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Using Chitosan as a Nucleation Agent in Thermoplastic Foams for Heavy Metal Adsorption

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Summary: Thermoplastics/chitosan-powder composite foams were prepared by extrusion using azodicarbonamide (ACA) as chemical blowing agent. The effect of chitosan content on morphology (cell size, nucleation density and foam density) of the foams was studied. Chitosan particles are located on the bubbles periphery. Morphological quantification showed that foam cell size decreased and cell population increased with addition of chitosan into polymeric matrix from 1 to 10%. Further, optimum chitosan content was obtained for each polymer. Polymers foamed with chitosan were tested as a chelating resin to adsorb chromium (Cr VI) from different concentration solutions.

Keywords: chitosan; cell diameter; foam; nucleation agent; polyolefin

Introduction

Heterogeneous foam nucleation is widely used in polymer systems containing additives. The bubble production efficiency depends on different factors such as shape and type of nucleating particles.[1] Chemical and physical blowing agents can be used for the extrusion-foaming process. Chemical blowing agents must decompose during the extrusion process producing the gas needed for foaming, which is then mixed with the polymer matrix. Nucleation occurs when the core of a polymer melt has been supersaturated with blowing agent. When cell nucleation takes place in the extrusion die, the cells grow and the foam density decreases as the available blowing agent molecules diffuse into the cells.[2] A nucleation agent is a favorable factor because it can induce an heterogeneous nucleating mechanism,[3] and it is responsible for smaller cell size formation and a more uniform cell size distribution. Different works[4–7] have used inorganic nucleation agents to enhance cell nucleation in foamed polymers in order to improve morphology and some mechanical properties.

Naguib et al.[4] studied the effect of talc addition in extruded Polypropylene (PP) foams and they found that the increased cell density at a high talc content increased the number of cells. Calcium carbonate was used by Anderson et al.[5] to promote the creation of nucleation sites in Polyvinyl Chloride (PVC) extruded foams with low levels of blowing agent. Buckmaster and Randa[6] used boron nitride and inorganic salts to obtain uniform small-diameter cell structure in fluoropolymer foams. Eggshells were recently used by Xu and Hanna[7] in thermoplastic starch foams, they saw that foam cell size, expansion ratio and compressibility decreased and that cell population increased with addition of eggshell into the starch matrix.

Additionally organic powders such as wood powder has been used by Rodrigue et al.[8] as nucleation agent in Low-density

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Polyethylene (LDPE) foams. In this study chitosan powder was used as nucleation agent. Chitosan is obtained by alkaline treatment of chitin at high temperature. The most common reaction of this system is carried out using NaOH as catalyst for chitin deacetylation. Chitosan and its derivatives have become useful polysaccharides in pharmaceutical, biomedical and environmental areas due to their biocompatible, biodegradable, and non-toxic properties.[9–11] Chitosan is one of the most abundant polysaccharides in nature. The chelating properties of chitosan are well known, thus is a good sorbent for metal ions in diluted effluents.[10–14] Yun et al.[15] demonstrated that chitosan and cross-linked chitosan were good for heavy metal remotion from solutions of Pb^{+2}, Cu^{+2} and Co^{+2} among others. The adsorption capacity for metal ions depends on the amine group (concentration and accessibility) of the chitosan for complex formation.[14–16] However, the most serious limitations for using chitosan alone as chelating resin are its relative high solubility on weak acids and its high cost.

In this work chitosan powder was used as nucleation agent for Low density and High density Polyethylene (LDPE, HDPE), Polypropylene (PP) and Polystyrene (PS) extrudated foams. Azodicarbonamide (ACA) was chosen as the chemical blowing agent. The main objectives of this paper were to demonstrate that chitosan acts as an effective nucleation agent for polymeric foams and to investigate the effects of its amount over cell population and size (morphology). Polymers foamed with chitosan were tested as a chelating resin to adsorb chromium (Cr VI) from solutions at different concentrations.

