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Characterization of hdpe/ha Composites Treated with Titanate and Zirconate Coupling Agents

Albano Carmen,[1,2] Perera Rosestela,*[3] Karam Arquímedes,[1] González Gema,[4] Domínguez Nohemy,[1] Sánchez Yanixia,[1] Brito Juaquín Luís[5]*

Summary: The development of new materials for bone substitution has been of great interest for the scientific community in the last years. High-density polyethylene (HDPE) and hydroxyapatite (HA) composites have been used in biomedical applications without any inflammatory response. However, the differences in nature of both materials have motivated the use of coupling agents to improve their interfacial interactions. In this work, the effects of adding three different commercial coupling agents (NZ12, Lica01, Lica12) to high-density polyethylene (HDPE)/hydroxyapatite (HA) composites were studied. Composites containing 20 parts per hundred (phr) of HA previously treated with the already mentioned coupling agents were characterized by mechanical tests and their morphologies were analyzed afterwards. Composites with 0.3 and 0.5 wt% of NZ12 unfolded an increase in their Young's modulus and tensile strength, as a consequence of an improved dispersion of the filler into the polymeric matrix. Analysis of the samples by XPS showed that the zirconate coupling agent interacted more with the HA, as reflected in the lower binding energies of the corresponding oxygen atoms, which agrees with their better performance from the mechanical point of view.

Keywords: compatibilization; composites; coupling agents; polyethylene; XPS

Introduction

Bones eventually need to be temporarily or permanently replaced due to diseases or traumatic situations. The search for a material that complies with the mechanical and biological requirements for that purpose has been the objective of the scientific community lately. Multidisciplinary studies have been carried out in metals, alloys, ceramics and polymers, being the last ones among the more extensively used materials.[1–3]

In the last few years, composites of high-density polyethylene (HDPE) reinforced with HA have been proposed as alternative materials to be used in orthopedic surgery.[4,5] However, due to the different chemical nature of HDPE and HA, only physical interfacial interactions between them are possible. The objective of this work was to study the influence of three different coupling agents of the neo-alcoxy type (NZ12, Lica 01 y Lica 12) on the behavior of HDPE/HA composites prepared in an internal mixer.

Experimental Part

The hydroxyapatite used in this work was prepared by a precipitation method through a wet chemical reaction using

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[1] Centro de Química, Laboratorio de Polímeros, Instituto Venezolano de Investigaciones Científicas (IVIC)
E-mail: calbano@ivic.ve
[2] Universidad Central de Venezuela, Facultad de Ingeniería
[3] Departamento de Mecánica, Universidad Simón Bolívar
[4] Centro Tecnológico, Instituto Venezolano de Investigaciones Científicas (IVIC)
[5] Centro de Química, Laboratorio de Fisicoquímica de Superficies (IVIC)

equimolar solutions of calcium hydroxide ($Ca(OH)_2$) and di-amonium hydrogen phosphate ($(NH_4)_2HPO_4$)[4] as follows:

$$10Ca(OH)_2 + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6OH_2 + NH_4OH + 6H_2O$$

The resultant suspension was washed with de-ionized water, separated by a centrifuge, its pH neutralized and dried at 80 °C for 48 hours afterwards.

The XRD pattern was recorded using a diffractometer (Siemens, Model D5005) in the range of 20–60°. Scanning Electron Microscopy (SEM) analyses of the HA was done using a Hitachi S4500.

A high-density polyethylene (HDPE) with a MFI of 4.88 g/min and a Mw of 77456 g/mol supplied by Coramer C. A. was used in the preparation of the composites. HDPE/HA composites containing 20 parts per hundred of the filler were made in a HAAKE Rheomix 600 at conditions previously optimized of 160 °C, 90 rpm and 5 min. Three different commercial coupling agents were used, in concentrations of 0.3, 0.5, 0.7 and 1.0 wt.% to the amount of filler: a zirconate (NZ12) and two titanates (Lica 12 and Lica 01). Their chemical structures are shown in Table 1.

