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Tribological and Mechanical Properties of Poly[(*R*)-3-hydroxybutyric acid] Grafted with Vinyl Compounds: Insight into Possible Application

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Biodegradable graft copolymers were prepared by gamma radiation-induced graft polymerization of two vinyl monomers, vinyl acetate and vinyl alcohol, onto poly[(*R*)-3-hydroxybutyric acid]. Success of the grafting reaction was verified by Fourier-transform infrared and nuclear magnetic resonance spectroscopy. Thermal remolding was used to create membranes from the copolymers. We determined tribological and mechanical properties of the membranes obtained. The lowest elongation at break in tensile testing is seen for P(3HB) and the highest for P(3HB-*g*-VA). Up to 5 N or so, the highest scratch resistance is exhibited by P(3HB-*g*-VA). Piezoelectric behavior is seen for P(3HB-*g*-VA) while P(3HB-*g*-VAc) and plain P(3HB) showed no electric response. Explanation of the piezoelectric behavior in terms of molecular structures is provided.

Keywords: Membrane tensile testing; Membrane tribology; Piezoelectricity; Poly(vinyl acetate); Poly(vinyl alcohol); Poly[(*R*)-3-hydroxybutyric acid]

INTRODUCTION

Polyhydroxyalkanoates (PHAs) are widely used in biomedical engineering due to their biocompatibility and biodegradability.[1] These polymers are gaining importance because different grafting copolymers can be developed to vary the original molecular structure and allow novel applications.[2,3] Poly[(*R*)-3-hydroxybutyric acid] (P(3HB)) is the most popular PHA and the first member of the "green polymer" family. Its mechanical properties are similar to those of

polypropylene, so it can be used to prepare medical devices, bioresorbable surgical sutures, biodegradable screws for bone fixation, periodontal treatment membranes, and similar applications.[4] However, practical applications of P(3HB) are limited by some adverse properties, namely relatively elevated hydrophobicity, high degree of crystallinity (about 65%), low elongation in tensile testing, and brittleness and instability at temperatures close to the melting point. In some cases, hydrophobicity is an advantage, but not for all kinds of applications.[5] Considerable efforts have been expended toward the development of new materials based on P(3HB) in order to enable a wider application range.[6] The grafting reaction is one of the most studied modifications since it permits dramatically changing the properties of the base polymers, thus leading to materials for desired uses.[7–9] There is a variety of methods of modification of the surfaces of polymeric membranes[10]; Zhang and coworkers reviewed the research on surface modifications on P(3HB) and its copolymers.[11] P(3HB) is among the most used thermoplastic polyesters, amenable to grafting.[12,13]

Previously, we successfully performed the gamma radiation–induced grafting of poly (vinyl acetate) and poly(vinyl alcohol) (PVA) onto poly[(R)-3-hydroxybutyric acid] and determined the properties of P(3HB) after such a modification.[14,15] P(3HB) cannot be grafted with PVA directly, so we proceeded by saponification of grafted poly(vinyl acetate) (PVAc). We studied in more detail the mechanism of grafting of VA onto P(3HB), by nuclear magnetic resonance (NMR) spectroscopy, and the effect of the solvent in the graft reaction.[13] Biodegradability was studied by us,[16] and extensively by Wada and colleagues.[17] However, tribological and mechanical properties of grafted P(3HB) have been barely explored; in particular, the tensile and tribological behavior of these mentioned materials have not been reported before. A tribological and mechanical study of P(3HB) nanocomposites with inorganic nanotubes has been reported; apparently, the subject is progressively gaining more importance because of the increasing relevance of finding novel applications for thermoplastics.[18]

In this present invetigation we studied films of vinyl acetate and vinyl alcohol grafted onto P(3HB) by thermal remolding, determining tribological and mechanical properties of the resulting membranes. Several techniques, such as Fourier-transform infrared (FT-IR) and NMR spectroscopy, were used to verify the successful grafting, comparing with our previous investigations.[14–16] Then, the grafted copolymer's tribology and mechanical properties were compared with those of the blank. Preliminary investigation was also conducted to explore possible applications of the membranes. Nonetheless, more efforts are needed to conclude if these membranes can extend the use of P(3HB) in biomedical engineering due to their tendency to produce electricity.

