrique" located in Algiers (Algeria).

Techniques

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the PVC-*g*-MA and PVC were recorded using an FTIR SHIMADZU FTIR-8400S in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹. The samples were analyzed using the KBr pellet method.

Scanning electron microscopy (SEM)

The morphology of composites was examined using FEI CONTA 200 electron microscope. The compression molded sheet was cryogenically fractured in liquid nitrogen. The micrographs were taken at a magnification of 200.

Tensile test

The tensile test for the composites was conducted according to standard "ISO 527, June 1993" at ambient temperature, using a tensile testing machine of the type "Zwick/Roell." Five measurements were conducted and average for the final result.

Thermogravimetric analysis

The thermal behavior of the various formulations was investigated. For thermal stability analysis, the decomposition rates were measured by a SETARAM TGT DTA 92 thermogravimetric apparatus. A sample of initial mass of 15–20 mg was introduced into a platinum crucible; the sample mass (TG) variation was then measured as a function of temperature (or time), and the rates of mass loss (DTG) were deter-

mined by using a thermobalance under an inert nitrogen atmosphere up to 600° C, at a heating rate of 20° C/min.

RESULTS AND DISCUSSION

Characterization of PVC and the PVC-g-MA

FTIR analysis of the PVC and the PVC-g-MA

Figure 1 shows the FTIR spectra of PVC and the prepared PVC-g-MA, respectively, focused on the range of wave number 2000–600 cm^{-1} . The characteristic absorptions (cm⁻¹) of 2973–2908 (v_{C-H}), 1432 (δ_{CH2}), and 837 (v_{CCl}) were attributed to the PVC.^{9,10} Since the unreacted MA gives rise to absorption bands in the same regions as the grafted anhydride,^{9,11} the complete elimination of the unreacted MA was of great importance. This was done by washing with distilled water during the precipitation process and drying at the temperature of 50°C in a hot air oven for 24 h. The absence of unreacted MA can be checked by the disappearance of the characteristic band at 1600–1500 cm^{-1} (C=C bond of MA). For the graft copolymer, a broad and intense characteristic band at 1797 cm⁻¹ and a weak absorption band at 1857 cm⁻¹ were observed. These bands can be assigned to grafted anhydride which are due to symmetric (strong) and asymmetric (weak) C=O stretching vibrations of succinic anhydride rings, respectively.9,12 This proves the presence of grafted anhydride on the PVC macromolecules.

Scanning electron microscopy (SEM)

The morphology of the PVC and PVC-*g*-MA powders was examined by using an electron microscope. The powders were compressed in the form of pastilles before being viewed. As shown in Figure 2(a),



Figure 1 FTIR spectra of the virgin PVC and PVC-*g*-MA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 2 Morphologies of (a) PVC and (b) PVC-g-MA.

the PVC used was a powder with a surface, which resembles to a honeycomb. Figure 2(b) showed that the treatment changed the morphology of the powder surface. Under the effect of grafting, we can found from SEM that the surface of the powder became smooth due to compatibility between PVC and AM. The AM could not react with the matrix inside the powders. That was just reacted on the surface of the powders according to Qiu et al.^{13,14}

Determination of the MA content

Quantification of the grafted MA on the macromolecular chains of PVC was performed using the titration method. The result allows us to estimate the AM content to an average of 2.32%.

Characterization of the composites

Scanning electron microscopy (SEM)

The morphology of fractured surfaces reflects the reasons for which the mechanical properties of the composites prepared are different. The morphological fractures of tensile fractured surfaces of 10 wt % alfa reinforced PVC composites investigated by SEM were shown in Figure 3. Noncoupled composites displayed a rough morphology with the presence of many voids and cavities resulting from fiber pullout [Fig. 3(a)]. This indicates poor interfacial adhesion that reveals the low affinity between the polymer matrix and the alfa fiber. The presence of the coupling agent changed the morphology of the composites. The addition of PVC-g-MA to the composites produced a more homogeneous surface with less voids and cavities. This indicated that PVC-g-MA

had a positive effect on the interfacial adhesion between fiber and matrix; a surface became very homogeneous especially for 3 and 5% of PVC-g-MA [Fig. 3(c,d)]. It was obvious that alfa fiber was more compatible with PVC in the presence of the PVC-g-MA as compared to the composites coupled with PP-g-MA [Fig. 3(e)] where pulled-out traces of filler particles are to be seen. This result can be explained by establishment of the bonds between hydroxyl groups on the fiber surface and functional from the PVC-g-MA presents the good wettability between fiber and the polymeric matrix.¹⁵

