NEW THERMOPLASTIC
ADHESIVE AND BARRIER RESINS

Terry Glass, Ha Pham, Marie Winkler*

The Dow Chemical Company

2301 Brazosport Blvd.

Freeport, Texas 77541

Abstract

BLOX™ Adhesive and Barrier Resins are the first commercialized polymers from a new family of thermoplastics, namely polyhydroxyaminoethers (PHAE). These resins offer a unique property set, including excellent adhesion to a variety of substrates, high gas barrier, superior clarity, and good mechanical strength and toughness. In addition, these resins are amorphous and can be easily processed using conventional thermoplastic processing techniques. Some commercial applications to-date utilizing PHAE resins include barrier packaging, starch-based foam packaging, and powder coatings.
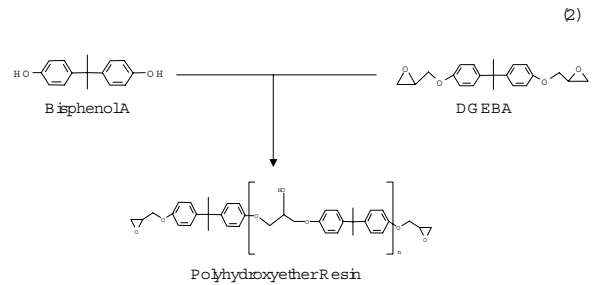
EPOXY-BASED THERMOPLASTICS

Phenoxy Type Products

Epoxy-based thermoplastic resins are not new materials, with polyhydroxyether polymers (PKHH™) (1) introduced commercially over thirty years ago. These phenoxy resins are produced in a batch process involving the reaction of

Advanced Epoxy Resins

Taffy Process

Depending on Bisphenol A / Epichlorohydrin ratio, different chain lengths are obtained. 'n' may vary from 0 to 60 in a normal Gaussian Distribution.

epichlorohydrin and bisphenol A in desired stoichiometric ratios to achieve high molecular weights. These resins are prepared in solvents with salt removal and solvent stripping/recovery, a costly manufacturing route which

contributes to their relatively high selling price (typically between $3.00 - $5.00/lb), thus relegating their use to low volume applications such as resin modifiers and specialty coatings.
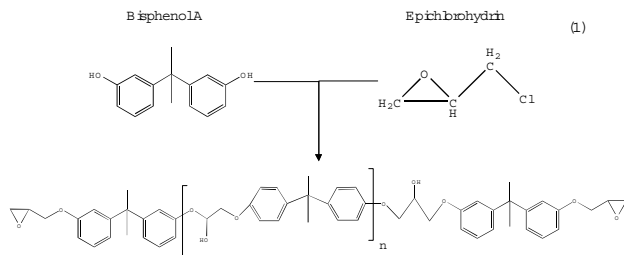
Advanced Epoxy Resins

Polyhydroxyether Resin

"Fusion (or Advancement) Process
Depending on DGEBA/BisA ratio, different chain lengths are obtained.
'n" may vary from 0 to 60, BUT EVEN VALUES DOMINATE, because of build up of chain (even number of BisA units from Bisphenol A and DGEBA added in each step).
Example : n (Average) = 5, contains n=2,4,6,8,10, with majority 4 and 6.
Although n (average) may be the same as Taffy Process, distribution of n will be different.

This cost limitation for epoxy-based thermoplastics has been altered through the development of reactive extrusion (REX) technology. With this processing technique, a conventional liquid epoxy resin, such as diglycidyl ether of bisphenol A (DGEBA), can be advanced to a solid, high molecular weight resin in a neat solventless process referred to as a "Fusion Process" (2).

Resins made via the REX process are fully converted in a matter of minutes, significantly reducing manufacturing costs. Additional benefits include reduced lot-to-lot variations in molecular weight distribution, the flexibility to make small lots of varying molecular weights with minimal waste, and the ability to custom make resins with a variety of additives such as pigments and flow modifiers. Perhaps most importantly, REX also allows for cost effective manufacturing of a variety of epoxy-based chemistries with different molecular weights and properties.

*TO WHOM CORRESPONDENCE SHOULD BE ADDRESSED

BLOX – TRADEMARK OF THE DOW CHEMICAL COMPANY

PKHH – TRADEMARK OF INCHEM CORPORATION

Table 1 details the physical and chemical properties of extruder-made polyhydroxyether products to solution-made, commercially sold polyhydroxyether resins.

