Cytec Industries Inc. 2012 Green Chemistry Challenge Award Nomination

Saturated polyester – phenolic resin systems for Bisphenol A-free interior can coatings for food packaging

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Milestones in Last 5 Years

The first commercial sales of DUROFTAL® PE 6607/60BGMP in the US occurred in 2008. The technology is protected by world-wide patent applications including the USA. First full scale production of the phenolic part of the system was run in Willow Island, WV in 2010. First commercial sales were done to US customers in 2011.

Focus Area: Design of greener chemicals

The technology presented in this paper fits into the focus area of the design of greener chemicals, because the new products are used as ***bisphenol A-free*** binders for interior coatings of 2-piece and 3-piece food packaging cans. The ***new products do not use bisphenol A (BPA) or bisphenol A diglycidylether (BADGE) as raw materials.*** Migration of BPA from liners of food cans is one of the major sources for consumer exposure to this chemical. The new technology is based on FDA 21 CFR §175.300 compliant polyester chemistry. Thus, the exposure of consumers to the potential endocrine disruptor BPA can be eliminated with the use of this technology.
This nomination does not meet the criteria for the small business or academia categories.

Collaboration

The new technology was developed at the Cytec R&D Centers for Liquid Coating Resins in Graz, Austria, and Stamford CT, USA. Scale up of the polyester resin manufacturing process was conducted at the Cytec site Werndorf, Austria. The phenolic resin was scaled up in Wiesbaden, Germany, and in Willow Island, WV.

Abstract

Recent studies revealed potential endocrine disrupting effects of bisphenol A (BPA) in animals. However, BPA is a key raw material for binders used in interior coatings for food cans. Thus, food cans are an important source for consumer exposure to BPA; therefore, the food industry is demanding BPA free coatings. Although a final regulatory decision about the further usage of BPA has not been made yet, the use of this monomer in interior can coating systems has become a matter of public interest and scientific discussion.

A new generation of saturated polyester resins has been developed for use as the main binder in conjunction with phenolic resins. This new resin system can be used in interior can coatings for the metal packaging goods industry. Coating systems based on these resins exhibit performance comparable to conventional high molecular epoxy systems, with the additional advantage of being completely free of residual BPA. The saturated polyester resin is compliant with FDA 21 CFR §175.300 and it is more flexible than conventional systems based on high molecular epoxy resins. Although the polyester resin is compatible with most existing cross linkers (predominantly phenolic resins and amino resins), for this special application a new tailor-made phenolic resin was designed so that the system can be completely BPA-free and match the performance of existing systems. Computer modeling indicates that the polyester resin does not exhibit estrogenic properties seen with BPA.

Introduction

BPA is used primarily to manufacture polycarbonate plastics and epoxy resins, both of which end up in a lot of different consumer products. Products made of polycarbonates range from baby bottles to bicycle helmets, from eye glass lenses to medical devices. Epoxy resins, commonly used as binders in protective coatings, protect the safety and integrity of canned foods and beverages when used in interior metal can coatings.

In recent years, studies have revealed that BPA is suspected to be an endocrine disruptor, which can mimic the body's own hormones and may lead to negative health effects (1)(2)(3)(4). In 2009, the Endocrine Society released a scientific statement expressing concern over current human exposure to BPA (5).

BPA has been known to leach from the coating lining of canned foods (6) and to a lesser degree, from polycarbonate plastics. A recent Health Canada study found that the majority of canned soft drinks in their test had low, but measurable levels of BPA (7). Nevertheless, there are also studies that disprove negative effects of BPA on human health, and the scientific debate is still open. Nevertheless, consumer groups recommend that people wishing to lower their exposure to BPA should avoid canned food and drinks, unless the package labeling indicates it is BPA free (8).

Development of BPA free coatings for food containers

Although most current epoxy based coating systems show low BPA migration values which are far below the limits stated in various food laws, the major food & beverage companies demand BPA free systems for food can liners. Cytec is committed to promote the development of products that reduce safety, health and environmental risks (9). Consequently, this leads to Cytec's effort aiming to replace epoxy resins by other suitable polymer backbones for food packaging coatings, especially interior can coatings. In Table 1, the main performance requirements of interior can coatings for metal cans are described (1 is most important, 5 is least important).

