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Computational simulation a system of waterborne polyurethane matrix by β-C induction with ZnO and $CaCO_3$ particles

Simulación computacional de una matriz de poliuretano base agua, con inducción de β-C y compuestos de ZnO y $CaCO_3$

AGUILAR-MARURI, Saul†´.´´, CONTRERAS-LÓPEZ, David´´, GALINDO-GONZÁLEZ, Rosario´´´ and FUENTES-RAMÍREZ, Rosalba´´*

´*Centro de Investigación en Materiales Avanzados S.C., Monterrey Unit, North Alliance No. 202, PIIT Park, C.P.66628, Apodaca, Nuevo Leon, Mexico.*
´´*Universidad de Guanajuato, Natural and Exact Sciences Division, Department of Chemical Engineering, Noria Alta S/N, Col. Noria Alta, C.P. 36050, Guanajuato, Guanajuato, Mexico.*
´´´*CONACYT cathedra in Universidad de Guanajuato, Natural and Exact Sciences Division.*

ID 1st Author: *Saul, Aguilar-Maruri* / **ORC ID:** 0000-0002-1656-472X, **CVU CONACYT ID:** 955004

ID 1st Co-author: *David, Contreras-López* / **ORC ID:** 0000-0003-1384-4766, **CVU CONACYT ID**: 38297

ID 2nd Co-author: *Rosario, Galindo-González* / **ORC ID:** 0000-0002-3612-1555, **CVU CONACYT ID:** 223987

ID 3rd Co-author: *Rosalba, Fuentes-Ramírez* / **ORC ID:** 0000-0003-0520-3387, **CVU CONACYT ID:** 202669

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Abstract

This work includes the search for the development of a composite of a WPU (waterborne polyurethane), β-CD (β-Cyclodextrin), PZnO (zinc oxide particles), and the presence of $CaCO_3$, to obtain new properties such as adhesion to multiple substrates of organic and inorganic origin. Therefore, a development sequence was proposed: Computational development: conformation of the polymeric matrix (with the intermediary polymers) and simulation of the interaction between β-CD and PZnO and Ca^{+2} and CO_3^{-2} ions, as well as insertions in β-CD, computational simulations were carried out with the help of ACD LABS™ (free version) software and by molecular dynamics with GROMACS™. With the above, we were able to determine properties such as interfacial tensions, surface tensions, and contact angles, and degrees of solvation and stability in waterborne emulsions. Therefore, it is important to point out that one of the main contributions of this research proposal is that there are no studies that combine these materials.

Waterborne polyurethane, ZnO particles, computational simulation

Resumen

El presente estudio desarrolla la factibilidad teórica computacional de desarrollar un compósito de una matriz de PUBA (poliuretano base agua), con la inserción de β-CD (β-Ciclodextrina), en la cadena polimérica, PZnO (partículas de óxido de zinc) y $CaCO_3$. Este material tendrá propiedades de adhesión a múltiples sustratos (orgánicos e inorgánico). La metodología de síntesis considera la simulación computacional: conformación de la matriz polimérica (con sus intermediarios) y simulación de la interacción entre la β-CD y las PZnO e iones Ca^{+2} y CO_3^{-2}, así como las inserciones en la β-CD, se realizaron simulaciones computacionales con ayuda del software ACD LABS™ (versión libre) y por dinámica molecular con GROMACS™. Con lo anterior, logramos determinar propiedades como tensiones interfaciales, tensiones superficiales, ángulos de contacto y grados de solvatación y estabilidad en emulsiones base agua. Este trabajo presenta un material que combina las interacciones de la β-CD, PZnO y $CaCO_3$, las cuales no se han conjuntado hasta el momento.

Poliuretano base agua, partículas de ZnO, simulación computacional

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* Correspondence to the author (Email: rosalba@ugto.mx)
† Researcher contributing as first author.

Introduction

Currently, PU´s (polyurethanes) are a class of versatile polymers (Christopher *et al*., 2016) with multiple synthesis routes and applications, which have been affiliated in different utilities such as the manufacture of liquid coatings, elastomers, elastic fibres, etc., (Akindoyo *et al*., 2016). These types of materials are chosen in the various industrial branches for their superior properties, such as mechanical properties (excellent rigidity, hardness, resistance to abrasion, and flexibility at low temperatures), chemical resistance (corrosion resistance), and resilience (Akindoyo *et al*., 2016). WPU systems represent non-toxic, non-flammable, and non-air polluting commercial products (Tornero *et al*., 2018). Booming research is looking for multiple synthesis routes for these materials, where blocks composed of polyols, diisocyanates, neutralizers, hydrophilic extensor chains, and additives will determine the structure of said PU and its properties (Kang *et al*., 2018). Therefore, there is a tendency to generate PU's with better elasticity, resistance to dry film abrasion, among other properties (Noble, 2018).