Table 1.

Comparative Polyhydroxyether Properties

Analysis	Solution Polymerization	Dow Extruder Resin
Mw	55492	53946
Mn	14237	14069
Mw/Mn	3.898	3.834
Hydrolyzable Chlorides (ppm)	233	618
Tensile Strength (psig)	10767	10995
HDT (°C), 264 psi	66.9	71.8
Notch Izod (ft-lb/in.)	0.97	1.00

The tensile strength, impact resistance, molecular weight, etc. are similar and should provide comparable performance in many applications.

PHAE Type Products

Of recent commercial interest are epoxy-based thermoplastics produced through the reaction of liquid epoxy resins and primary amines. This highly exothermic chemistry is ideally suited for REX, and the resultant polyhydroxyaminoether (PHAE) polymers exhibit intriguing performance characteristics. This new family of thermoplastics has a property envelope that includes excellent barrier to atmospheric gases, optical clarity, remarkable adhesion to a variety of substrates, notable melt strength and good mechanical behavior. A series of PHAE products have became items of commerce under the trade name BLOX Adhesive and BLOX Barrier Resins and is the basis for the following discussion.

Basics of PHAE Polymer Chemistry

The parent polyhydroxyaminoether (PHAE 1) of the PHAE family is manufactured by reactive extrusion (2) of DGEBA with ethanolamine as indicated in eq 3, a melt polymerization approach that allows stoichiometric control of product molecular weight. As emphasized in the introductory comments, PHAE 1 can be a genuinely high-polymeric thermoplastic; at stoichiometric balance, eq 3 yields a polymer with an absolute weight average molecular weight (Mw) of around 60,000 and a polydispersity (Mw/Mn) of about 3.5. This value is higher than the Mw/Mn= 2 expected for an ideal step-growth process (3) and indicates that some

branching accompanies the primarily linear chain growth of eq 3 by a mechanism discussed in detail elsewhere (4).

PHAE 1 is an almost colorless (YI = 2.0), transparent amorphous resin that undergoes a glass transition near 80°C. The material dissolves in highly polar solvents such as dimethylformamide but is basically unaffected by aliphatic or aromatic hydrocarbons; solvents of intermediate polarity, such as acetone, swell but do not dissolve the resin.

Because of its thermoplasticity, PHAE 1 can be conventionally processed by injection molding, cast film extrusion, blown film extrusion, thermoforming, extrusion foaming and blow molding. Coextrusion of the material with polyethylene terephthalate (PET) and various polyolefins (which require an adhesive layer, such as a maleated polypropylene) also is straightforward. Fabrication conditions for 1 is process dependent, and molecular weight of the materials can affect process parameters. In general, however, PHAE resins, including 1, are easily processed between 180° and 220°C. Higher temperature processing may require incorporation of one of several available proprietary stabilizer packages.

Mechanically, PHAE 1 is a moderately ductile, rather robust thermoplastic with sufficient integrity for disposable and many durable end uses. With a break stress of about 7000 psi (Table 2), injection-molded PHAE is stronger than comparably ductile, high-impact polystyrene (HIPS) or ABS (both of which show tensile elongations resembling that of
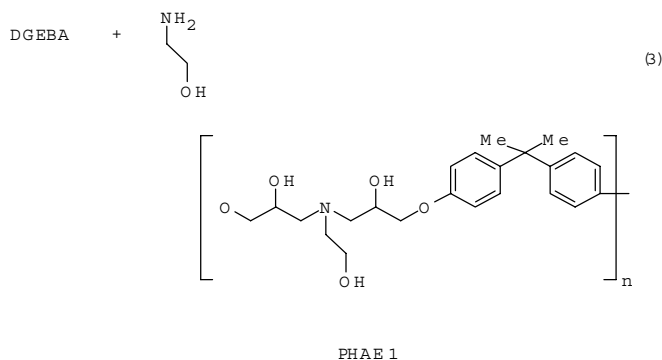
PHAE 1

PHAE 1) and similar to general purpose polystyrene, which is considerably more brittle than polymer 1. Table 2 indicates that the polyhydroxyaminoether is a rather stiff thermoplastic (its modulus is close to that of PET), yet has good practical toughness, demonstrated by the polymer's ductile rather than brittle failure in Dynatup experiments. These tests reveal penetration energies (86 ft-lb) for polymer 1 that are only slightly lower than values of about 100 ft-lb measured for injection-molded polycarbonate, a well-known engineering resin that combines rigidity and impact resistance. However, toughness in polymer 1 is sensitive to scratches and surface damage (the material is "notch sensitive"). The notched Izod impact energy for injection-molded PHAE is a respectable 2 –

3 ft-lb/in and comparable to those of widely-used ABS and HIPS

Table 2.