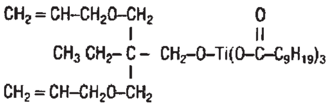
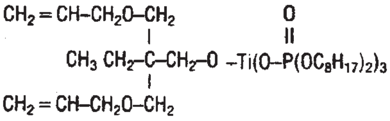
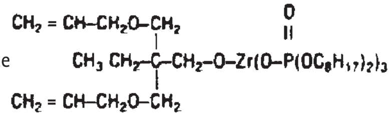
The treatment with the different coupling agents to which the filler were subjected to consisted of the following: the required volume of coupling agent (to reach 0.3, 0.5, 0.7 and 1.0 wt.%) was diluted with an equal amount of hexane, thus obtaining a 1.1 solution. This solution was then slowly sprayed over the filler, for 15 min periods, which was contained in a rotating mixer of the Sigma type. The rotation direction of the mixer was changed every 5 min to ensure distribution of the agent in the filler. Afterwards, the excess of hexane was eliminated by means of a Heindolph rotavapor.

The obtained composites were characterized by mechanical and morphological studies, performing tensile tests and transmission electron microscopy analyses.

Samples for mechanical testing were cut from compression-molded sheets of 1 mm in thickness, following ASTM D-638 standard. A universal testing machine EZ-20 was used for that purpose at a cross speed of 50 mm/min. Transmission Electron Microscopy (TEM) analyses were done using a Phillips CM10 microscope. Samples were prepared by ultramicrotomy without any further conditioning.

The analysis of the samples by XPS was carried out with an ESCALAB 220i-XL

Table 1.
Chemical description and structure of the coupling agents used in this study (Ken-React Reference Manual, 1993).

Commercial name	Chemical Description	Chemical Structure
Lica 01	Neopentyl(diallyl)oxy, trineodecanonyl Titanate	
Lica 12	Neopentyl(diallyl)oxy, tri(dioctyl)phosphate Titanate	
NZ12	Neopentyl(dyallyl)oxy, tri(dioctyl)phosphate Zirconate	

instrument, equipped with a dual (non-monochromatic) Mg/Al anode, operated at 400 W. The Al anode (1486.6 eV) was employed for the experiments reported here. All measurements were performed under UHV, better than 10^{-8} torr. Calibration of the instrument was performed employing the Au $4f_{7/2}$ line at 83.9 eV. Quantification of the XPS signals and curve fitting of the spectra was carried out with the XPS PEAK 4.1 and XPS GRAPH routines after baseline subtraction by the Shirley method, employing an 80% Gausian-20% Lorentzian combination.

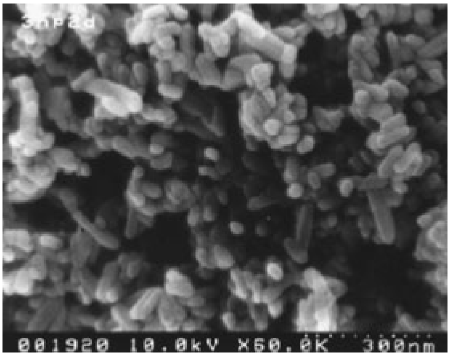


Figure 2.
SEM of HA particles.

Results and Discussion

Figure 1 shows the diffraction spectrum of the synthesized HA. The bands' widths of this spectrum are larger than those reported by Panda et al.,[6] which is an indicative that the particle sizes are nanometric. This result was corroborated by Scanning Electron Microscopy (SEM) where the particle sizes measured about 20 × 60 nm (Figure 2).