Experimental Part

Materials

Industrial grade powder chitosan (America Alimentos, Jalisco, Mexico) with average particle size (Horiba LA-950, Laser Scattering) of 173 μm, and 95% deacetylation (Infrared Spectroscopy Analysis Method).

High density polyethylene (HDPE) 65050 and low density polyethylene (LDPE) 20020P were provided by PEMEX (Mexico). Polystyrene (PS) Styron 685D and Polypropylene (PP) 1112 were purchased from Dow Chemicals and Pinnacle polymers respectively. Some properties of each polymer are shown in Table 1. The chemical blowing agent azodicarbonamide (ACA) and zinc oxide (ZnO) were obtained from Aldrich. $K_2Cr_2O_7$ from AccuStandard Inc. was used to prepare chromium solutions.

Sample Preparation

Blends of 1, 2, 5, 7 and 10% chitosan (wt/wt) in each polymer with 0.5% and 0.1% (wt/wt) of ACA and ZnO respectively were prepared with a Leistritz micro 26 GL/GG twin-screw extruder of 36 L/D operating in the co-rotating mode, obtaining cylindrical profiles in a 3 mm circular die. The temperature profile and the screw speed for each polymer are shown in Table 2.

Morphology

A morphological analysis of the samples was performed to obtain the size of the cells. The samples were fractured in cross-sectional area of the machine direction using liquid nitrogen. Polarized light micrographs were taken using an Olympus Mic-D microscope. Each picture was analyzed quantitatively via Image-Pro Express

Table 1.
Physical properties of utilized polymers.

Polymer	Density (kg/m^3)	Melt index (g/10 min)	Tg (°C)	Tm (°C)
HDPE 65050	966	5	−70	128
LDPE 20020P	921	1.8	−25	115
PS Styron 685D	1050	1.5	100	–
PP 1112	900	12	10	173

Table 2.
Processing conditions for each polymer.

Polymer	Zone Temperature (°C)									Screw speed (rpm)
	1	2	3	4	5	6	7	8	9	
HDPE 65050	160	160	165	165	165	169	174	175	161	10
LDPE 20020P	120	130	140	150	160	169	174	175	161	10
PS Styron 685D	165	165	170	170	170	169	174	175	161	30
PP 1112	165	165	170	170	170	174	179	180	166	30

(Media Cybernetics) to measure the bubbles dimensions. The mean cell diameter (D) was calculated as the average of at least 100 cells, and cell density (N_f) defined as the number of cells per cubic centimeter of foam as:[17]

$$N_f = \left(\frac{n}{A}\right)^{3/2} \tag{1}$$

where n is the number of cells in a micrograph of area A in cm^2.

Chromium Adsorption

Solutions of Cr(VI) at different concentrations (from 50 to 500 mg/L) using $K_2Cr_2O_7$ at pH 6.00, all in deionized water were prepared. The pH of the solutions was adjusted by adding either 0.1 N NaOH or 0.1 N HNO_3 as needed. Batch adsorption experiments were carried out in 15 mL glass vials by mixing together 1 g of chitosan-polymer blend foam with 10 mL of metal solution (of each concentration used). The contents in the vial were agitated in a Shaker bead (Barnstead Shke5000-7) at constant temperature (25 °C) and contact time of 8 h at speed of 150 rpm. The contact time was evaluated after chitosan-polymer is saturated with the highest metal solution and concentration at equilibrium remains the same. After sample filtration, Cr(VI) concentrations into recovered solutions were analyzed. The metal solution concentration before and after the reaction, were determined with an atomic adsorption spectrophotometer (Varian SpectrAA 220) with air-acetylene oxidizing flame; wavelength 357.9 nm, working range 0.06-15.0 μg/mL; lamp current 7 mA and slit width 0.2 nm.

The adsorption isotherm at a particular temperature was obtained by varying the initial concentration of Cr ions. The amount of ions adsorbed (q_e, reported per gram of chitosan or composite), based on the difference of metal concentration in aqueous solutions before and after adsorption, the volume of aqueous solution, and the amount of adsorbent used by weight, was calculated using the following equation:

$$q_e = \frac{V(C_o - C_f)}{W} \tag{2}$$

where V is the volume (L) of metal solution,$C_o$the initial metal concentration (mg/L), $C_f$the final metal concentration (mg/L) and W is the weight (g) of the adsorbent used.