EXPERIMENTAL SECTION

Synthesis of P(HB-g-VAc) and P(HB-g-VAc) Membranes

P(3HB) from Sigma Aldrich was purified by precipitation in ethanol from chloroform solutions. The vinyl acetate monomer, VAc (Merck, Darmstadt, Germany), was distilled before use. Because of the instability of vinyl alcohol (VA), poly(vinyl alcohol) (PVA) was made indirectly by polymerization of VAc, followed by hydrolysis of the ester bonds.

The synthesis reaction was carried out in a special glass device in a vacuum. The irradiation experiments were performed at room temperature. First, 200 mg of P(3HB) was added to 0.5 mL of VAc in bulk. The sample VAc was subjected to ^{60}Co gamma rays at 10 kGy and 1.62 kGy/h, respectively, as the dose and the dose rate. The time of exposure of the sample to irradiation was about 6 h. The P(3HB) grafted with VAc was extracted with a Soxhlet apparatus using acetone for 96 h to remove residues of VAc monomer and poly (vinyl acetate) obtained as collateral products. The P(3HB-g-VAc) was dried under vacuum conditions at 40°C to reach constant weight. The hydrolysis of P(3HB-g-VAc) was carried out in methanol solutions of 0.05 M sodium hydroxide (NaOH) for 10 h. P(3HB-g-VA) was washed with enough water, filtered, and dried under vacuum conditions before further characterization. Each sample preparation was repeated four times to ensure reproducibility under the same graft reaction conditions. Films of P(3HB) and grafted polymer were obtained by thermal remolding. The polymers were produced using a Teflon template. The melt pressing was performed at 160°C and 10^5 kg/m^2 for 10 min. After cooling, the products were cut into pieces of 1 cm^2 size, with the thickness ≈ 1 mm.

Fourier-Transform Infrared Analysis

Fourier-transform infrared attenuated total reflectance (FT-IR-ATR) spectra were recorded using a Bruker Vertex 70, with 4 cm^{-1} resolution, eight scans, wavenumber range 700–4000 cm^{-1}, and less than 50 mg of each sample.

Nuclear Magnetic Resonance Study

^{1}H-NMR and ^{13}C-NMR spectra were obtained using Mercury 400 BB equipment with a resonance frequency of 300 MHz. The polymeric materials were dissolved in hot deuterated trifluoroacetic acid (CF$_3$COOD).

Tribological Study of the Grafted Copolymers

Scratch resistance was determined using a Micro-Scratch Tester (MST) from CSM (Peseux, Switzerland). This technique has been described previously.[19,20] We applied a progressive load from 0 to 15.0 N for a length of 5.0 mm. Averages of ten scratches were calculated from each sample at the scratch speed of 5.33 mm/min. The conical diamond intender had a diameter of 200 μm and a cone angle of 120°. We determined the instantaneous or penetration depth R_p and the residual (healing) depth R_h 2 min after the passage of the indenter. The error bars on the penetration depth are about ±9 μm, while for the recovery depth they are about ±3 μm.

Tensile Test Measurement

Tensile testing was carried out using an Adamel Lhomargy DY.22 machine at room temperature (25°C), with a load cell of about 5000 N (maximum capacity). The membrane's

sample strips mentioned in the experimental section were used to determine the stress-strain curves. The variables of deformation (mm) and force (N) were obtained at a speed of 0.5 mm/min. The capturing and storing of data were attained through an interface connected to a computer program, which allows obtaining the values of Young's modulus, E/GPa, the stress at break, σb/MPa, the strain at break, εb/(%), and the area S under each curve in an Excel worksheet.

Preliminary Study of the Application Proposal

For piezoelectric evaluation, the samples were put between electrically isolated steel plates to ensure appropriate electrical responses. Then the system glass/steel/polymer/steel/glass was connected to a digital interphase Tektronic TX3 True RMS apparatus with RS-232 optical connection. Electrical measurements were performed as a function of the pressure applied across the polymer sample, the pressure being registered simultaneously on a computer.