Mechanical properties of injection-molded polyhydroxy-aminoether 1

| Property	Performance
Physical Form	Pellets
Density	1.2 g/ml
Tg (amorphous)	78° C
Yield Strength	8300 psi
Break Strength	6900 psi
Elongation	46 %
Flexural Modulus	351,000 psi
Notched Izod Impact Energy	2 ft-lb/in
Dynatup Impact Energy	86 ft-lb (ductile failure)
Heat Distortion Under Load (HDUL)	70 °C (66 psi)

but much lower than the value of 17 ft-lb/in that is typical of polycarbonate. The heat distortion temperature (HDUL) of 1 (70°C) is slightly below its Tg. This low softening temperature makes polymer 1 ideal for its use in multilayer PET based containers, which are blow molded around 100°C but it is a disadvantage for many durable applications. Consequently, new PHAE with the potential for higher HDUL presently are under development.

A major impetus into polyhydroxyaminoethers was the likelihood that the pendant hydroxy groups that populate the backbones of these polymers would contribute to strong interchain hydrogen bonding, high intermolecular cohesive energy density, and ultimately good barrier to oxygen and other atmospheric gases (4, 5, 6, 7), making the materials attractive for protective packaging. As indicated at the outset, such is indeed the case. At 60% relative humidity and room temperature, films of polymer 1 exhibit an oxygen transmission rate (O_2TR) of 0.8 cc-mil/100 in^2-day-atm (O_2) (Barrier Units or BU; Table 3) and a carbon dioxide transmission rate (CO_2TR) of 3.9 BU (0% relative humidity). Thus, PHAE 1, has 4 - 5 times the oxygen and carbon dioxide barrier of the PET (O_2TR = 4 - 5 BU and CO_2TR = 25 - 30 BU) (8) commonly used in soft drink packaging. (To put these O_2TR values in perspective, most commercial thermoplastics are quite permeable with O_2TR of 50 to 500 BU). Truly high-barrier characteristics in the PHAE family can be achieved by copolymerizing ethanolamine with DGEBA and resorcinol-diglycidyl ether (RDGE) to yield polymers such as 2 - 5 in Table 3.

These amorphous thermoplastics, which have increased opportunity for interchain hydrogen bonding compared with polymer 1, exhibit O_2TR as low as 0.04 BU barrier performance. This is comparable to that of the ethylene vinyl alcohol

Table 3.

Oxygen transmission rates of RDGE modified polymers
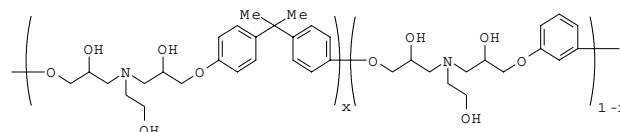
Structure No.	x	O_2TR *
2	1.0	0.80
3	0.75	0.38
4	0.7	0.20
5	0.5	0.04

*cc-mil/100 in^2-atm-day

copolymers (EVOH), barrier nylons (based on adipic acid and xylylene diamine) or polyvinylidene chloride resins currently used in rigid and flexible barrier packaging. Polymers 2 - 5 also are excellent barriers to carbon dioxide with CO_2TR of less than 2.5 BU. Values, which represent oxygen transmission rates (O_2TR) as cc-mil/100 in^2-day-atm (O_2) (expressed here as Barrier Units or BU) were determined according to ASTM method D 3985-81 for 3 - 5-mil films at 23 °C and 60% relative humidity.