Structural modifications to PU´s provide specific performance properties to the coating, that has been explored with the addition of nanoparticles or various chain extenders to the polymeric matrix. It has been found that including ZnO nanoparticles (synthesized by sol-gel method) in the matrix of a WPU is an ecological alternative to delay corrosion in AISI 1018 CS substrates due to the increase in the impedance displayed in the EIS (Electrochemical impedance spectroscopy) (Salazar-Bravo *et al*., 2019). Other analysis by EIS determined that the β-CD/WPU film blocks the corrosive medium to the substrate, especially in the presence of $CaCO_3$, which verifies an anti-corrosive system with effective self-healing on metallic substrates (Hua et al., 2019).

Furthermore, the use of computational simulations has allowed economic and risk-free validation, aspects such as experimental synthesis or determination of conformations of new proposed polymeric structures.

This work establishes the computational feasibility of a WPU synthesized by induction via β-CD, and with the addition of $CaCO_3$ and PZnO, as a precursor of a coating with significant adhesion to polymeric and inorganic materials, it will possess a self-healing mineralization and possible protection against UV radiation. And by means of computational simulation (considering the synthesis conditions, ZnO and $CaCO_3$ addition sites, and emulsion feasibility of the polymeric matrix in water), some structural and physicochemical characteristics can be predictively analysed.

Methodology

Computational simulation:

1. Using AVOGADRO (optimizing with the following parameters: UFF as Force Field and Steepest Descent as algorithm, 9 optimizations or until obtaining an energy difference between simulations of 0.5%), the structures corresponding to β-CD, ZnO, and Ca^{+2} and CO_3^{-2} ions were drawn, obtaining the corresponding structures in *pdb* files (Brookhaven Protein DataBank format).

2. Subsequently, in GROMACS™ (using the corresponding topology), the effective interaction of β-CD with PZnO and $CaCO_3$ was established. Molecular dynamics simulations considered one molecule of β-CD, 200 molecules of water, 50 of Ca^{+2}, 50 of CO_3^{-2}, and 100 of ZnO, using a long-range Van der Waals interaction model, which has Lorentz-Berthelot corrections. Nine simulations were carried out to obtain a variation of minimization of total energy of 0.5%, between continuous simulations.

3. The synthesis stages of Hua *et al*., (2019) were considered for the simulation of the conformation of the polymeric matrix. These stages consider the mole equivalents, with which it was possible to determine some polymeric intermediates that could be expected in the synthesis stage.

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4. The formation of the polymer corresponding to each reaction stage was simulated in ACD LABS™ (free version) with the molecular mechanics algorithm based on the parameterization of the force field, CHARMM, with modifications and simplifications to increase the stability and speed of calculation of the model of (Brooks, B. *et al*., 1983), obtaining the estimation of the surface tension.

5. The final structure of step 4 was transferred to GROMACS™ with which the feasibility of solvation of the proposed system was established, using *gro* files. Fifteen simulations were carried out to obtain a variation of minimization of total energy of 0.5%, between continuous simulations.

Results

The result of the molecular dynamics simulations, for the effective interactions between β-CD, ZnO particles and calcium carbonate ions were successful, is shown in Figure 1.

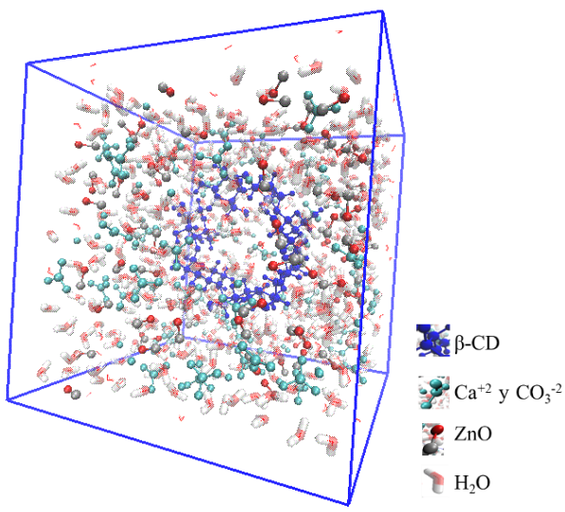

Figure 1 Configuration resulting from the balanced simulation of molecular dynamics of the interaction of ZnO, Ca^{+2}, CO_3^{-2}, and β-CD in aqueous medium, carried out in GROMACS™. Analysis volume of 14.33 nm^3
Source: Own work [VMD (Visual Molecular Dynamics) program]

With concentration calculations and considering the average density obtained from the simulation (1898.23 kg/m^3, as shown in the Figure 2), it would imply the possibility of an interaction of β-CD with 112073 ppm of Ca^{+2}, 455136 ppm of ZnO and 167807 ppm of CO_3^{-2}.