Table 1: Specific film properties required for interior can liners

Coating properties	Importance
Compliance to food laws	1
Resistance against retorting	1
Flexibility / Deep-draw ability	2
Adhesion to metal (aluminum, tinplate, tin-free steel)	2
Reactivity (cycle 10 min / 200 °C)	2
Reactivity (cycle 40 s / 240 °C PMT)	2
Scratch resistance	3

Compliance to various food regulations is an indispensable pre-requisite for any can liner system. Retort resistance is required, because all food cans are filled and subsequently sterilized at high temperature. During the sterilization, acidic foodstuffs can attack the liner and remove it from the metal surface of the can, resulting in metal corrosion and spoilage of the food. This process can only be avoided, if can liners show sufficient adhesion to the metal surface and a high degree of cross-linking. A high degree of cross-linking is a direct consequence of the reactivity of the can coating system at the temperature applied for curing. Highly reactive coating resins yield highly cross-linked can liners which in term provide for high retort resistance.

The coatings on the interior and exterior side of the can are applied and cured on a long band of sheet metal (“coil”) which then undergoes a multi-step process including cutting and molding operations, e.g. deep-drawing, crimping, etc., before the can is finally ready for filling. Therefore, can liners must be flexible enough to avoid cracks and removal from the metal during molding.

Technical Approach

Specially designed polyester resins seemed to be the most feasible approach. Other technologies like alkyd or acrylic resins, polyvinyl butyral, polyurethanes, cyclic rubber etc. are either lacking the balance between flexibility and resistance or do not comply with US and European food laws.

Polyester resins are generally prepared from oligo-functional carboxylic acids, and oligo-functional alcohols or phenols in a condensation process (esterification) under formation of water. Polyesters that are predominantly made of flexible monomers, such as linear aliphatic alcohols and linear aliphatic acids, are usually also flexible. Polyesters based on aromatic or cycloaliphatic or highly branched aliphatic moieties are usually hard and brittle. Neither the flexible nor the hard polyesters provide the right balance of impact resistance and adhesion that is required for coating films on metal substrates subjected to molding.

Our investigations revealed that combinations of “hard” and “soft” monomers in at least one class (acid-functional or hydroxyl-functional), yield polyesters that provide good elasticity and impact resistance as well as good adhesion and hardness against abrasion and indentation. In a preferred embodiment both, the acid component and the hydroxy component comprise each of at least one hard and at least one soft compound.

Examples of "hard" dihydroxy-functional compounds are 1,2-propylene glycol, 1,2-dihydroxy butane, neopentyl glycol, 2,2,4-trimethylpentane diol-1,3, and 1,2-dihydroxycyclohexane. Hard tri- or oligohydroxy compounds are e. g. pentaerythritol, trimethylol ethane, trimethylol propane, and trimethylol butane. Examples of “soft” dihydroxy-functional compounds are 1,2-ethandiol, 1,6-hexandiol.

Examples of "hard" diacid compounds are maleic acid, fumaric acid, itaconic, citraconic and mesaconic acids, 2,3-dimethylsuccinic acid, tetra- and hexahydrophthalic acid and isomers of these. Hard tri-acid compounds are monocyclic or oligocyclic aliphatic acids, such as hexahydro-trimesic acid, and also aromatic acids such as trimellithic acid and trimesic acid.
Examples of “soft” diacid compounds are e.g. adipic acid, glutaric acid, succinic acid, sebacinic acid, and dimer fatty acids.

The performance characteristics required for can coating have been achieved by the synthesis of the polyester resin with a predominantly linear structure and a relatively low molar mass (Mw approx. 10,000). All monomers comply with food contact laws and are listed in the respective positive lists of raw materials. In order to design an optimal resin, several structure-properties needed to be considered:

Very high hydroxyl values of more than 300 mg/g and acid values between 25 mg/g and 35 mg/g (on solid resin) in combination with a hard (durable) phenolic resin result in a densely cross-linked but still flexible network and good retort resistance. The relatively low molar mass (compared to other polyester resins) and the right balance of flexibility and hardness in the polymer backbone account for good deep-draw ability.