Figure 3 unfolds the Young's modulus changes when the three different coupling agents were used in different concentrations. An increase of about 25 to 30% in this parameter was obtained when the coupling agent NZ12 was used at concentrations of

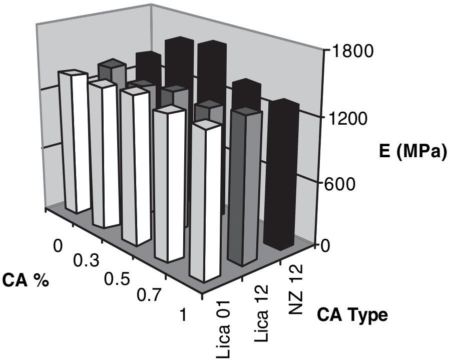


Figure 3.
Young's modulus (E) of the coupled composites (CA: coupling agent).

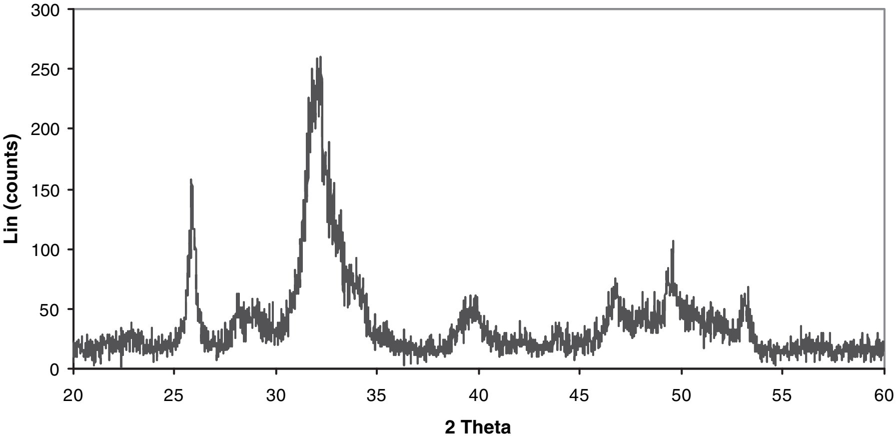


Figure 1.
XRD patterns of the synthesized HA.

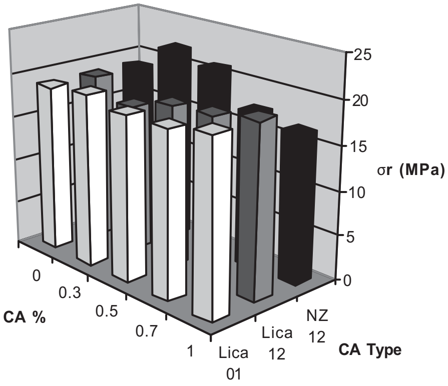


Figure 4.
Tensile strength (σr) of the coupled composites (CA: coupling agent).

0.3 and 0.5 wt.%. At the other concentrations tested, no significant changes were found. This could be an indicative that at such concentrations, the NZ12 produced a compatibilizing effect that improved the interfacial interactions between the polyethylene and the filler particles thus improving their dispersion into the polymeric matrix. As a consequence, an increase in the stiffness of the composite was achieved. This effect is also evident in the tensile strength values reported in Figure 4, where a similar trend can be observed. The other coupling agents (titanates) did not produce any improvement.

Table 2 shows the elongation at break of composites containing all the different coupling agents. When either Lica 01 or Lica 12 was added to the composite, no significant changes were obtained in this parameter. On the other hand, treatments with NZ12 produced a slight decrease in the toughness when its concentration was increased.

Table 2.
Elongation at break of the coupled composites.

