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Istraživanja mogućnosti uporabe uzgojina u proizvodnji plastičnih dijelova na *Kansas Polymer Research Center*

Jedan od najsnažnijih trendova u proizvodnji plastičnih tvorevina je svakako uporaba uzgojina, proizvoda iz tla ili iz obnovljivih izvora, za njihovo pravljenje. U tome je vrlo uspješan Kansas Polymer Research Center koji djeluje u okviru Pittsburg State University u SAD. Posebno se to odnosi na područje poliuretana. Odluka da se prikažu rezultati tog centra temelji se na činjenici da je osnivač Centra dugogodišnji suradnik časopisa Polimeri, prof. Zoran S. Petrović, važan član Centra je i te još jedan suradnik u časopisu, dr. sc. Ivan Javni.

Uredništvo

Bio-environmental Research at Kansas Polymer Research Center

Prepared by: Zoran S. PETROVIC and Ivan JAVNI

Introduction

Kansas Polymer Research Center (KPRC) is a Kansas Technology Enterprise Corporation (KTEC) Center of Excellence, involved primarily in the development of materials from renewable resources. *KPRC* was started by Zoran Petrovic in 1994. Originally, it was a one-man operation, located in a converted student dormitory and without laboratories and equipment. *Pittsburg State University (PSU)* is a non-PhD granting school offering MSc as the highest degree. However, it is one of the few undergraduate universities in the USA with a strong accredited plastics technology program. The students have an opportunity to work on large machines for injection molding, extrusion, thermoforming, compression molding and blow molding as well as on machines for fabrication of composites. Processing machines are frequently donated by manufacturers and after a time they are replaced with newer models. Therefore, students are provided an introduction to the latest technology in plastics processing. *KPRC,* on the other hand, is purely a research institution which complements practical work at the plastics technology program.

Development of *KPRC*

The first *KPRC* client was *Titleist- FootJoy,* a leading manufacturer of golf equipment. That cooperation was very fruitful resulting in six US patents. Dr. Ivan Javni contributed greatly toward several new developments on this project. Dr. I. Javni, formerly from *Soda-So,* Tuzla and Zagreb, joined the *KPRC* in 1995. The January 1998 issue of *Golf Digest* featured two of our gels used in golf shoes as the most advanced developments in golf equipment the previous year. One was a reversible, responsive gel, a liquid at room temperature which takes the shape of a foot and gels upon reaching body temperature. When the foot is removed, the gel goes back to a liquid state. The other gel was a light, soft material consisting 90% of mineral oil, used in shoes as midsole. The real breakthrough in research came after the *United Soybean Board (USB)* decided to fund our work on polyols for polyurethanes based on soybean oil. This relationship has been maintained today and it has been most helpful in securing funding for bio-based polyols.

Other projects have involved the aircraft industry. Since Wichita, Kansas is a world center of aviation industry (*Boeing, Hawker-Beechcraft, Cessna, Learjet, Raytheon, Airbus* etc) the *KPRC* has also been involved in projects on composites and nanocomposites.

Over time, the volume of work has grown and we have increased the space, acquired crucial equipment, installed several laboratories and hired new researchers. New projects came from the *US Department of*

Agriculture (USDA) and an especially large project was obtained from the *US Department of Energy (DOE)*. Our initial partner on the *DOE* project was *BF Goodrich,* which spun the polymer business into a new company - *Noveon.* Since *Noveon* could not commercialize our development we partnered with *Cargill* Inc., one of the world's largest private companies. *Cargill* is today making a family of polyols under the trade name *BiOH*® licensed by *KPRC*. In 2007, *Cargill* and *KPRC* received the *Presidential Green Chemistry Challenge Award* (Figure 1) for commercialization and development of soy-based polyols for flexible and rigid polyurethane foams. This year, the *American Oil Chemical Society* awarded three researchers of *KPRC* with the *Glycerin Innovation Award* for the development of a family of polyols based on glycerin resulting from the bio-diesel production. Great impetus to *KPRC* research came after one of the world leading polyurethane chemists, Mihail Ionescu from Romania, joined the institute five years ago. His book on polyols was published by *RAPRA* in 2005.[1]

FIGURE 1 – *Cargill* and *KPRC* scientists at the *Presidential Green Chemistry Challenge Award* (Petrović, first on the left and Javni fourth from the right)

Today, the *KPRC* has grown to 11 researchers and a variable number of students. The group is quite international but most of the researchers are from former Yugoslavia. The *KPRC* enjoys world recognition as one of the leaders in vegetable oil-based polyurethanes. *KPRC* operates almost as a private company since about 80% of funding is provided from industry research and government scientific projects. *KPRC* is a holder of 12 US patents and it has over 100 invention disclosures, some of which will be converted to patents. Two years ago, the *KPRC* moved to a newly constructed building designed specifically for its research and is the best equipped polymer laboratory in this part of the country (Figure 2).

