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POLIÓIS VEGETAIS: MATÉRIA-PRIMA VERSÁTIL PARA PREPARAÇÃO DE POLÍMEROS

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Resumo: Polióis derivados de óleos vegetais tem sido preparados através de rotas sintéticas simples, como hidroxilação e transesterificação, e utilizados na preparação de poliuretanas, resinas epóxi e resinas alquídicas. Mais recentemente, polióis vegetais fosforilados foram empregados na formulação de espumas rígidas de poliuretano (PU) e suas propriedades como retardantes de chama e revestimentos anticorrosivos investigadas. Os polióis fosforados foram obtidos a partir da reação do óleo de soja epoxidado com ácido fosfórico. Os polióis obtidos foram caracterizados e usados na preparação de espumas de poliuretano e também em revestimentos. Os resultados demonstraram que os polióis fosforados obtidos a partir de fontes renováveis apresentam potencial como retardantes de chama tão bons quanto os comerciais, propriedades anticorrosivas e têm grande potencial para outras aplicações de PU's.

Palavras-chave: *Polióis vegetais, espumas de poliuretano, retardantes de chama, revestimentos anticorrosivos.*

Vegetable Polyols: Versatile Raw Material for Polymer Preparation

Abstract: Polyols derived from vegetable oils have been prepared by simple synthetic routes such as transesterification and hydroxylation, and used in the preparation of polyurethanes, epoxy resins and alkyd resins. Recently, it has been investigated the utilization of phosphorylated polyols, derived from vegetable oils, in the formulation of rigid polyurethane (PU) foams and their property as flame-retardants and anticorrosive coatings. In order to obtain the phosphorylated polyols, soybean oil was reacted with phosphoric acid and used in the preparation of polyurethane foams and also polyurethane coatings. The results demonstrated that phosphorylated polyols present flame-retardancy potential as good as the commercial ones and also anticorrosive properties and have great potential for others PU's applications.

Keywords: *Vegetable Polyols, polyurethane foams, retardant flames, anticorrosive coatings.*

Introduction

The preparation of polymers from renewable sources is of major economical and scientific importance. Vegetable oils are mostly composed of triacylglycerides which present characteristics that can be utilized in the production of polymeric materials, as epoxy resins, alkyd resins and polyurethanes [1-3].

Reactions of polyisocyanates with polyols originate polyurethanes (PUs) [4], which are polymers with high content of cross-linked bonds and also possess particular characteristics suitable for many applications [5].

Hydroxylated vegetable oils, whether synthetic or natural ones (castor oil), have been used for the preparation of polyurethanes through the reaction of hydroxyl groups with isocyanates [6]. Castor oil is made up of 87-90% ricinoleic acid which has a secondary hydroxyl at the 12-position of the carbon chain. Using a mixture of castor oil and glycerin not only increase the number of hydroxyl groups but also the presence of primary hydroxyls (originated from glycerin) favoring the preparation of rigid PU foams with good physical-mechanical properties [7].

Veronese and collaborators [8] performed structural modifications in both castor oil and soybean oil so that they could be used in the preparation of rigid PU foams. Soybean polyol was obtained by hydroxylation reaction of soybean oil with formic acid and hydrogen peroxide and subsequent transesterification with a polyfunctional alcohol in order to increase OH functionality.

Castor oil was transesterified with triethanolamine or glycerin in 1:3 (oil:alcohol) molar ratio. The mechanical properties of foams prepared with modified vegetable polyols showed similar properties to those prepared from commercial polyols, presenting potential application in the preparation of rigid PU foams, since they were obtained from a renewable source.

One of the disadvantages of using PU foams is their high flammability and flame-retardant additives are normally added in their formulation to attenuate their flammability. Flame-retardants diminish the risk of fire by decreasing the combustion rate and flame propagation in the presence of fire [5].

Guo and collaborators [9] carried out ring-opening hydrolysis reactions of epoxydized soybean oil in the presence of phosphoric acid and water. They synthesize soybean polyols with different hydroxyl values and different functionalities of phosphate esters (mono, di and tri esters) by controlling the type and quantity of polar solvent and the percentage of phosphoric acid utilized in the synthesis.

In this work, it has been investigated the utilization of phosphorylated polyols, derived from vegetable oils, in the formulation of polyurethane foams and their property as flame-retardants for foams and anticorrosive coatings.