The optimization leads to a negative value of the total energy of the system at the simulation temperature (300 K), which means that the system is bounded and stable, because the energy that is optimized in a greater proportion is the potential energy and not kinetics, obtaining an average value of -7708.39 kJ/mol, as shown in Figure 3.

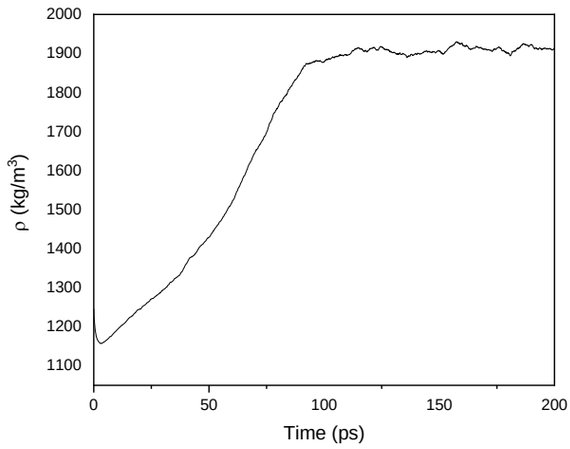

Figure 2 Density of the system balanced by molecular dynamics, in GROMACS™, for the interaction of ZnO, Ca^{+2}, CO_3^{-2} and β-CD in an aqueous medium
Source: Own work [OriginPro 9]

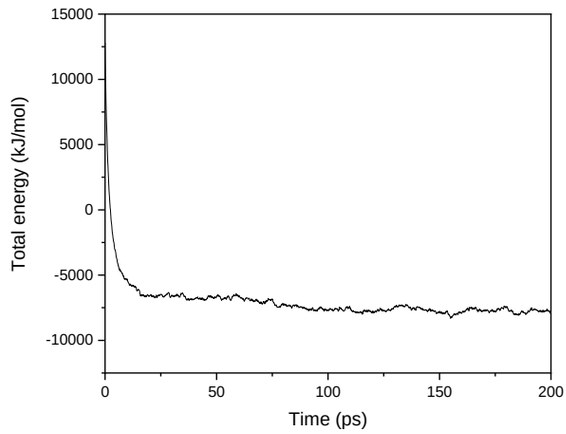

Figure 3 Total energy of the system balanced by molecular dynamics, in GROMACS™, for the interaction of ZnO, Ca^{+2}, CO_3^{-2} and β-CD in an aqueous medium
Source: Own work [OriginPro 9]

The molecular dynamics simulations, Figure 4, estimated a surface tension of 625 bar nm for the system, which is equivalent to 62.5 mN/m. The surface tension of the water is 73 mN/m therefore, the system has a slight variation in the intramolecular cohesion forces that occur.

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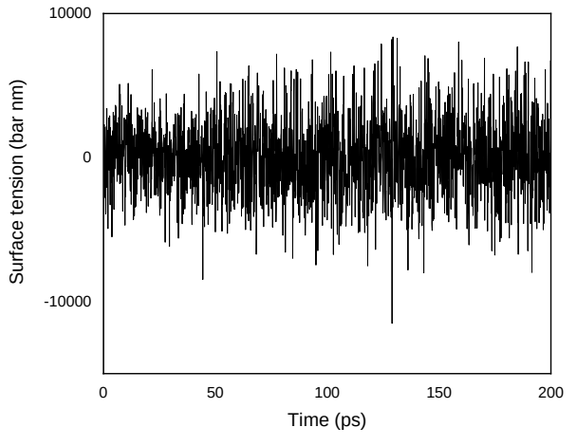

Figure 4 Surface tension of the system balanced by molecular dynamics, in GROMACS, for the interaction of ZnO, Ca^{+2}, CO_3^{-2} and β-CD in aqueous medium
Source: Own work [OriginPro 9]

The analysis of the radial distributions of ZnO, water, Ca^{+2} and CO_3^{-2}, by means of the simulations of molecular dynamics carried out in GROMACS™, indicate that β-CD was found with the first ZnO species at 0.56 nm (Figure 5), with Ca^{+2} at 1.27 nm (Figure 6), with CO_3^{-2} at 0.25 nm (Figure 7) and with water at 0.52 nm (Figure 8). This indicates a good interaction of β-CD with ZnO and CO_3^{-2} (because β-CD is composed of seven d-glucopyranose residues linked by α-1,4-glycosidic bonds with a structure with a hydrophobic internal cavity and a hydrophilic exterior), and above all a good solvation of the system.