Vegetable oil-based polyurethanes

Vegetable oils are an excellent substrate for chemical transformation. The points of chemical attacks are double bonds, ester bonds and allylic hydrogen. The review of the polyols and polyurethanes from vegetable oils was published recently.[2] One way of creating polyols is to epoxidize oil and ring open with alcohols, acids or water. The reaction is shown in Figure 3.

FIGURE 2 - ***Kansas Polymer Research Center*** with national flags of researchers

An elegant way of direct conversion of oils to polyols is hydroformylation. In this procedure double bonds are reacted with carbon monoxide and hydrogen to form aldehydes which are then reduced to hydroxyls by hydrogenation (Figure 4)

The beauty of this reaction is that all the components end up in the product. The polyol has also an extra carbon per OH group. These polyols at the same hydroxyl number give softer polyurethanes than those by epoxidation.

Transesterification may involve glycerolysis as in preparation of alkyds. The results are a mixture of mono- and diglycerides. These are inexpensive but low quality polyols. They may be useful for the preparation of urethane oils which dry by oxidation and are applied as coatings.

The first polyols on the market were made by oxidation of oils (blown oils). In this process, oxygen attacks the allylic position to double bonds forming a range of oxidation products ranging from peroxides, hydroxyls, ketones and acids. The problem in these polyols is a very strong smell, low reactivity and generally poor properties of polyurethanes.

Vegetable oils can be polymerized by heating at high temperature, cca 330 °C. That causes migration of double bonds and helps Diels-Alder addition. Under these drastic conditions the oil may lose 30% of its weight due to degradation, but the polymeric oil after purification has a light color. We have developed a low temperature process of cationic polymerization of oils with no mass loss.[3]

Ozonolysis is a very precise method for cutting double bonds. Reducing ozonides leads to polyols and a range of monols, while oxidation leads to polyacids and monoacids. Polyurethanes obtained from ozonolysis polyols display excellent properties useful in coatings and adhesives.[4] Ozonolysis of oils is a useful process for the preparation of hydroxy acids, monomers for esterification.[5]

Novel thermoplastic polyurethanes (TPU) were developed from hydroxy fatty acids. One of such acids is ricinoleic, a main component of castor oil. TPUs are segmented polyurethanes with alternating hard and soft segments. We prepared polyester diols of different molecular weights and reacted with diisocyanate and butane diol to obtain TPUs with different soft segment concentration.[6] Such polyurethanes are potentially biodegradable. Their potential use is in sport shoe soles, medical tubing, adhesive films etc.

Oils are naturally branched molecules and by linking them, one can prepare hyperbranched structures useful in coatings or foams. We have prepared hyperbranched polyols as substituents for copolymer polyols.[7]

Very interesting epoxy resins are also obtained from vegetable oils. They are useful flexibilizers for reducing brittleness of standard epoxy resins. Internal epoxy groups like those in epoxidized oils cannot be cured with amines but they react with anhydrides and acids.[8] We have used both urethanes and epoxy resins from vegetable oils to obtain polymer concrete, fiber-reinforced composites and nano-composites. The application of new resins is limitless.

An interesting work was conducted on the non-isocyanate route to polyurethanes. It involves formation of polycarbonate oils from epoxidized oils and their reaction with amines. The results are some hydrophilic urethanes.[9]

In order to understand the effect of structure on properties of oil-based products, it is necessary to carry out the work with model compounds.[10] It has been shown that oils as well as polyols from vegetable oils have very heterogeneous structures. Such heterogeneity is not detrimental in highly crosslinked systems but it has negative effects in elastomers.[11]

This short presentation shows a cross section of some of the works performed at the Kansas Polymer Research Center. Most of the work for industrial partners is confidential and we are unable to discuss it here.