	εr (%)		
	NZ12	Lica 01	Lica 12
0	6.8 ± 1.7	6.8 ± 1.7	6.8 ± 1.7
0.3	4.6 ± 0.9	6.5 ± 1.1	7.2 ± 2.1
0.5	4.7 ± 1.1	6.1 ± 0.6	6.7 ± 0.8
0.7	5.7 ± 1.7	4.7 ± 1.1	7.2 ± 1.2
1.0	4.3 ± 1.0	6.3 ± 1.7	6.3 ± 1.7

Coupling agents act as molecular bridges at the interface between two substrates. Titanium and zirconate-derived coupling agents are unique in that their reaction with the free protons at the inorganic interface results in the formation of monomolecular layers on the inorganic surface. The absence of polymolecular layers at the interface along with the chemical structure of the titanates and zirconates create novel substrate surface energy modifications and polymer phase interactions often resulting in viscosity reductions in filled polymer composites.[7] Figure 5 depicts the monomolecular layer formed by the mechanism of alcholysis reactions of a neoalkoxy triorganofunctional titatante coupling agent with the idealized inorganic surface bearing a proton. The Ti or Zr's center of the coupling agent may also act as an electron donor or acceptor causing a catalytic rearrangement and redistribution of the molecular structure and molecular weight of the polymeric phase. On the other hand, the R2 of the molecules of these agents (Table 1) provide Van der Waals's entanglements via the long carbon chains of the thermoplastic, likely originating a plasticizing effect or polymer compatibilization.

Figures 6 displays how the use of NZ12 at a concentration of 0.3 wt.% improves the distribution and dispersion of the filler into the polymeric matrix when compared to the distribution and dispersion of the composite without any coupling agent (Figure 7), which in turn explains the improvements in the Young's modulus and tensile strength values. No improvement was obtained when the HA was treated with the titanates (Lica 01 and Lica 12).

Typically, titanate or zirconate-treated inorganics are hydrophobic, organophilic and organofunctional. When incorporated into polymeric systems they often promote adhesion, improve dispersion and rheology and do not produce embrittlement,[7] if they form a monomolecular layer on the inorganic surface. From the mechanical test

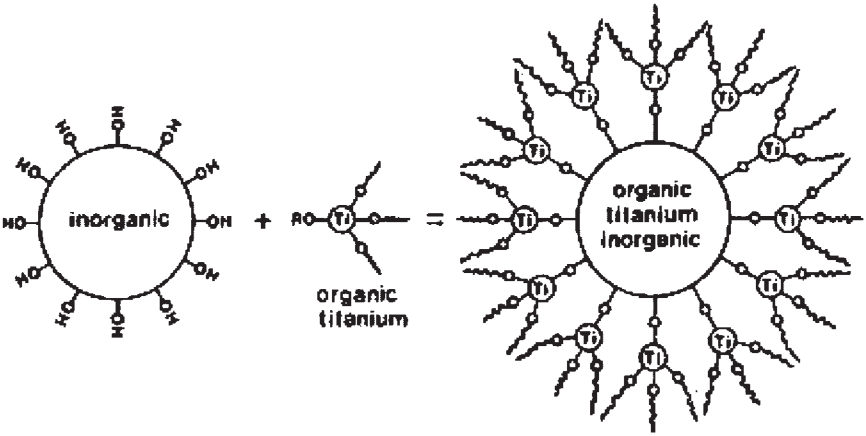


Figure 5.
The reaction of a neoalkoxy triorganofunctional titanate coupling agent with the inorganic surface.[7]

results, it could be inferred that the used titanates might be forming a multilayer at the interface, which implies that some alkoxy groups do not react, giving rise to some negative effects such as a loss of adhesion of the coating. Excess of titanates frequently provides lubrication and superplasticizing effects, such as increases in the elongation at break.

Some theoretical models were used to analyze the tensile data. The Young's modulus was predicted using the Guth-Smallwood equation.[8,9]

$$\frac{E_c}{E_m} = 1 + 2.5\Phi_f + 14.1\Phi_f^2 \qquad (1)$$

where E_c is the Young's modulus of the composite (MPa), E_m is the Young's modulus of the matrix (MPa) and ϕ_f is the filler volume fraction. To calculate ϕ_f, the values of 0.94 g/ cm^3 as the HDPE's density[10] and 3.16 g/cm^3 as the density of the HA were used.[11]

Furthermore, to predict the theoretical values of the tensile strength, the equation of Nicolais-Narkis was employed[12]:

$$\frac{\sigma_c}{\sigma_m} = (1 - 1.21\Phi_f^{2/3}) \qquad (2)$$

where σ_c is the composite's tensile strength (MPa) and σ_m is the matrix tensile strength (MPa).