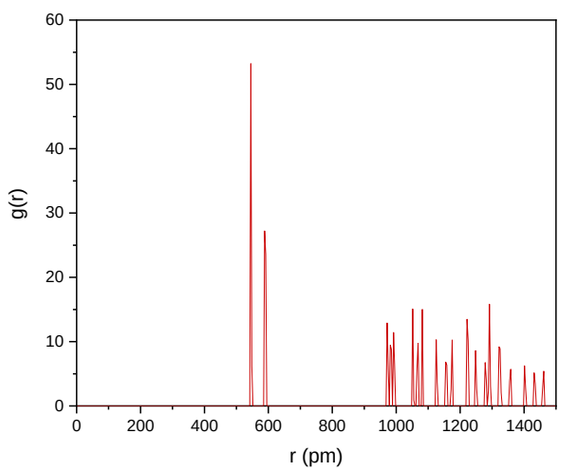

Figure 5 Radial distribution function of ZnO in the system balanced by molecular dynamics, in GROMACS™, for the interaction of ZnO, Ca^{+2}, CO_3^{-2} and β-CD in aqueous medium
Source: Own work [OriginPro 9]

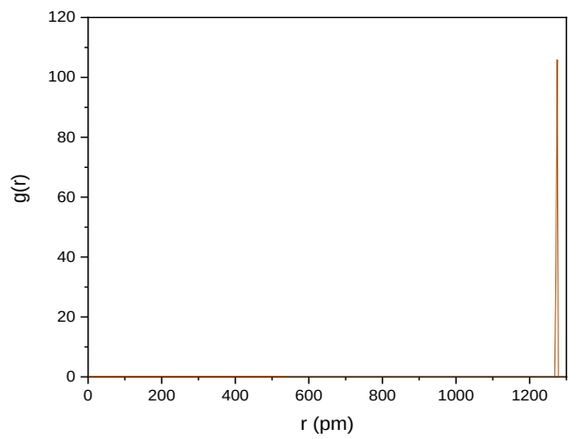

Figure 6 Radial distribution function of Ca^{+2} in the system balanced by molecular dynamics, in GROMACS™, for the interaction of ZnO, Ca^{+2}, CO_3^{-2} and β-CD in aqueous medium
Source: Own work [OriginPro 9]

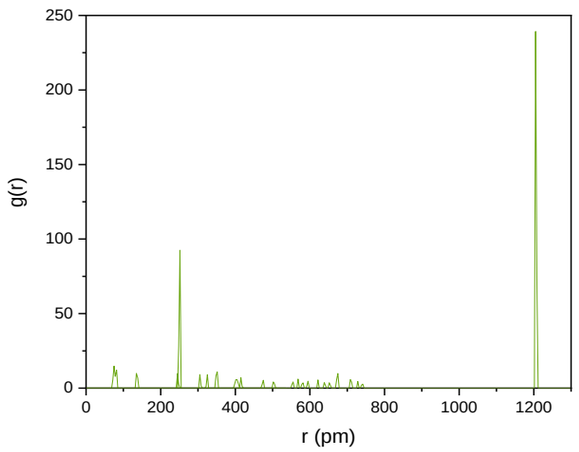

Figure 7 Radial distribution function of CO_3^{-2} in the system balanced by molecular dynamics, in GROMACS™, for the interaction of ZnO, Ca^{+2}, CO_3^{-2} and β-CD in aqueous medium
Source: Own work [OriginPro 9]