Results and Discussion

Morphology

Experimental mean bubble diameter (± standard deviation) for all foamed material prepared in this work, are shown in Table 3. It is shown that LDPE has the smallest cell diameter among the thermoplastics used here. In most cases, cell diameter decreases asnucleation agent content increases, and this is in agreement with the findings reported by Yang and Han,[18] for the system LDPE-fluorocarbons using Calcium carbonate, Calcium hydroxide, calcium stearate, zinc stearate, aluminum stearate and talc as nucleation agents.

LDPE showed the smallest size dispersion among the studied foamed polymers when nucleation agent was added. The remaining polymers also show a tendency to form smaller bubbles as Chitosan addition increases. Polystyrene produced the largest bubbles. Density of the foamed

Table 3.
Mean cell diameter of polymer foamed as function of amount of chitosan.

Chitosan (%wt)	LDPE 20020P D (μm)	HDPE 65050 D (μm)	PS 685D D (μm)	PP 1112 D (μm)
0	94 ± 33	143 ± 40	224 ± 61	168 ± 68
1	133 ± 42	164 ± 59	204 ± 69	161 ± 58
2	82 ± 24	132 ± 53	200 ± 74	150 ± 47
5	81 ± 21	115 ± 38	127 ± 57	118 ± 51
7	63 ± 20	112 ± 41	113 ± 52	117 ± 48
10	59 ± 19	80 ± 21	109 ± 53	65 ± 22

material was also changing as nucleation agent addition increased.

The general pattern for density changes is as follows: As nucleation agent was added, density started to diminish up to a minimum, and then it went back towards the density of the pure polymer, without reaching the density of the pure polymer. The minimal density for these polymers was around 0.40 g/cm^3.

Nucleation density results (Table 4) show a slight increase on the amount of bubbles once the 1% plateau is passed, as reported by Colton and Suh,[19–21] with the largest nucleation density around 7% Chitosan for all the polymers except PP which only needs 5% to reach the highest nucleation density.

According to Colton and Suh,[19–21] such ‘‘critical concentration’’ depends on the nucleation agent solubility for a transient regime for controlled nucleation from homogeneous to heterogeneous; as the nucleation agent concentration increases once the critical concentration is surpassed, the amount of bubbles diminishes maybe due to openings from where the gas might escape without forming bubbles inside the extruder. Thus less bubbles and higher density of the foamed material are obtained. LDPE presented the highest nucleation density on its critical concentration followed by HDPE, PS and PP.

The chitosan used here as nucleation agent follows the expected trends reported by other research groups using other powders or material as nucleation agent. When adding the biopolymer, we not only diminished the bubble size and increased the amount of bubbles, we also get bubbles with more homogeneous mean distribution sizes, similar to the findings of Hansen and Martin,[22–23] Rodrigue et al.[24] and McClurg.[25] The density of the foam, depends on the amount of bubbles thus, our results indicate that the density of the materials produced is directly related to the amount of chitosan used. The increase on density of the foamed material at higher Chitosan concentrations is explained by the fact that the bubbles are small in size and we have fewer bubbles per volumetric unit increasing this way the density which approaches that of the pure material. In other words, Chitosan stops being effective as nucleation agent, and starts working as solid filler which does not provide any more active sites for bubble formation in an heterogeneous nucleation.