Tables 3 and 4 display the dependence of the Young's modulus and tensile strength

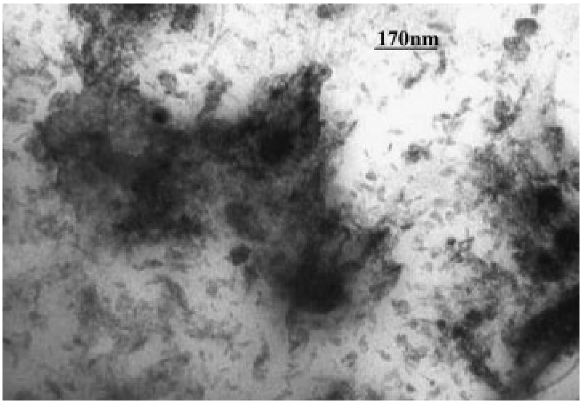


Figure 6.
TEM micrograph of HDPE/HA composites coupled with NZ12 at a concentration of 0.3 wt.%.

Figure 7.
TEM micrograph of the HDPE/HA composite without a coupling agent.

values (E_c, σ_c) of the composites normalized to the respective values of the Young's modulus and tensile strength values of the matrix.

When the results presented in Table 3 are analyzed, it can be concluded that the values of E_c/E_m of the composites obtained through equation (1) are reasonably well related to the experimental results, indicating that the incorporation of HA in a proportion of 20 wt.% increases the rigidity of the HDPE, through the restriction in the mobility of the polymer molecules. Furthermore, changes in E_c/E_m with the addition of the coupling agent are not important, except when 0.3 and 0.5 wt.% of NZ12 were incorporated, indicating enhanced interaction of the filler and HDPE matrix.[7] According to Chan et al.,[13] the interactions between the polymer and filler are due to the large interfacial area between them, as well as to the fact that there are two-counter balanced forces that are affecting the mechanical properties of the nanocomposites. They are the reinforcing and nucleating effects of the filler nanoparticles.

Table 3.
Comparison of experimental data with theoretical predictions from the Guth-Smallwood equation for different contents of coupling agents (in wt.%).

Composites	Ec/Em experimental for different ccentrations of coupling agents			
	0.3	0.5	0.7	1
PEHA-NZ12	1.6342	1.6875	1.4283	1.3514
PEHA-Lica01	1.3975	1.4365	1.3781	1.3811
PEHA-Lica12	1.3084	1.3709	1.3340	1.3811

Theoretical Ec/Em = 1.1848.
Without coupling agent, experimental Ec/Em = 1.3986.

Table 4.
Comparison of experimental data with theoretical predictions from the Guth-Smallwood equation for different contents of coupling agents (in wt.%).

Composites	σc/σm experimental for different concentration of coupling agents			
	0.3	0.5	0.7	1
PEHA-NZ12	1.0891	1.0446	0.8663	0.8267
PEHA-Lica01	0.9604	0.9208	0.9208	0.9653
PEHA-Lica12	0.8317	0.9059	0.9208	0.9653

Theoretical σc/σm = 0.8226.
Without coupling agent, experimental σc/σm = 0.9356.