It is assumed that an interpenetrating network is formed at curing, where the soft-hard polyester backbone stands for the matrix and the hard durable phenolic resin for the framework. This special structure in the cured film dissipates the mechanical stress, generated during the molding process of the coated metal. So, very flexible coatings, free of porosity are formed by this dual behavior of the internal structure.

Glycols containing only primary hydroxyl groups were used as raw materials in order to maintain high reactivity during the coating cure and to allow complete conversion to the resin during the manufacture. The polyester resin is supplied in butylglycol/methoxypropanol to eliminate the use of high boiling aromatic hydrocarbons like solvent naphtha.

Primarily, this polyester resin is designed to be used in solvent borne applications. However, due to its acid value between 25 mg/g and 35 mg/g, it is also soluble in water, after neutralization with an appropriate amine or with ammonia. Waterborne coatings capability provides a significant advantage in delivering low VOC, eco-friendly coatings.

Specially developed phenolic resins are used as cross linkers for this polyester resin in metal-packaging interior coating formulations. The phenolic resin presented in this paper displays a very high reactivity combined with excellent chemical (retort) resistance. This resin does not contain “critical” monomers like BPA, nonylphenol or butylphenol, either, but consists solely of cresol monomers. It complies with FDA 21 CFR § 175.300 and is suitable for food contact according to the European regulation.

The retort resistance of an interior can coating system based on DUROFTAL PE 6607/60BGMP and PHENODUR® PR 516/60B was tested against standard food simulants like 2 % lactic acid, 3 % citric acid, 3 % sodium chloride and 2 % sodium chloride plus 2 % acetic acid (see Figure 1). As the resistance of the formulation with the polyester resin is comparable to the epoxy resin benchmark in the test with 3 % sodium chloride, 3 % citric acid and the mixture of 2 % sodium chloride plus 2 % acetic acid, the polyester coating is even more resistant against 2 % lactic acid with nearly 100 % un-affected surface area.

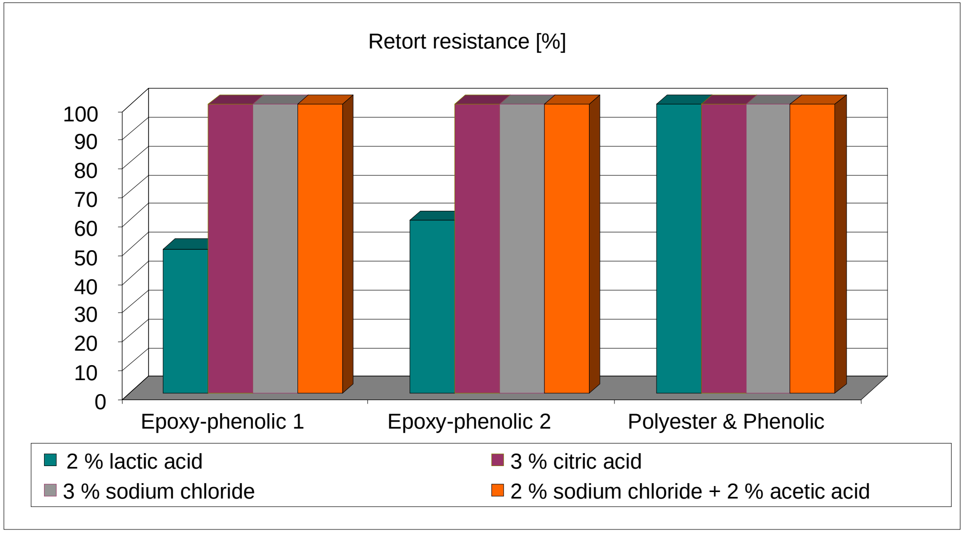

Figure 1: Retort resistance of DUROFTAL PE 6607/60BGMP and PHENODUR PR 516/60B, curing cycle 12 min / 200 °C

Toxicity of DUROFTAL PE 6607/60BGMP

The toxicity of DUROFTAL PE 6607/60BGMP is based on the toxicity of its components, which include a high molar mass polymer and several solvents. The toxicity, therefore, is exclusively based on these solvents and can be summarized as follows: The estimated acute oral (rat) LD50, acute dermal (rabbit) LD50 and 4-hour inhalation (rat) LC50 values for this product are 1260 mg/kg, 940 mg/kg and 5.8 mg/L, respectively. Direct contact with this material may cause moderate eye and skin irritation. Overexposure to vapors may cause irritation of the respiratory tract and eyes and central nervous system effects.