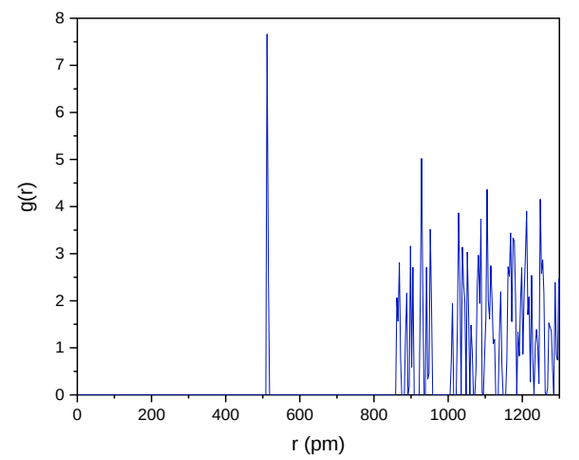

Figure 8 Radial distribution function of water in the system balanced by molecular dynamics, in GROMACS™, for the interaction of ZnO, Ca^{+2}, CO_3^{-2} and β-CD in aqueous medium
Source: Own work [OriginPro 9]

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The radial distribution functions obtained in Figures 5-8 indicate that the system will have a very close interaction with respect to the studied particles (ZnO, CO_3^{-2} and water), especially for the CO_3^{-2} and ZnO particles, with which the β-CD is an interaction-retention site, as other works have already reported for CO_3^{-2} (Hua *et al*., 2019). And from the correct interaction with PZnO, the polymer matrix is expected to acquire resistance properties from exposure to UV radiation, as has been reported in the bibliography (Hua *et al*., 2019).

The stages of synthesis of polymer matrix consider the mole equivalents, this indicate someone reagents are in excess and is possible occurrence parallel reactions like show in Figure 9, this polymer resulting from the reaction between 6 molecules of IPDI (Isophorone diisocyanate) and 3 of PD (polycaprolactone diol average Mn ~ 2000 g/mol), resulting in an optimized system in AVOGADRO with a final energy of 7817.56 kJ/mol and a molecular weight of 7028.76 g/mol. The result of these simulations was visualized with VMD.

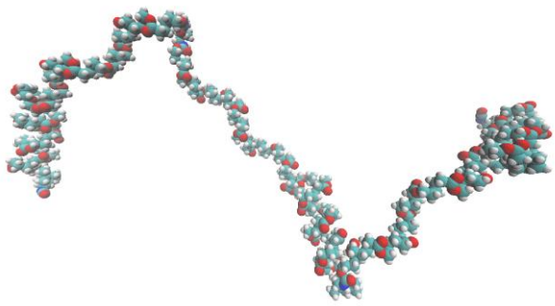

Figure 9 Polymer resulting from the reaction between 6 molecules of IPDI and 3 of PD, hydrogen (white), oxygen (white), carbon (light blue) and nitrogen (navy blue)
Source: Own work [VMD (Visual Molecular Dynamics) program]

The final polymer, Figure 10, in GROMACS™ reports a cell volume of 169.22 nm^3, with a density of 1005.25 g/L and optimal solvation with 5323 water molecules. The percentage of solids that our water-based coating would have is estimated, which is 6.21%, which is a good percentage for a coating that will be applied by spraying with a pressure of 2.5 kg/cm^2, although the layer that will be deposited in the surface of the substrate would be very small for which it would arise to apply several layers.

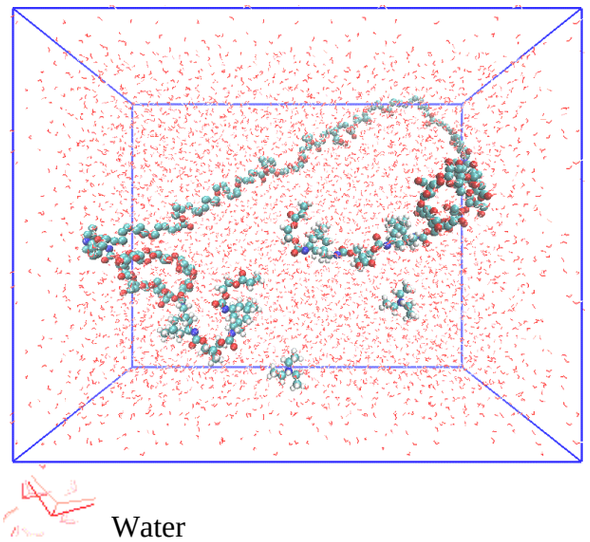

Figure 10 Configuration resulting from WPU final in solvation, in GROMACS™, hydrogen (white), oxygen (white), carbon (light blue) and nitrogen (navy blue)
Source: Own work [VMD (Visual Molecular Dynamics) program]

Making an analysis of the results obtained in the simulations with ACD LABS/ChemSketch™ (free version) and considering equations 4 and 5 of the work of (Good, R. J., & Girifalco, L. A., 1960), Figure 16 is obtained. The program cannot estimate properties of the final polymer because it does not have a continuous structure.