Mechanical properties

Hardness

Hardness of a particular sample refers to its stiffness or resistance of being broken to have its shape changed permanently when load is applied to it. Figure 4 shows the effect of the PVC-g-MA and load factor on the hardness of the composites. The incorporation of alfa reinforced composites increased their hardness and then showed only a slight increasing trend upon further increases in fiber content. This indicates a decrease in fiexibility and an increase in stiffness of the composites with increasing fiber content.^{16,17}

The treated composites were found to show better hardness compared to those of the untreated ones. This could be due to better fiber-matrix interfacial wetting after the reaction of esterification between the fiber and the anhydride, which confer certain hardness larger than that of the untreated composites.¹⁸ This may be too attributed to better dispersion of the fiber into the matrix with minimization



Figure 3 SEM micrographs of fracture of composites (10 wt % alfa) as a function of compatibilisant agent content and types at ×200. (a) 0% PVC-*g*-MA, (b) 1% PVC-*g*-MA, (c) 3% PVC-*g*-MA, (d) 5% PVC-*g*-MA, and (e) 3% PP-*g*-MA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of voids and stronger interfacial adhesion between the matrix and the fiber.¹⁷

The evolution of hardness according to the load factor and the nature of the compatibilisant agent



Figure 4 Influence of fiber load and the compatibilisant agent (PVC-*g*-MA) at various contents on the hardness of PVC/alfa composites.

are illustrated in Figure 5, the addition of PP-g-MA generally brings an increase in the hardness of the composites. This can be due to the hardness of the PP evaluated about 73, which is higher than that of PVC evaluated about 61. In fact, the presence of a



Figure 5 Hardness of PVC/alfa composites as a function of compatibilisant agent types.



Figure 6 Influence of fiber load and the compatibilisant agent (PVC-*g*-MA) at various contents on the tensile strength of PVC/alfa composites.

more fiexible matrix usually causes the resultant composites to exhibit lower hardness.¹⁷

Tensile strength

The measurement of the mechanical properties is a means of making possible to evaluate the degree of interaction creates between matrix PVC and alfa fiber. The effect of the fiber and compatibilisant agent on the mechanical properties in particular, the tensile, the elongation, and the Young modulus of the composite materials PVC/Alfa were studied.

We obtained a value of 26.19 MPa for the tensile strength of virgin PVC and 12.64, 11.45, and 9.24 MPa for the composites containing 10, 20, and 30% of alfa, respectively (Fig. 6). The tensile strength of the composites decreased with an increasing of fiber loading due to the weak interfacial adhesion and a low compatibility between the hydrophilic fiber and hydrophobic PVC. An increase in the fiber content increases the microvoides between the fiber and the matrix, which weaken the fiber-matrix interfacial adhesion.¹⁶ As a result, the values of tensile strength show a decreasing trend with increasing of fiber content in the composite. The tensile strength of the composites with various rates of PVC-g-MA was appreciably higher than those of the composites untreated because of increased interfacial adherence. The synergy between fibers and the matrix reinforces material and increases energy necessary to break it. The highest value of tensile strength was obtained with 5 wt % PVC-g-MA. The tensile strength value determined for this sample was more than 21% higher than that obtained for the noncoupled composite. This can be explained by the fact that the addition of low fiber content in the matrix leads to

its good dispersion. However, with raised concentrations, the particles occupy a more significant volume, which weakens the composites.

Vilaseca et al.¹⁹ studied the effect of different amounts of PP-g-MA (2, 4, 6, and 8%) on the tensile properties of abaca strands–PP. The effectiveness of PP-g-MA as coupling agent was clearly seen. The addition of PP-g-MA coupling agent improved the ultimate tensile strength in all cases. Concretely, the addition 6 wt % of PP-g-MA provided increments of about 22–29% in the ultimate tensile strength of PP-g-MA -modified composites compared to the same composite formulations without coupling agent. Compared to the plain matrix, the addition of 6 wt % of PP-g-MA produced increments of 28, 63, and 76%, respectively, for composites containing 20, 30, and 40 wt % of reinforcement.