RESULTS AND DISCUSSION

Synthesis Evaluation

Spectroscopy was performed to evaluate the success, or otherwise, of the grafting. Both FT-IR and NMR spectra are presented in Figure 1. The graft of PVA (see Figure 1(a) and 1(b), B) onto P(3HB) (Figure 1(b), A) was verified by FT-IR spectroscopy. Figure 1 shows the FT-IR transmittance spectra of P(3HB) and grafting copolymers P(3HB-g-VAc) and P(3HB-g-VA) (Figure 1(b), C) obtained in bulk. We see that P(3HB-g-VA) exhibits the characteristic bands of P(3HB) as well as novel bands that correspond to the new product. A detailed characterization follows: the band at 725 cm^{-1} corresponds to the bending out of the plane of C-H (γ C-H) of the base polymer, the band at 980 cm^{-1} is characteristic of P(3HB) and corresponds to the stretching vibration of C-H, the bands at 1051, 1100, and 1132 cm^{-1} are assigned to υ $_{C-C}$ and δ $_{C-H}$, the bands at 1228 and 1181 cm^{-1} are assigned to the anti-symmetric stretching of the ester (C-O) groups, the band at 1380 cm^{-1} is assigned to the CH$_3$ symmetric scissoring vibration, the band at 1454 cm^{-1} is assigned to aliphatic CH$_2$ scissoring vibration, the band at 1724 cm^{-1} is attributed to the carbonyl stretching vibration, the band at 2890 cm^{-1} is related to the stretching of carbons SP-H, and the bands at the region 2930–2980 cm^{-1} are assigned to the stretching vibration of carbons SP3-H and SP2-H. The bands named above are common to P(3HB) as well as to grafted materials. We also see new bands: the stretching and bending bands that are attributed to alcohol groups of PVA grafted onto P(3HB), observed respectively at 3000–3500 cm^{-1} (wide band centered at 3540 cm^{-1}) and 1560 cm^{-1}. The bands at 2364 cm^{-1} seen in the copolymers are not evidence of grafting but signals of an asymmetrical stretching vibration of CO$_2$. The FT-IR spectra thus clearly confirm the synthesis of P(3HB-g-VA).

As mentioned, we also determined the NMR spectra of P(3HB-g-VA); see Figure 1(c) and 1(d). ^{1}H-NMR spectra show broad bands of polymerized materials, while the intensity also
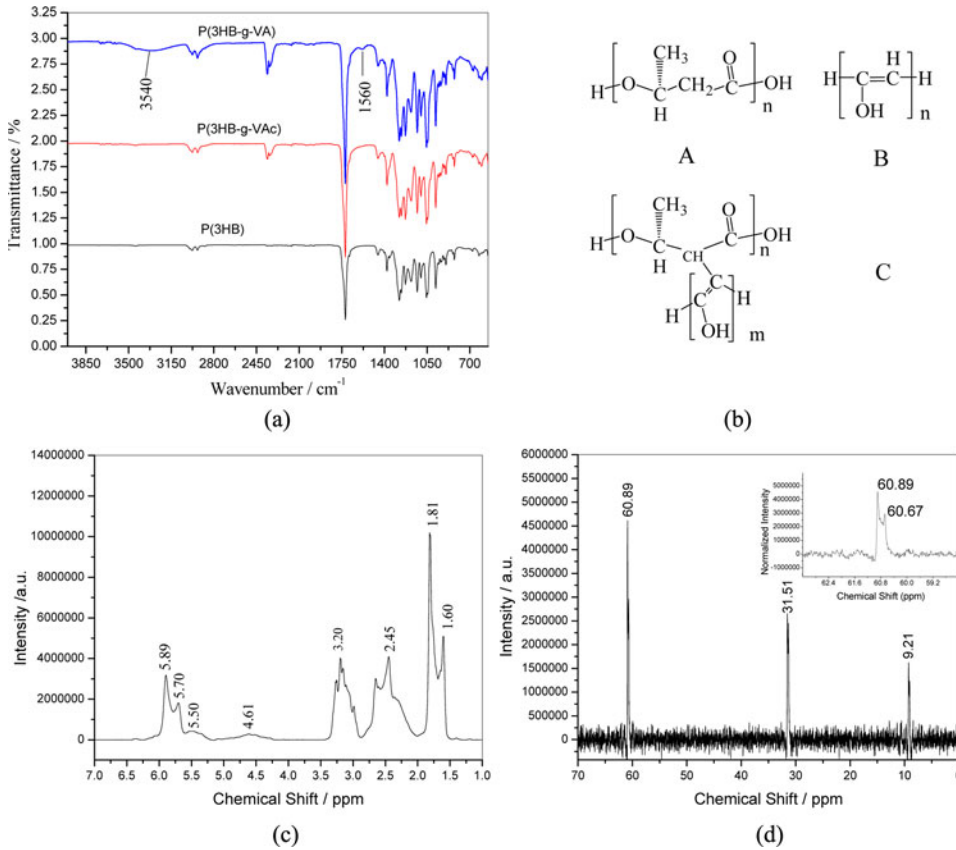
FIGURE 1 From left to right: top left, (a) FT-IR transmittance spectra of P(3HB) and grafting copolymers; top right, (b) chemical structure of A (P(3HB)), B (PVA), and C (proposed P(3HB-g-VA)); bottom left, (c) ^{1}H-NMR spectrum of P(3HB-g-VA); bottom right, (d) ^{13}C-NMR spectrum of P(3HB-g-VA).