The tensile strength of the composites was analyzed using the theoretical model of Nicolais-Narkis, in order to understand the generation of discontinuities or weak points in the structure of theses two-phase systems. The predicted value of the ratio σ_c/σ_m is smaller than the experimental one for composites without coupling agents. In those samples treated with the different coupling agents at different contents the σ_c/σ_m values are similar to that of the composite without coupling agent (Table 4) except for those with 0.3 and 0.5 wt.% of NZ12. The Nicolais-Narkis equation describes structures where the adhesion is poor, because the weightage factor (1.21) is believed to be dependent on the adhesion quality between the matrix and the inclusion. A value of 1.21 of the weightage factor is stated to be valid for the

Table 5.
Values of the stress concentration parameter "P" (Eq. (2)) for the composites for different content of coupling agents (in wt.%).

Composites	"P"for different concentrations of coupling agents			
	0.3	0.5	0.7	1
PEHA-NZ12	−0.6073	−0.3037	0.9110	1.1809
PEHA-Lica01	0.2699	0.5399	0.5399	0.2362
PEHA-Lica12	1.1472	0.6411	0.5399	0.2362

Without coupling agent "P" = 0.4386.

Table 6.
Values of the proportionality constant "a" (Eq. (3)) for the composites with different contents of coupling agents (in wt.%).

Composites	"a" for different concentrations of coupling agents			
	0.3	0.5	0.7	1
PEHA-NZ12	−1.5189	−0.7756	2.5531	3.3857
PEHA-Lica01	0.7190	1.4683	1.4683	0.6275
PEHA-Lica12	3.2794	1.7577	1.4683	0.6275

Without coupling agent "a" = 0.1836

extreme case of poor adhesion and spherical inclusions.[14] Equation (2) was follow using a factor P instead of the value of 1.21, being the values of P negative for HDPE/HA composites with 0.3 and 0.5 wt.% of NZ12 as seen in Table 5, because the composite's tensile strength is higher than that of the matrix. According to Maiti & Lopez,[14] the polymer-filler adhesion improves as the "P" values decrease. Hence, it can be concluded that a good interfacial adhesion is present in composites of HDPE with HA treated with 0.3 and 0.5 wt.% of NZ12. This fact was confirmed when the Kunori & Geil equation was used.[14] This equation relates the tensile strength with a proportionality parameter "a", which is a stress concentration parameter. A higher value of "a" corresponds to a stronger stress concentration. The Kunori & Geil equation is as follows:

$$\frac{\sigma_c}{\sigma_m} = \exp(-a\Phi_f) \tag{3}$$

The values of "a" determined from equation (3), are shown in Table 6. As it can be seen, those values are negative for samples of HDPE/HA composites treated with 0.3 and 0.5 wt.% of NZ12, which leads to the same conclusion as before, that is, the stress concentration at the interface decreased and hence, there seems to be a good interfacial adhesion in the composites.

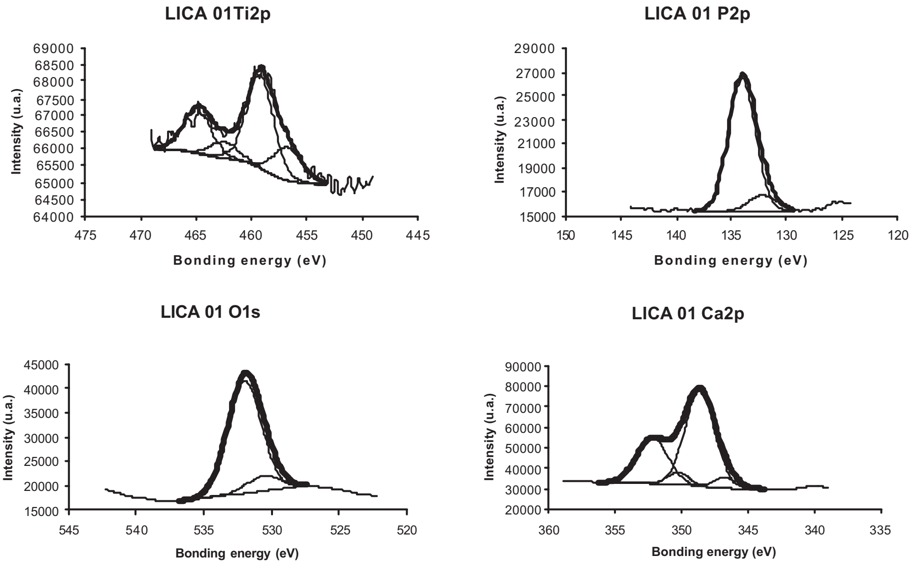


Figure 8.
XPS of HA-Lica 01.