Han y Ma[26] found optimal conditions at a concentration of 0.25% (wt/wt) in tests from 0 to 1%, when using talc as nucleation

Table 4.
Nucleation density (cells/cm^3)

Chitosan (%wt)	LDPE 20020	HDPE 20020P	PS 685D	PP 1112
0	1.22E + 05	2.56E + 04	8.57E + 03	1.53E + 04
1	6.57E + 04	8.84E + 03	6.84E + 03	1.16E + 04
2	1.86E + 05	1.68E + 04	7.02E + 03	1.73E + 04
5	2.29E + 05	3.21E + 04	1.95E + 04	2.65E + 04
7	4.37E + 05	3.44E + 04	2.78E + 04	2.55E + 04
10	2.56E + 05	2.90E + 04	2.10E + 04	6.99E + 03

agent in a system of LDPE with fluorocarbons, demonstrating that for each system and nucleation agent, there is an inflection point based on the amount of nucleation agent at which the density of bubbles is the best. Moving away of that point, the generation, amount, size and distribution of the bubbles would stop being optimal. In our case, for the studied thermoplastic materials, the optimal concentration of chitosan was 7%, except in the case of the PP in which the optimal concentration is 5%.

Lee[27,28] also observed a critical concentration which is related to the particle size of the nucleation agent. Rodrigue et al.[24] extruded foams of poly(methyl methacrylate) at several concentrations (0–5%) and particle sizes (1, 3 and 17 μm) of calcium carbonate, finding the critical concentrations between 0.7 and 1.3 for calcium carbonate. In agreement with the works of Han and Ma,[26] Lee[27,28] and Rodrigue et al.[24] it is possible to suggest that for large particles of nucleation agent, the critical concentration will be in higher percentages.

The morphology of some foamed LDPE is shown in Figure 1, it is possible to observe the availability of some chitosan particles on the composite surface. At low chitosan concentration (1%) the particles are located preferably on the periphery of the bubbles, as shown in Figure 1a, which is an advantage for the desired application in the present study.

Figure 1b shows a photograph of the same material as on Figure 1a after a procedure to solubilize the chitosan by means of acetic acid with the purpose to demonstrate its availability on the surface. When chitosan concentration is increased (5% Figures 1 c and d), the density of the bubbles also increases and the size of the cells diminish. It is also observed in Figure 1d that while the chitosan concentration is increased, certain amount of chitosan is exposed on the surface. Even though the chitosan is in some cases within the bubble, when the material is pelletized the chitosan is exposed.

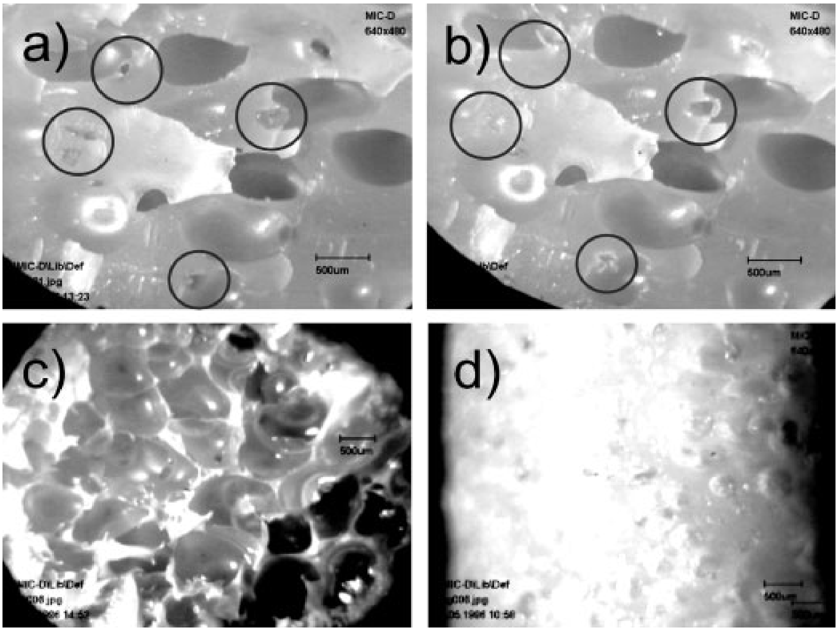

Figure 1.

Morphology of foamed LDPE. a) 1% Chitosan located on the outside surface of the bubbles, b) 1% Chitosan after extraction with acetic acid, c) Transversal view with 5% Chitosan d) longitudinal view with 5% Chitosan.