Experimental

Phosphorylated polyols were used in different proportions with other polyols, such as castor oil, glycerin and glycol polyesters. In order to obtain the phosphorylated polyols, epoxydized vegetable oil was reacted with phosphoric acid. The obtained polyols were characterized by infrared spectroscopy (IR), nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), hydroxyl index (OH), acid value (AV), and inductively coupled plasma optical emission spectrometry (ICP-OES). The polyurethane foams were prepared using a NCO/OH molar ratio 1.2:1 and poured into a box using pentane as blowing agent and polymeric diphenylmethane diisocyanate (MDI). They were characterized by means of apparent density, scanning electron microscopy (SEM), flammability test and simultaneous thermal analysis coupled with Fourier transform infrared spectrometry (SDT-FTIR). The polyurethane coatings were prepared by reacting the polyols with (toluene diisocyanate) TDI with different OH/NCO proportions (2.0; 1.5 and 1.0) on steel SE 1020 plates and left 48 hours to complete the reaction. Subsequently, the plates were subjected to corrosion tests, being submerged in a solution of NaCl in the concentration of 3.5% wt, simulating the conditions of seawater. Electrochemical impedance measurements were performed to evaluate the resistance and capacitance of the film throughout the period of immersion.

Results and Discussion

Phosphorylated polyols obtained in this work (ESOPN1 and -PN2) constitute a mixture of mono, di and phosphorylated triglycerides and, in minor proportion, products not containing phosphorus and polyethers, derived from polymerization reactions of epoxide ring-opening and containing 1.32 and 2.55 % wt of phosphorus, respectively.

PU flammability was evaluated by means of oxygen index (OI). In order to verify the potentiality of the flame-retardant effect of phosphorylated polyols, commercial phosphorylated flame-retardants TEP and FYROL-HF4 were used to prepare PUs. The results of this test are presented on Table 1. It is possible to observe that: (1) when the phosphorylated polyols were used as flame-retardants in the formulation of PUs, OI values were higher than that of PU1; (2) in PUs 2 to 5, where the content of phosphorus contained in the total PU formulation was about 0.4%, the PUs that contained the phosphorylated polyol (PU2 and PU3) presented OI results similar to and/or

better than those of PUs that contained commercial flame-retardants (PU4 and PU5); (3) in PUs 6 to 9, with approximately 0.8% phosphorus, this behavior was also observed, that is, PUs with phosphorylated polyols presented OI values similar to and/or even better than PUs in which were used commercial flame-retardants and (4) OI value increased with the increasing phosphorus content used in the PU when compared with PUs in which polyol-PN2 was utilized.

Table 1. Characterization of PU's.

| PU | Polyol (% weight) | | | P cont. (%) | O ₂ index (standard deviation) (% O ₂) |
|------|--------------------------|--------|----------------|-------------------|--|
| | Phosphorylated polyol | CO | Voranol GLY | | |
| PU1 | - | - 100 | - | - | 18.7 (0.1) |
| PU2 | ESOPN1 (75) | - 25 | - | 0.41 | 20.1 (0.1) |
| PU3 | ESOPN1 (80) | 1 5 | 5 | 0.42 | 20.5 (0.2) |
| PU4 | TEP* | - 100 | - | 0.42 | 20.1 (0.2) |
| PU5 | FYROL-HF4* | - 100 | - | 0.43 | 19.6 (0.2) |
| PU6 | ESOPN2(100) | - - | - | 0.86 | 21.8 (0.2) |
| PU7 | ESOPN2 (90) | - 10 | - | 0.77 | 21.3 (0.2) |
| PU8 | TEP* | - 100 | - | 0.82 | 21.3 (0.2) |
| PU9 | FYROL-HF4* | - 100 | - | 0.83 | 20.8 (0.2) |
| PU10 | ESOPN2 (75) | - 25 | - | 0.66 | 21.2 (0.2) |
| PU11 | ESOPN2 (60) | - 40 | - | 0.35 | 20.2 (0.2) |
| PU12 | ESOPN2 (25) | - 75 | - | 0.22 | 19.4 (0.,2) |

* Commercial flame-retardants.

SE 1020 steel specimens coated with PU's containing a relationship $[OH]/[NCO] = 2.0$ and immersed in 3.5% NaCl solution presented high values of capacitance and low values for the film resistance determined by Electrochemical Impedance spectroscopy. The results are due to a higher hydrophilicity of the coatings, damaging the stabilization of protective layer on the metal surface. Moreover a lower crosslinking resulted in a porous or poorly bonded film and, consequently, in a little effective protection.

Lower capacitance, larger values of film resistance and less negative corrosion potentials were obtained for phosphorylated resins with a ratio $[OH]/[NCO] = 1.0$; evidencing a greater efficiency of the protection afforded by these.

Conclusions

Phosphorylated polyols obtained from renewable sources present flame-retardancy and also anticorrosive properties and have great potential for PU's applications.

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