To analyze in a more detailed fashion whether an interaction between the HA and the HDPE matrix does exist when the NZ12 coupling agent is present, XPS studies were performed in those composites where the coupling agents were used at concentrations of 0.5 wt. %. Figure 8 shows selected high resolution XPS spectra of the Ca 2p, O 1s, P 2p, Ti 2p and Zr 3d regions. Each region was curve fitted with peak parameters derived from a pure hydroxyapatite sample and literature data for Ti and Zr. The resulting deconvoluted spectra are shown in Figure 6 for Lica 01. The data for binding energies (B.E.), peak areas and full width at half maximum height (fwhm) for the three coupling agents are shown in Table 7.

The C 1s region showed several superimposed peaks, reflecting the different carbon species present in the polymer and coupling agents. Thus, referencing of the spectral data was not made with the C 1s peak as customary; instead, the O, Ca or P main signals (due to the hydroxyapatite) were employed for adjusting the binding energy scale. The main peaks shown in Table 7 as B, (D_1, D_2), and F for O, Ca and P, respectively, relate well to the data for pure hydroxyapatite.

The lower B.E. signals A, (C_1, C_2) and E could be attributed to the effect of the

Table 7.
XPS data for HA-Lica 01, HA-Lica 12 and HA-NZ12 samples.

Element	Signal	Peak position (eV)	Area (a.u.)	FWHM (eV)
LICA 01				
O	$A = 1s$	530.5	9560	3.0
	$B = 1s$	532.0	72111	2.9
Ca	$C_1 = 2p_{3/2}$	346.6	14677	2.1
	$C_2 = 2p_{1/2}$	350.1	7667	1.9
	$D_1 = 2p_{3/2}$	348.5	129397	2.6
	$D_2 = 2p_{1/2}$	352.1	64699	2.8
P	$E = 2p$	132.0	4018	2.9
	$F = 2p$	133.9	34034	2.9
Ti	$G_1 = 2p_{3/2}$	456.7	3318	3.0
	$G_2 = 2p_{1/2}$	462.4	1659	3.0
	$H_1 = 2p_{1/2}$	459.2	8896	2.8
	$H_2 = 2p_{1/2}$	464.9	4448	3.0
LICA 12				
O	$A = 1s$	530.7	24189	3.0
	$B = 1s$	532.0	150200	3.0
Ca	$C_1 = 2p_{3/2}$	346.6	33571	2.6
	$C_2 = 2p_{1/2}$	349.7	16785	2.6
	$D_1 = 2p_{3/2}$	347.9	165311	2.6
	$D_2 = 2p_{1/2}$	351.5	82655	2.6
P	$E = 2p$	132.4	4218	3.0
	$F = 2p$	133.9	39042	3.0
Ti	$G_1 = 2p_{3/2}$	456.4	4641	3.0
	$G_2 = 2p_{1/2}$	462.1	2321	3.0
	$H_1 = 2p_{3/2}$	459.1	9521	2.7
	$H_2 = 2p_{1/2}$	464.8	4761	3.0
NZ 12				
O	$A_1 = 1s$	528.0	23210	3.0
	$A_2 = 1s$	529.9	12640	2.2
	$B = 1s$	532.0	110824	2.8
Ca	$C_1 = 2p_{3/2}$	347.0	23643	3.0
	$C_2 = 2p_{1/2}$	350.5	11822	2.9
	$D_1 = 2p_{3/2}$	347.9	110113	2.8
	$D_2 = 2p_{1/2}$	351.6	41146	2.6
P	$F = 2p$	133.8	34750	3.0
Zr	$J_1 = 3d_{5/2}$	183.3	21665	3.0
	$J_2 = 3d_{3/2}$	185.7	14444	3.0