increases relative to P(3HB). On one hand, the bands at 1.81 ppm, the one centered at 2.45 ppm, and the one at 5.89 ppm are characteristic of P(3HB) and correspond to CH_3 protons, CH_2 protons, and CH protons, respectively. On the other hand, the spectrum also reveals the presence of new bands: (i) the band at 1.60 ppm, corresponding to the CH_3 protons in their new environment; (ii) the bands at 2.99–3.27, centered at 3.20 ppm, corresponding to the CH_2 protons of the new molecule; and (iii) the bands at 4.61, 5.5, and 5.70 ppm, showing the existence of at least four different kinds of CH protons. It is on this basis that we propose the structure shown in Figure 1(b), C. In addition, the ^{13}C-NMR spectrum shows a novel band at 60.07 ppm, corresponding to CH carbons (see amplified zone in Figure 1(d)). The signal is quite small; we conclude that the grafting degree is low, relative to the number of grafted carbons on the P(3HB). The grafting degree calculated by the mass increase is 69.8 and 42.9% for P(3HB-g-VAc) and P(3HB-g-VA), respectively. Although the number of grafted carbons seems low, the grafted chain can grow to achieve a large size. We also observe that the graft

copolymer bands (31.51 and 9.21 ppm) in the ^{13}C NMR spectrum follow the same trend, showing doublet splitting patterns; they also are displaced relatively to the base polymer while new signals appear due to the change of the chemical environment. We conclude that ^{1}H-NMR as well as ^{13}C-NMR spectra of P(3HB-g-VA) are consistent with successful grafting of VA onto P(3HB).

Scratch Resistance Determination

In scratch resistance determination, one obtains the instantaneous or penetration depth R_p and the healing (final, residual) depth R_h. The latter is always smaller in viscoelastic materials. The percentage viscoelastic recovery f is calculated as:[19,20]

$$f = \left[(R_p - R_h) \cdot 100\% \right] / R_p \qquad (1)$$

The results are presented in Figure 2.

The load range from 0.03 to 15.0 N was chosen because of film thickness, which is 1.0 mm. Since penetration depth of the groove is transient, the healing depth R_h is what remains. We see that up to 5 N or so P(3HB-g-VA) has the best resistance to scratching. At higher loads, it is the unmodified P(3HB) that has the shallowest groove. As far as the percentage recovery is concerned, the situation is similar with the recovery depth, both below and above 5 N loads.

Tensile Behavior

Typical stress versus strain curves of P(3HB) and grafting polymers are shown in Figure 3. Table I provides values of Young's modulus, E/GPa, the stress at break, σ_b/MPa, the strain at break, ε_b'(%), and the area S under each curve obtained from Figure 3.

We recall that the brittleness of materials is defined[21,22] as:

$$B = 1/\left(E_b' \right) \qquad (2)$$

where E' is the storage modulus determined by dynamic mechanical analysis (DMA) at 1.0 Hz and the temperature of interest. While we do not have at our disposal DMA results, we see that P(3HB) has the lowest tensile elongation at break, while P(3HB-g-VA) has the highest.

Insight into Possible Application: Electrical Behavior

P(3HB) and P(3HB-g-VAc) have not shown an electric response under stress. By contrast, the third material does display piezoelectric behavior. Therefore, in Figure 4, we show diagrams of voltage versus time and voltage versus stress for the P(3HB-g-VA) membrane.