$$\theta = cos^{-1}\left[2\Phi\left(\frac{\gamma_{Prepolymer}}{\gamma_{water}}\right)^{\frac{1}{2}} - 1\right] \quad (1)$$

$$\gamma_{Prepolymer-water} = \gamma_{Prepolymer} + \gamma_{water} - 2\Phi\left(\gamma_{Prepolymer}\gamma_{water}\right)^2 \quad (2)$$

Where:

- θ is the contact angle between the prepolymer and the water.
- γ surface tension in mN/m.
- $\Phi = \frac{4\left(V_{prepolymer}V_{water}\right)^{\frac{1}{3}}}{\left[\left(V_{prepolymer}\right)^{\frac{1}{3}}+\left(V_{water}\right)^{\frac{1}{3}}\right]^2}$
- V is the molecular weight (g/mol) of the species divided by its density (g/cm^3).

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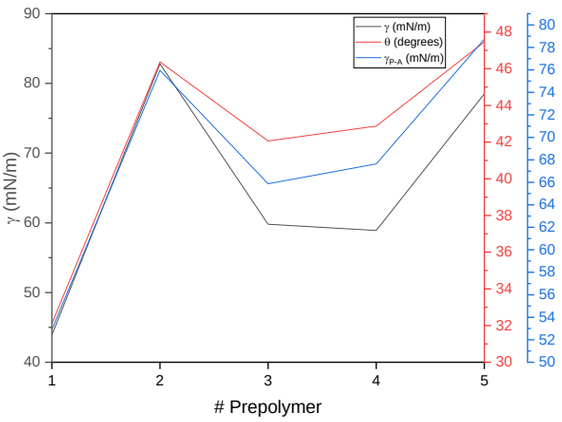

Figure 11 Variation of γ, θ and $\gamma_{P\text{-}A(Prepolymer\text{-}water)}$ of the prepolymers generated by computational simulations and 3-D CHARMM-type of force field optimization in ACD LABS/ChemSketch™ (free version)
Source: Own work [OriginPro 9]

The θ found for each prepolymer analyzed indicates that there is an interface between water and the polymeric matrix and suggests a measure of the wettability of the polymer by water. When carrying out the analysis of the variability of $\gamma_{P\text{-}A}$ we found values between 52 and 79 mN/m, which indicates dispersed systems with a larger particle size and a reduction in interfacial tension favours the formation of a dispersed system from the point from an energetic point of view. The evaluation of θ and γ with substrates of different chemical origin with prepolymer 5 (m-P5) is summarized in Table 2.

Material	$\gamma_{material}$ $\left[\frac{mN}{m}\right]$ *	θ_{m-P5} [°]	γ_{m-P5} $\left[\frac{mN}{m}\right]$
Polyethylene	30-32	57.13	63.25
Polypropylene	30-35	56.60	63.43
Steel	40-55	58.87	84.03
Glass	70-73	48.30	80.54
* Data extracted from (Pye, 2016)			

Table 2 Evaluation of $\gamma_{material}$, $\gamma_{m\text{-}P5}$ and θ for the generated prepolymer 5 and proposed materials
Source: Own work [Microsoft Office Word]

For all the θ shown in Table 2, we can infer that there is a polymer with a medium degree of wettability, which favours the mass transfer mechanism within the roughness of the proposed substrates, benefiting an interfacial adhesion between two immiscible systems. Although based on the results of $\gamma_{m\text{-}P5}$ we can consider that the polymeric system will have a higher interfacial resistance for substrates such as steel and glass.

Conclusions

The polymerization process between IPDI and PD was studied, and as chain extenders β- CD, dimethylolpropionic acid and ethyl acrylate, and from the polymers formed laterally with the minimization of energies by the conjugate gradient in the AVOGADRO software.

The theoretical feasibility of the formation of the polymeric matrix and the insertion of PZnO, Ca^{+2} and CO_3^{-2} ions, with the formation of an emulsion (in a waterborne system) of the polymeric matrix and the adhesion to organic and inorganic substrates (polyethylene, polypropylene, steel, and glass), and an equilibrium model with long-range Van der Waals interactions, using molecular dynamics with GROMACS™ software.

The simulations carried out of the polymeric matrix, in GROMACS™, demonstrate its viability as a coating that can be applied by spraying, under standard industrial operability conditions, due to the feasibility of creating a system with a 5% total solids percentage.

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