Plasma surface modification of nanoparticles to prepare polymer nanocomposites with enhanced properties.

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Abstract

In the last 10 years, we had worked at CIQA (México) with plasma modification of different types of particles and nanoparticles such as carbon nanofibers, carbon nanotubes, graphene, graphite, copper, silver, silica, titanium, agave, etc. Nanoparticles generally present excellent mechanical, thermal, electrical and antibacterial properties, however, due to their high surface energy they form clusters or agglomerates and generally they are not compatible with polymeric matrices. At our laboratory, particles had been plasma modified in a simple RF (13.56 MHz) plasma reactor, varying plasma power, gas flow rate and time of treatment mainly. Although, last year we also had performed surface modification of nanoparticles at atmospheric pressure. Three plasma reactors with different geometry had been used mainly, to carry out the modification of different types of particles.

The process to perform the modification of particles had been mainly plasma polymerization, where a thin coating of polymer is deposited at the surface of the particle. Although in some cases, the particles and nanoparticles had been also modified using reactive or inert gases, such as: air, oxygen, nitrogen, argon, ammonia, etc. Particles had been modified mainly to increase their chemical compatibility towards different polymers, since polymers and particles are generally of different chemical nature, and it is necessary to carry out the surface modification of particles in order to improve the compatibility between the two phases, and the distribution on the particles inside the polymer matrix. Pristine and treated nanoparticles were analyzed by different analytical techniques (FTIR, TGA, XPS, SEM, TEM, X-ray Diffraction, dispersion in solvents, etc.)

The polymer nanocomposites obtained after mixing the modified particles with different polymers by melt mixing (extrusion, injection) or by *in situ* polymerization. The polymer composites obtained, had been analyzed by thermal analysis (DSC and TGA), crystallinity was evaluated by x-Ray Diffraction and the mechanical properties of the composites had also been obtained, mainly Young modulus and in some cases antimicrobial properties had also been evaluated. In general had been observed that polymers containing modified particles or nanoparticles present better properties than those containing pristine particles. Plasma treatment improves the compatibility between polymer and particles and as a result, the properties of the composites are enhanced. We had also found that when the nanocomposites (their surface) are etched in a plasma reactor, some properties, such as electrical, thermal or antibacterial are also improved.

References of the author :

1.- Nanocomposites Prepared with High Density Polyethylene and Carbon Nanofibers Modified by Ethylene plasma. M. G. Neira-Velázquez, J. J. Borjas-Ramos, E. Hernández-Hernández, C. G. Hernández-Ramos, R. I. Narro-Céspedes. *Plasma Processes and Polymers*, 2015, 12, 477-485.

2.- Plasma functionalization of CNF´s with vapors of ammonia/water, Ernesto Hernández-Hernández, María G. Neira-Velázquez, Hilda Guerrero-Alvarado, José F. Hernández-Gámez, Pablo González-Morones, Carlos A. Ávila-Orta, Yibran A. Perera-Mercado, José J. Borjas-Ramos, Marissa Pérez Álvarez, Anna D. Iliná, Pascual Bartolo-Pérez, Plasma Chemistry and Plasma Processing, 2015.

3.- Effect of Plasma Polymerization of Copper Nanoparticles using Acrylic monomers on their antibacterial properties. M. Navarro-Rosales, C. A. Ávila-Orta, M. G. Neira-Velázquez, H. Ortega-Ortiz, E. Hernández-Hernández, P. González-Morones, S. G. Rosales-Solís, R. M. Jiménez-Barrera, B. L. España-Sánchez. *Plasma Processes and Polymers*, 2014, 11, 685–693.

4.- Improving stability of TiO_2 particles in water by RF-plasma polymerization of poly(acrylic acid) onto particle surface Araceli Solís-Gómez, M. Guadalupe Neira-Velázquez, Juan Morales, Marco Antonio Sánchez-Castillo, Elías Pérez *Colloids and Surfaces A: Physicochem. Eng. Aspects* 451 (2014) 66–74.

5.- Enhanced Antibacterial Activity of Melt Processed Poly(propylene) Ag and Cu Nanocomposites by Argon Plasma Treatment, Beatriz L. Espana-Sánchez, Carlos A. Avila-Orta, Felipe Padilla-Vaca, María G. Neira-Velázquez, Pablo González-Morones, Jose A. Rodríguez-Gonzalez, Ernesto Hernández-Hernández, Angeles Rangel-Serrano, Enrique Díaz Barriga-C., Luis Yate, Ronald F. Ziolo, Plasma Process. Polym. 2014, 11, 353–365.