The tensile strength of composites treated with PVC-*g*-MA was the highest (Fig. 7) due to the suficient MA grafted on PVC (2.32%) compared to the insuficient level of PP (1.71%).²⁰

Elongation at break

The dependence of elongation at break on the fiber loading of PVC composites with and without the presence of coupling agent was shown in Figure 8. It indicated that the incorporation of alfa into the PVC composites reduced the elongation at break. With increase in fiber loading, the stiffness and brittleness of the composites increase. This will reduce composites resilience and toughness and lead to lower resistance at break.²¹

However, the elongation at break of the composites treated with PVC-g-MA is slightly higher than that of the untreated composites. Indeed, the elongation at break for the F2 (PVC/10% alfa/0% PVC-g-MA) formulation is surroundings of 49% whereas



Figure 7 Tensile strength of PVC/Alfa composites as a function of compatibilisant agent types.

Journal of Applied Polymer Science DOI 10.1002/app



Figure 8 Influence of fiber load and the compatibilisant agent (PVC-g-MA) at various contents on the elongation at break of PVC/alfa composites.

that of F11 (PVC/10% alfa/5% PVC-g-MA) is 75% an improvement of surroundings of 53%. The addition of the coupling agent allows a profit in deformation compared to the untreated composites, but not in term of total deformation compared to virgin PVC. This east improvement can be due to a good dispersion of alfa fiber by the addition of the coupling agent, which contributes certain flexibility to material.

The elongation at break for compound with PVCg-MA is slightly higher than PVC compound with PP-g-MA due to the better interaction of the PVC matrix with the PVC segment of PVC-g-MA.²¹ We estimate a loss of elongation at break of surroundings of 3, 28, and 51% for the formulations of 10, 20, and 30% of alfa fiber, respectively, with 3% of PP-g-MA compared to 3% of PVC-g-MA (Fig. 9).

Young modulus

The Figure 10 represents the evolution of Young's modulus according to the alfa fiber loading and PVC-g-MA content. We notice that the Young modulus increases with the increase in the content of alfa fiber; it varies from 287.4 to 514.7 MPa when the load factor increases from 10 to 30%, respectively, in the standard deviation of measurement. This increase in the Young modulus indicates that the rigidity of the composites increased.²² The addition of PVC-g-MA in the preparation of the PVC/alfa composites made it possible to increase only the formulation with 10% of alfa fiber. The modulus increases very moderately with the increase in PVC-g-MA. One would not expect much change in this property, since stiffness is not very sensitive to the modification of interfacial adhesion. The considerable decrease in stiffness can be explained only from the



Figure 9 Elongation at break of PVC/Alfa composites as

a function of compatibilisant agent types.

change of deformation mechanism. In fact, changes in interaction and chain mobility would not justify such a large decrease in modulus.²² According to Liu et al.²³ Young modulus is known to be less sensitive to interfacial interaction. They noted that the addition of PE-g-MA or EPR-g-MA (ethylene/propylene elastomer) carried out a moderate reduction of the module of the HDPE/fiber composites of bamboo, indeed the module of the untreated composites, which is of 3.64 GP, decreased by 7 and 17.6% for the composites treated with PE-g-MA and by EPR-g-MA, respectively.

This result was also applied for PP-g-MA (Fig. 11). It gave a module less raised compared to the composites untreated and treated with PVC-g-MA. It can be due to the high rigidity of PVC compared to that of PP.



Figure 10 Influence of fiber load and the compatibilisant agent (PVC-g-MA) at various contents on the Young modulus of PVC/alfa composites.



Figure 11 Young modulus of PVC/alfa composites as a function of compatibilisant agent types.

Thermogravimetric analysis

Thermal behavior of the PVC

TGA is one of the thermal analysis techniques used to quantify weight change and thermal decomposition of the sample. TGA curves of the pure PVC resin (and its composites loaded with 10, 20, and 30 wt % afa fiber) are shown in Figure 12. For virgin PVC sample, it can be observed that there are two weight loss stages (I and II). In the first stage, the decomposition starts at about 260.8°C and ends around 330°C. During this first decomposition stage, the sample weight loss is about 63%, due to the phenomenon of dehydrochlorination (HCl evolution). Under the effect of temperature, chlorine radicals resulting from scission of -C-Cl labile bonds take off an hydrogen radical from adjacent -C-H groups to form a covalent H-Cl bond. This chemical mechanism induces double bonds along the polymer