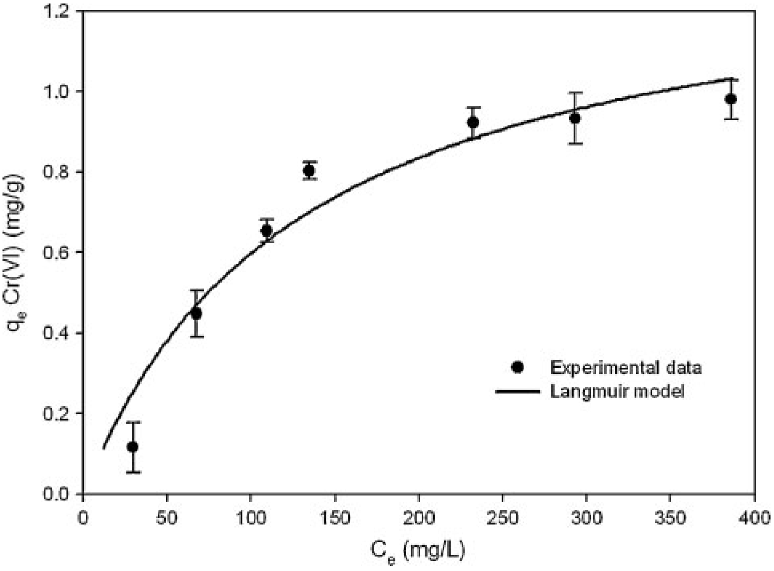

Figure 2.
Langmuir isotherm for LDPE/chitosan-powder composite after chromium sorption at pH = 6.0

Chromium Adsorption

Using the best foamed material with the most chitosan exposed in foams (LDPE 20020P with 7% wt chitosan), adsorption experiments are reported in Figure 2, as an example. The adsorption equilibrium experiments were conducted as indicated in experimental part, using an optimal pH of 6, a complete pH effect is given elsewhere.[29] The contact time was determinated after chitosan-polymer was saturated with the solution of highest metal concentration and equilibrium concentration remains the same (data not shown). The amount of metal adsorbed on the chitosan is calculated using equation 2.

The Langmuir adsorption isotherm represented by the linearized equation (3) was used here to fit the experimental adsorption data:[30]

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{3}$$

where q_e is the solid phase metal concentration (mg/g), C_e is the aqueous phase metal concentration at equilibrium (mg L^{-1}), q_{max} is the maximum metal uptake (mg g^{-1}) and b is a coefficient related to the strength of adsorption, $b = k_a / k_d$ (k_a is the rate constant of adsorption, k_d is the rate constant of desorption).

The amount of chitosan exposed was calculated by weight difference, thus this biopolymer is responsible for Cr(VI) adsorption, obtaining 86.4 mg Cr(VI) adsorbed by each g of chitosan. In chitosan, the main functional group responsible for metal ion adsorption is the amine group ($-NH_2$). The $-NH_2$ group of the chitosan has one pair of electrons from nitrogen, which primarily act as an active site for the formation of chitosan-metal-ion complex. The results of this study will certainly help to optimize and improve the processing conditions, especially to increase the chitosan content in order to improve the adsorption capacity and diversify the application of this material. Chitosan exposure on the foams surface is crucial for metal ion adsorption.

Conclusions

Chitosan powder was successfully used as nucleation agent in thermoplastic foams. As observed by microscopy, chitosan particles are located on the bubbles' periphery. From the morphological characterization, it is shown that the foam cell size decreased and cell population increased with chitosan content until a critical concentration (7% for HDPE, LDPE and PS and 5% for PP). LDPE foams with chitosan powder were tested as an effective chelating resin to adsorb metallic ions. The adsorption experimental data for Cr(VI) solutions were described by the Langmuir model. Maximum adsorption capacity for Cr(VI) is 84.6 mg/g Chitosan. Our results suggest the potential use of low-cost material in the removal of toxic heavy metals aqueous streams.

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