6.- Chemical Modification of Carbon Nanofibers with Plasma of Acrylic Acid. María G. Neira-Velázquez, Ernesto Hernández-Hernández, Luis F. Ramos-de Valle, Carlos A. Avila-Orta, Yibran A. Perera-Mercado, Silvia G. Solís-Rosales, Pablo González-Morones, Arturo Ponce-Pedraza, Miguel Avalos-Borja, Rosa I. Narro-Céspedes, Pascual Bartolo-Pérez. *Plasma Processes and Polymers*. Volume 10, Issue 7, pages 627–633, July 2013.

7.- Surface Modification of Nanoclays by Plasma Polymerization of Ethylene, M. Guadalupe Neira-Velázquez, L. Francisco Ramos-de Valle, Ernesto Hernández-Hernández, Arturo Ponce-Pedraza, S. Guadalupe Solís-Rosales, Pascual Bartolo-Pérez, Virgilio A. González González. *Plasma Processes and Polymers Volume 8(9), 842–849, 2011.* ISSN: 1612-8869.

8.- Silver nanoparticle deposition on hydrophilic multilayer film surface and its effect on antimicrobial activity. S. Sánchez-Valdes, J. Mendez-Nonell, L. F. Ramos-de-Valle, H. Ortega-Ortiz, M. Mondragón-Chaparro, E. Ramírez-Vargas, M. G. Neira-Velázquez, *Journal of Applied Polymer Science, Volume 123, Issue 5, pages 2643–2650, 5 2012.*
ISSN: 1097-4628.

9.- Changing the Surface Characteristics of CNF, from Hydrophobic to Hydrophilic, Via Plasma Polymerization with Acrylic Acid E. Hernández-Hernández, M. G. Neira-Velázquez, L. F. Ramos-de Valle, A. Ponce and D. Weinkauf ; Journal of Nano Research, 9, 45-53, (2010).

10.- Surface modification of carbon nanotubes with ethylene glycol plasma. *C. A. Ávila-Orta, V. J. Cruz-Delgado,* M. G. Neira-Velázquez, *E. Hernández-Hernández, M. G. Méndez-Padilla and F. J. Medellín-Rodríguez*, Carbon, 47(8), 1916-1921, (2009)

11.- Surface Modification of CNFs Via Deposition of an Ultra-Thin Coating of Plasma Polymerized Poly (Acrylic Acid) and Its Effect on the Properties of PA6/ CNF Nanocomposites *E. Hernández Hernández,* M. G. Neira Velázquez *and L. F. Ramos-de Valle,* Journal of Applied Polymer Science, 112 (6), 3510-3518, (2009)

12.- Surface Modification of CNFs by Plasma Polymerization of Methylmethacrylate and Its Effect on the Properties of PMMA/CNF Nanocomposites Neira-Velázquez María Guadalupe*, Ramos-de Valle Luis Francisco, Hernández-Hernández Ernesto, Zapata-González Ivan Journal: e-polymers, No. 162, 2008 ISSN 1618-7229

13.- Surface modification of CNFs via plasma polymerization of styrene monomer and its effect on the properties of PS/CNF nanocomposites L. F. Ramos de Valle*, M. G. Neira-Velázquez, E. Hernández Hernández, Journal of Applied Polymer Science, October, 2008.Volume 107 (3), 1893-1899. *ISSN*: 0021-8995

14.- Plasma modification and dispersion of multiwalled carbon nanotubes (MWCNT) in high impact polystyrene based nanocomposites: analysis by electron microscopy (TEM and SEM) E. Díaz Barriga-Castro, S. A. Zertuche-Martínez, A. O. Castañeda-Facio, J. A. Cepeda-Garza, M. G. Neira-Velázquez, R. Díaz De León-Gómez, F. Soriano-Corral. Acta Microscopica Vol. 23, No.3, 2014, pp. 168 – 175.

15.- Control of the chemical composition and thickness of deposited coatings over carbon nanotubes using acrylic acid plasma P. Gonzalez Morones, C. A. Avila Orta, D. Navarro Rodriguez, and M. G. Neira Velazquez, *Afinidad* LXX, 563, 201-205, 2013.

16.- Preparation of Polymer Nanocomposites with Enhanced Antimicrobial Properties. Beatriz L. España-Sánchez, Carlos A. Ávila-Orta, Maria G. Neira-Velázquez, Silvia G. Solís-Rosales and Pablo González – Morones. *MRS Proceedings* / Volume 1479/2012.

17.- Caracterización de nanofibras de carbón modificadas superficialmente con plasma de etileno. J. Borjas Ramos, M. Téllez Rosas, F. Ávalos Belmontes, G. Neira Velázquez, F. Ramos de Valle, Revista Prospectiva, Colombia. SSN: 1692-8261 Prospect. Vol. 9, No. 2, Julio - Diciembre de 2011, págs. 54-58.