Figure 12 TGA and DTG thermograms of unfilled PVC samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 13 TGA thermograms of PVC and PVC/Alfa composites (10, 20, and 30 wt % alfa fiber) without compatibilisant agent. F1 (PVC); F2 (PVC/10% alfa/0% PVC-g-MA); F3 (PVC/20% alfa/0% PVC-g-MA); F4 (PVC/30% alfa/0% PVC-g-MA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chain and may lead to conjugated polymeric chains. Between 330 and 400°C, the sample becomes thermally stable, that is, it does not lose weight in this temperature range. Indeed, after HCl evolution, conjugated double bonds are obtained and a new polymer, the polyacetylene, is formed. This polymer is more heat stable than PVC. From 400 to 480°C, a second decomposition stage is observed, much shorter than the first one and corresponding to polyacetylene cracking (scission of covalent and multiple bonds). Above 480°C, a stable residue is formed that corresponds to carbon black.²⁴

Thermal behavior of the PVC/Alfa composites

Effect of the load factor

Figure 13 represents the thermograms TGA of the PVC resin and its composites loaded with 10, 20, and 30 wt % alfa fiber. The shapes of the curves are similar for all the samples. It can be observed that there are two stages of decomposition of the composites as shown in Figure 13. The incorporation of the alfa fiber in matrix PVC decreases the onset decomposition temperature and this reduction is the largest since the content of load increases. Onset temperature of the decomposition was estimated at 260.8°C for virgin PVC, 231.1, 226.3, and 209.1°C for a load factor 10, 20, and 30 wt %, respectively. This reduction can be attributed to the decomposition of the hemicellulose, which is less stable than cellulose and lignin; they are generally degraded at temperatures ranging between 200 and 260°C.²⁵ The first stage of decomposition for the various composites corresponds to the dehydrochlorination, evaporation of

4360



Figure 14 TGA thermograms of PVC and PVC/Alfa composites (10 wt % alfa fiber) as a function of compatibilisant agent content and types. F2 (PVC/10% alfa/0% PVC-*g*-MA) F5 (PVC/10% alfa/1% PVC-*g*-MA); F8 (PVC/10% alfa/3% PVC-*g*-MA); F11 (PVC/10% alfa/5% PVC-*g*-MA); F14 (PVC/10% alfa/3% PP-*g*-MA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the plasticizer and the decomposition of the holocellulose (cellulose and hemicellulose), which are degraded in this range of temperature. More precisely, the thermal decomposition of cellulose occurs primarily starting from a temperature of 310°C and is done by depolymerization.²⁶ Finally, a superposition of decomposition of lignin and cracking of polyacetylene takes place between 400 and 470°C and which ends in the formation of a stable residue corresponding to the carbon black.

Effect of treatment

Figure 14 represents the thermograms of the TGA of the samples of the composites with 10% of load factor for various contents of PVC-g-MA (1, 3, and 5%) and 3% of PP-g-MA according to the change of the temperature. We see clearly that the profiles of thermal degradation of composites were similar. The curves of the TGA of the elaborate samples show two principal phases of decomposition. Each phase was characterized by a degradation rate of specific loss of mass. With equal content of alfa fiber, the onset decomposition temperature for the composites treated with 1, 3, and 5 wt % of PVC-g-MA and 3% of PP-g-MA are about 230.5, 231.2, 247.1, and 211.2°C, respectively, compared with that of untreated composite (231.1°C). It appears that the addition of 5% of PVC-g-MA has a significant effect on thermal degradation of the composites. It generates a profit of 16.1°C in the temperature of decomposition. Alireza Ashori²⁷ noted that the increase in microcrystalline cellulose content substantially reduced the thermal stability. In all cases, the degradation temperatures shifted to higher values after addition of PP-g-MA. The maximum improvement on the thermal stability of the composites was achieved when 5% PP-g-MA was used. This indicates that the compatibility and the interfacial bonding increased by mixing both components in the presence of the compatibilizing agent.

CONCLUSION

Based on the result of this study, the following conclusion can be drawn. The presence of maleic anhydride grafting on PVC was made evident by infrared analysis. After that, we characterized the PVC/alfa composites with and without PVC-g-MA or PP-g-MA. The results obtained reveal that: for untreated composites, the values of tensile strength were found to decrease gradually with an increase in fiber loading. However, mechanical properties such as tensile strength and hardness of treated composites are found to be much higher than those of the untreated ones. This result was evident from our SEM study.