We need to explain why two out of our three materials do not show piezoelectric behavior. Return, therefore, to their chemical structures displayed in Figure 1(b). The high concentration of hydroxyl groups in P(3HB-g-VA) is striking. Tables of dipole moments show that propane has the dipole moment of 0.084 Debye; the respective value for 1-propanol is 1.68 Debye, for
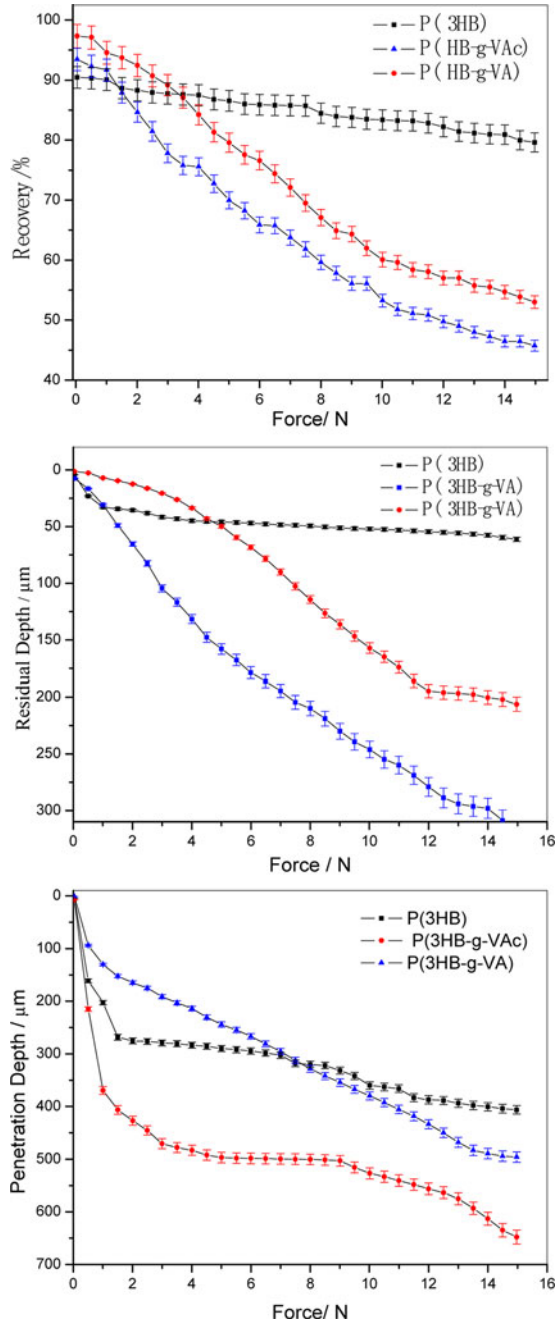
FIGURE 2 Scratch resistance determination results. Top: penetration depth at progressive load; middle: residual depth at progressive load; bottom: viscoelastic recovery.
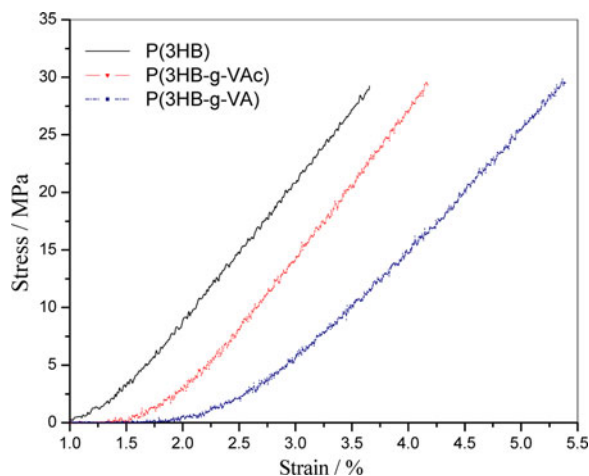
FIGURE 3 From left to right, stress vs. strain curves for P(3HB), P(3HB-*g*-VAc), and P(3HB-*g*-VA) polymers.

2-propanol, 1.66 Debye. Moreover, P(3HB-*g*-VA) has sided chains, and the other polymers do not. As discussed by Mirfakhrai and coworkers,[23] graft copolymers with polar side chains investigated for inverse piezoelectric behavior can produce substantial strains, an essential condition for artificial polymer muscles. Side chains are known to create greater chain relaxation capability (CRC),[24] thus higher chain mobility. We have seen in the previous section that P(3HB-*g*-VA) has the highest elongation at break.

The P(3HB-*g*-VA) sample shows an increase in the piezoelectric potential value up to 14.39 s, where the maximum piezoelectric potential of 0.012 V is reached. Figure 4 shows that the generated piezoelectric potential has a Gaussian-like behavior, similar to the voltage versus time diagram above it. When the device is stressed to 21.7 MPa, the system exhibits the maximum voltage; afterwards, the voltage decreases. Apparently, first P(3HB-*g*-VA) undergoes a gradual stress compression (0.5 mm/min of test speed), and the thickness of the film is reduced considerably; consequently, the dipole orientation of the molecules is affected, resulting in an electrical response by changing the output voltage polarity. In the second stage, the piezoelectric potential decreases because the stress is so high that it hinders the reorientation of the molecules. Free volume goes down, and along with it the CRC goes down. Therefore, the capacity of P(3HB-*g*-VA) film to change the output voltage polarity decreases.