coupling agent on the elements of HA or the components of the agent itself. Interestingly to note, the amount of the (C_1, C_2) Ca species respect to the main (D_1, D_2) ones is lower in the case of LICA 01 than in those for Lica 12 or NZ 12. Similarly, the size of the A Oxygen signal respect to the main B one is lower for Lica 01 than for the other two coupling agents. This fact could reflect a weaker interaction between Lica 01 and the HA than that of the other two compounds with the HA.

The lower B.E.s of the A_2 Oxygen signals in NZ12, as compared with those of the A Oxygen in the Lica containing composites, could indicate that the former ones possess more electronic density available to interact with HA sites. In consequence, the hydrophilic part of the NZ12 coupling agent must be covering the HA surface in a better way, thus improving the HA-NZ12 interaction. Zirconium in NZ12 is richer in electronic density than Ti in Lica, meaning that it could transfer more electron density to the hydrophobic part of the NZ12 chain, rendering it less polar and thus more alike the polymeric matrix. In this way, it can interact better with HDPE than the hydrophobic part of the Lica coupling agents.

Conclusions

At low NZ12 concentrations (0.3 and 0.5 wt.%), an improvement in the tensile properties was obtained, especially in the Young's modulus and in the tensile strength. The coupling agents of the titanate-type did not produce significant changes in the mechanical behavior of the composites. The prediction of the mechanical properties such as tensile strength and Young's modulus indicates a good polymer-filler interaction. Furthermore, it can be concluded that the zirconate coupling agent performed better than the titanates did from the mechanical properties point of view, because the former has a higher electronic richness of the metal-oxygen bonds involved in the interactions with both filler and polymer.

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[1] G. E. Zaikov, K. Z. Gumargalieva, A. Polishchuk, A. A. Adamyan, *Polym.-Plast. Technol. Eng.* **1999**, *38*(4), 621.
[2] M. Buchanan J., *Key Engineering Materials*, **2002**, *218–220*, 487.
[3] G. William, *British Ceramic Transactions*, **1996**, *95*(5), 212.
[4] K. E. Tanner, R. N. Downes, W. Bonfield, *British Ceramic Transactions*, **1993**, *93*(3), 104.
[5] M. Wang, D. Porter, W. Bonfield, *British Ceramic Transactions*, **1994**, *93*(3), 91.
[6] R. Panda, M. Hsieh, R. Chung, T. Chin, *The Japan Society of Applied Physics*, **2001**, *40*, 5030.
[7] S. J. Monte, Kenrich Petrochemical, INC., "Ken-React(R) Reference Manual-Titanate, Zirconate and Aluminate Coupling Agents", Third Revised Edition, March 1995.
[8] H. M. Smallwood, *J. Appl. Phys*, **1944**. *15*, 758.
[9] E. J. Guth, *Appl. Phys*, **1945**. *16*, 20.
[10] J. Brandrup, E. H. Immergut, "*Polymer Handbook*", Interscience Publishers, John Wiley & Sons, New York **1966**.
[11] R. Joseph, W. J. McGregor, M. T. Martyn, K. E. Tanner, P. D. Coates, *Biomaterials*, **2002**, *23*, 4295.
[12] L. Nicolais, M. Narkisw, *Polym. Eng. Sci.* **1971**, *11*, 194.
[13] C. M. Chan, J. Wu, J. X. Li, Y. K. Cheung, *Polymer*, **2002**, *43*, 2981.
[14] T. Kunori, P. H. Geil, *J. Macromol. Sci., Phys. B*, **1980**, *18*, 135.