The cured coating based on DUROFTAL PE 6607/60BGMP does not contain any significant levels of free solvent if properly cured (dried) as this is a requirement of compliance with 21 CFR § 175.300. Therefore, the neat DUROFTAL PE 6607/60BGMP polymer would not exhibit the toxic effects described above due to the removal of solvent from the polymer. This is a high molar mass saturated polyester polymer with a minimal oligomeric fraction below 500 Daltons and, as such, should not be absorbed to a significant degree. Therefore, the DUROFTAL PE 6607/60BGMP polymer, when present in the cured coating, is not expected to be toxic by ingestion, inhalation or absorption.

In addition, computer modeling (cat-SAR models: ESCREEN v 2009 and NCTRER v 2009), has indicated that the DUROFTAL PE 6607/60BGMP polymer without any structural repeating units (e.g., the lowest molar mass structure) is not expected to have endocrine disruption effects. The results of this modeling are listed below:

<u>ESCREEN MCF-7 cell proliferation Assay</u>: Estimated NOT to stimulate the proliferation of MCF-7 cells.

<u>Estrogen receptor ligand model (NCTRER)</u>: Estimated NOT to be ligand for the estrogen receptor.

Description of Cat-SAR Models

Below is a brief summary of the cat-SAR models used in the analysis.

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- ESCREEN, MCF-7 Relative Proliferate Effect (RPE**).** The ESCREEN relative proliferative effect (RPE) model for estrogen-like activity is based in s sets of 122 chemicals tested and published by Soto and colleagues (10-11). The RPE learning set consisted of 73 active and 49 inactive chemicals. Cat-SAR models based on these data have been published (12).
- FDA National Center for Toxicological Research Estrogen Receptor Binding (NCTER ER). This model is based on estrogen receptor binding data developed by the National Center for Toxicological Research (see [13, 14]). The data for this model was obtained from the EPA's Distributed Structure-Searchable Toxicity (DSSTox) Public Database Network (15) and consisted of 323 compounds, of which 139 are designated as ligands and 93 as non-ligands.

Ecotoxicity of Duroftal PE 6607/60BGMP

The ecotoxicity of DUROFTAL PE 6607/60BGMP is based on an evaluation of its components. Based on ecotoxicity data, biodegradation and EPIWIN modeling for one or more of the product's components, DUROFTAL PE 6607/60BGMP is not expected to exhibit toxicity in the environment and is appropriately classified as "not dangerous for the environment".

Benefits of BPA-free can coatings technology:

- The polyester polymer in DUROFTAL PE 6607/60BGMP has been modeled for human toxicity and was not found to be an endocrine disruptor as reported for BPA.
- Commercial sales started in 2011. As a result, about 10 t of BPA were replaced by DUROFTAL PE 6607/60BGMP in the US in 2011.
- The BPA free can coating system has the potential to replace 18,000 t/a of BPA in North America or 55,000 t/a of BPA globally.
- The molar masses of polyester resins are usually lower when compared to standard high molecular epoxy resins type # 7 and # 9, allowing for higher solids content of the coatings with less solvent needed for dilution. Thus, there is a potential reduction in VOC of 22,000 t/a in North America and 68,000 t/a globally.
- This product has the potential to replace BPA based linings on the interior of infant formula packaging.
- Polyester resins are a common technology for exterior lacquers (pigmented basecoats and overprint varnishes) in can coating applications. Thus, the new system can be used for both, interior and exterior can coatings. Food contact compliance is becoming more of a requirement for the exterior layers of food packaging cans in order to exclude contamination of the interior surface with non food contact compliant materials.
- Duroftal PE 6607/60BGMP is water dilutable after neutralization with suitable amines and can be used to formulate water borne lacquers.
- BPA-free formulas often do show a better substrate wetting and leveling, respectively lower porosity.

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