The whole of the data collected concerning the thermal properties show clearly that the presence of alfa fiber enhanced the thermal stability of the PVC. Another important feature observed was the higher degradation temperature of the polymer matrix in the composites containing the PVC-*g*-MA. The temperature of degradation of the polymer matrix increased about 16°C in comparison to the non-coupled composite, indicating that PVC-*g*-MA improved the thermal stability of the polymer.

The whole of the results obtained makes it possible to conclude that the introduction of a coupling agent seems crucial. However, for the sight of the results, it should be noted that the comparative study showed that the best adhesion with the interface was obtained with PVC-g-MA than with PP-g-MA. This study confirms that the choice of the coupling agent must be made according to the matrix and to the application aimed for composite material.

References

- 1. Araujo, J. R.; Waldman, W. R.; De Paoli, M. A. Polym Degrad Stab 2008, 93, 1770.
- Kim, H. S.; Lee, B. H.; Choi, S. W.; Kim, S.; Kim, H. J. Compos A 2007, 38, 1473.
- 3. Mohanty, S.; Nayak, S. K. Mater Sci Eng A 2007, 443, 202.
- 4. Chand, N.; Jain, D. Compos A 2005, 36, 594.
- 5. Keener, T. J.; Stuart, R. K; Brown, T. K. Compos A 2004, 35, 357.
- 6. Lope, X. L.; Tabil, G. J Polym Environ 2007, 15, 25.
- 7. Lu, J. Z.; Wu, Q.; Negulescu, I. Wood Fiber Sci 2004, 36, 500.
- Mishra, S.; Naik, J. B.; Patil, Y. P. Compos Sci Technol 2000, 60, 1729.
- 9. Nakason, C.; Kaesaman, A.; Supasanthitikul, P. Polym Test 2004, 23, 35.

- 10. Kameda, T.; Fukuda, Y.; Grause, G.; Yoshioka, T. J Appl Polym Sci 2010, 116, 36.
- Hong, C. K.; Kim, M. J.; Oh, S. H.; Lee, Y. S.; Nah, C. J Ind Eng Chem 2008, 14, 236.
- Vicente, A. I.; Campos, J.; Bordado, J. M.; Ribeiro, M. R. React Funct Polym 2008, 68, 519.
- 13. Li, W.; Yuan, M.; Yang, M. Eur Polym J 2006, 42, 1396.
- 14. Qiu, W.; Endo, T.; Hirotsu, T. Eur Polym J 2005, 41, 1979.
- 15. Nachtigall, M. B.; Cerveira, S.; Rosa, M. L. Polym Test 2007, 26, 619.
- Nazrul Islam, Md.; Rezaur Rahman, Md.; Mominul Haque, Md.; Monimul Huque, Md. Compos A 2010, 41, 192.
- 17. Rezaur Rahman, Md.; Monimul Huque, Md.; Nazrul Islama, Md.; Hasan, M. Compos A 2009, 40, 511.
- Georgopoulos, S. Th.; Tarantili, P. A.; Avgerinos, E.; Andreopoulos, A. G.; Koukios, E. G. Polym Degrad Stab 2005, 90, 303.

- Vilaseca, F.; Valadez-Gonzalez, A.; Herrera-Franco, P. J.; Pèlach, M. A.; López, J. P.; Mutjé, P. Bioresour Technol 2010, 101, 387.
- Kim, H. S.; Lee, B. H.; Choi, S. W.; Kim, S.; Kim, H. J. Compos A 2007, 38, 1473.
- 21. Ismail, H. A.; Rusli; Rashid, A. Polym Test 2005, 24, 856.
- 22. Dányádi, L.; Móczó, J.; Pukánszky, B. Compos A 2010, 41, 199.
- 23. Liu, H.; Wu, Q.; Han, G.; Yao, F.; Kojima, Y.; Suzuki, S. Compos A 2008, 39, 1891.
- Bishay, I. K.; Abd-El-Messieh, S. L.; Mansour, S. H. Mater Des 2011, 32, 62.
- 25. Zainudin, E. S.; Sapuan, S. M.; Abdan, K. M.; Mohamad, T. M. Mater Des 2009, 30, 557.
- Bledzki, A. K.; Letman, M.; Viksne, A.; Rence, L. Compos A 2005, 36, 789.
- 27. Ashori, A.; Nourbakhsh, A. Compos B 2010, 41, 578.