TABLE I
Mechanical properties of P(3HB), P(3HB-*g*-VAc), and P(3HB-*g*-VA) polymers

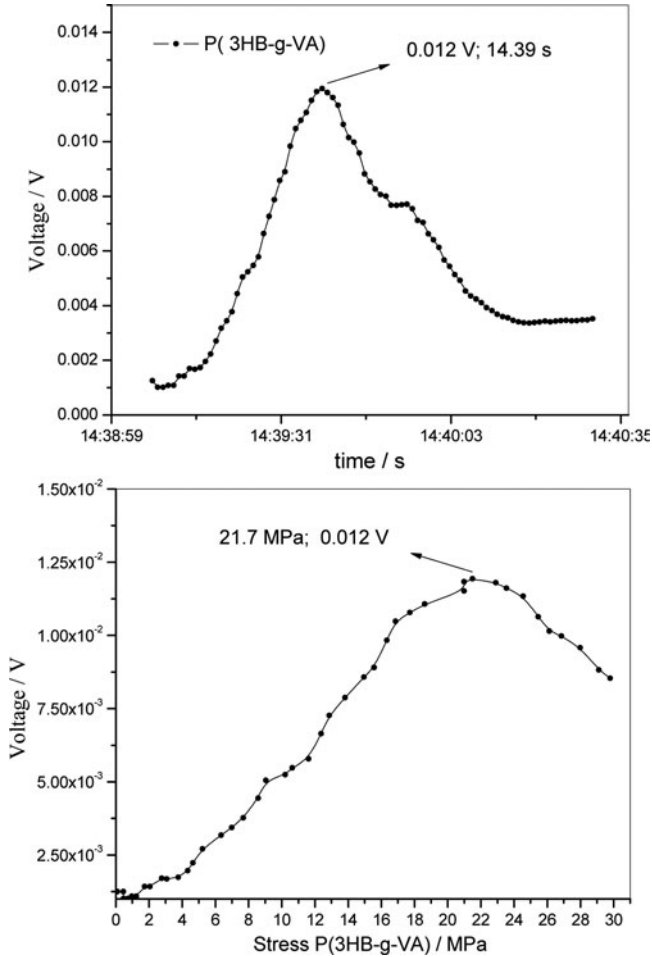| Sample	E *(Gpa)*	σ_b *(MPa)*	ε_b *(%)*	S
P(3HB)	0.60	28.4	3.64	35.0
P(3HB-*g*-VAc)	0.54	29.5	4.17	34.1
P(3HB-*g*-VA)	0.35	29.7	5.36	29.8

FIGURE 4 Top: voltage vs. time diagram for the P(3HB-*g*-VA) membrane; bottom: voltage vs. stress diagram for the same membrane.

Unfortunately, the piezoelectric potential value is relatively lower than expected, so practical application cannot be established under these conditions. However, a complete piezoelectric characterization is still under progress, and the results will be reported in the near future.

CONCLUSIONS

Membranes obtained by radiation-induced graft polymerization of vinyl acetate onto P(3HB) and membranes obtained by hydrolysis of the former membranes were first verified by FT-IR and NMR in agreement with our earlier works.

Evaluations of the grafted membranes were then carried out through tribological and mechanical research. The tribology test indicated that up to 5 N P(3HB-*g*-VA) has the best resistance to scratching, and at higher loads, it is the unmodified P(3HB) that has the shallowest groove. A similar trend was followed by the percentage recovery and the recovery depth over all graphs. Additionally, mechanical study revealed that P(3HB) has the lowest tensile elongation at break, while P(3HB-*g*-VA) has the highest.

Moreover, preliminary experiments were undertaken to search for piezoelectricity. The results indicated that P(3HB-*g*-VA) is a potential candidate for biomedical applications such as artificial polymer muscle. Nevertheless, their piezoelectric properties were found to be too low to make ensure possible applications, so more effort will be undertaken, since, for the moment, our results are inadequate to this end.

ACKNOWLEDGEMENTS

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