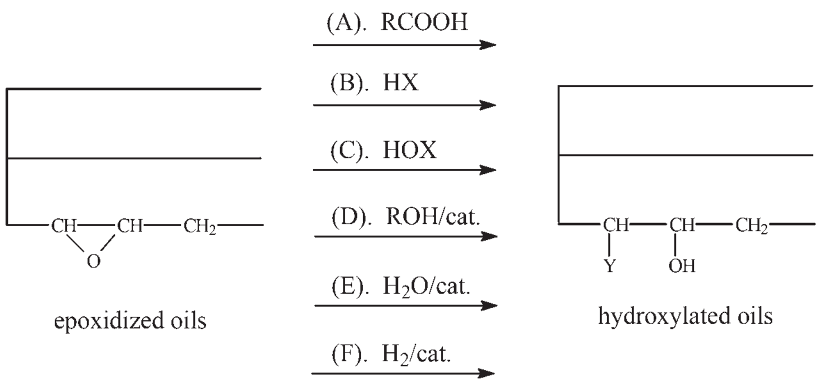

FIGURE 3 – Hydroxylation reactions of epoxidized oil, where Y = -O-C(O)R for (A); X for (B); -OX for (C); -OR for (D); -OH for (E) and -H for (F), and X = Cl or Br.

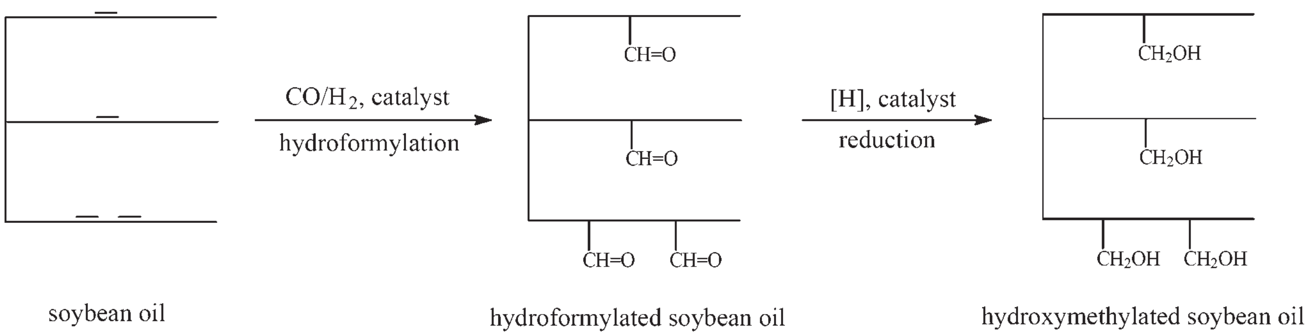

FIGURE 4 - Hydroformylation of soybean oil.

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Vijesti

Priredio: Tvrtko VUKUŠIĆ

Novi koncentrat za zaštitu kabelskih plašteva od glodavaca

PolyOne je razvio novi, univerzalni koncentrat *masterbatch* (MB) za zaštitu kabelskih plašteva (npr. PVC, PE) od ugriza glodavaca.

ANTIRODENT MASTERBATCH 87477 NP EVA, na bazi kopolimera EVAC, fiziološki je i ekološki prihvatljiv, ne pokazuje znakove migracije u vodu, ne otapa se u vodi te je postojan u tlu i kemijski inertan. Sadržava 5 % nehigroskopne aktivne tvari (zaštićeni naziv *RODREPEL*), koja u koncentratu ima višestruko djelovanje. Kod glodavaca (miševi, zečevi, štakori) izaziva osjećaj odbojnosti zbog gorkog okusa, djeluje nagrizajuće na sluznicu te ulijeva strah zbog oslobađanja neugodnog mirisa koji je istovjetan mirisu urina nekih grabežljivaca (tigrov urin).

Dodaje se u koncentraciji 1 – 5 % u kabelske materijale, a istraživanja provedena u *PolyOne* pokazuju da se dodatkom ovoga koncentrata u kabelske materijale (npr. PVC, PE) broj ugriza na kabelima smanjio u istom razdoblju (180 dana) za 95 % u odnosu na iste materijale u kojima nije bilo ovog dodatka.

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INHOL BV – umreživе kabelske smjese za solarne kabele

INHOL BV iz Nizozemske razvio je dvije nove beshalogene, zaštićene od gorenja i dimljenja umreživе kabelske smjese - *POX 21169-1 PV SOLAR* (za izolaciju) te *POX 21169-2-PV SOLAR* (za plašteve), koje se upotrebljavaju za izradu solarnih kabela koji služe za prijenos energije, dobivene iz sunčeve energije, s pomoću fotovoltaika.

Kabeli izrađeni od ovih materijala pokazuju vrlo dobra mehanička i električna svojstva, postojanost na UV zračenje, ozon i vodu. Kabeli se upotrebljavaju u radnom području od -40 do +120 °C, a certificirani su u *TŰV* laboratoriju, prema *TŰV 2Pfg 1169/08/2007.*

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