In addition to their unusual barrier properties, PHAE strongly adhere to a variety of substrates, a probable consequence of the ability of pendant hydroxy functions on these macromolecules to undergo interfacial, polar interactions with other materials. For example, the lap shear strength of polymer 1, bonded at 180 °C to cold-rolled steel, is about 3500 psi. This behavior is consistent with that of two-part epoxy thermosets which can have lap shear strengths across the range of 1500 to 5000 psi (9). In addition, polymer 1 shows evidence for bonding to PET at temperatures well below the melting point of the polyester. Fracture energies or G_{Ic} (10), measured for the interface of 2 - 5 molded to PET at 220 °C, vary from 45 to 60 J/m^2; in contrast, high-barrier nylon shows virtually no adhesion to PET with G_{Ic} less than 10 J/m^2. On an absolute basis perhaps, these differences appear small, but in drop tests of blow-molded, multilayer PET bottles incorporating various barrier layers, those based on PHAE are ten times more resistant to delamination than are constructions containing EVOH or barrier nylon.

The adhesive properties of PHAE also manifest themselves in the behavior of the polymers filled with mineral and renewable fillers. In filled thermoplastics in which adhesion between the matrix polymer and the filler is poor, mechanical properties, particularly tensile stress, decrease with increased loading. Polyhydroxyaminoethers bond effectively with a

number of fillers and actually display increased strength when loaded with mica, talc, calcium carbonate, wood flour and even granular starch. As an example, break stress of compression-molded, 40-mil plaques of polymer 1 climbs from about 6300 psi unfilled to over 11,000 psi after the material is melt blended with 30% hardwood flour with a particle size of less than 125 μm. Tensile modulus increases from 415,000 psi to 813,000 psi have been measured in these specimens as well. In fact, tensile strengths as high 13,000 psi for polymer 1 filled with 20% mica or talc have been measured.

COMMERCIAL APPLICATIONS

Rigid Containers

Plastic PET beverage containers are a staple packaging medium for carbonated soft drinks and have been commercially available since the 1970s. Although an adequate barrier material, PET barrier properties are usually not sufficient for small containers (less than 20 ounce stored at room temperature), or for beverages whose flavor and shelf life are very sensitive to oxygen exposure, such as beer and juices. For these applications, multi-layer containers of PET and a high barrier polymer are currently under development. The most commercially advanced multi-layer containers contain either EVOH, MXD6 nylon, or polyethylene naphthalate (PEN). These resins all provide adequate shelf life for oxygen sensitive beverages. Significant differences center on pricing, processability, and adhesion to PET. Adhesion to PET is a significant advantage of PHAE, allowing for greater packaging design flexibility and superior resistance to delamination due to shipping and handling.

LOOSE FILL

In a totally unrelated packaging application, PHAE has found commercial value as a binder in environmentally friendly, starch-based foam packaging such as loose fill (i.e., packing "peanuts") and corrugated sheet. This epoxy-based thermoplastics exhibits excellent adhesion to the starch matrix, offers good ductility and resiliency to the foam product, allows for easy processability of the starch, enables a larger percentage of the inexpensive, renewable resource in the formulation, and improves overall economics over competing commercial formulations.

The excellent adhesive characteristics of PHAE are a probable consequence of the ability of the pendant hydroxy functions to undergo interfacial, polar interactions with materials such as metal, glass, other polar polymers, and cellulosics such as cotton, paper, and starch. In addition to excellent adhesion to starch, PHAE offers the rheological profile and thermal characteristics necessary for starch foam

extrusion. Not often thought of as an extrudable thermoplastic, starch can be melt processed with sufficient plasticizer, temperature, and shear conditions to denature the granules into a thermoplastic mass. Additional needs for foam extrusion include sufficient blowing agent and pressure drop across the die for adequate cell size and structure. Adding to this complexity is that water is used as both a cost effective plasticizer and blowing agent, which means the two roles cannot be independently controlled. A binder system, a necessity for final product resiliency and toughness, must therefore conform to the delicate balance of rheological and thermal history requirements of starch processing. And finally, a major attribute of PHAE/starch loose fill over other commercial formulations is the PHAE enables inexpensive native starch to be used in the formulation, and at higher levels, favorably impacting economics. In fact, the economics of PHAE technology allows for the potential of starch-based foam packaging to favorably compete against its polystyrene rival.

POWDER COATINGS

Another interesting commercial application for this new family of epoxy-based thermoplastics is in powder coatings, an area where thermoplastics struggle primarily because of inadequate adhesion to substrates such as metal, glass, and wood. PHAE has found a niche as an economically attractive replacement for high performance nylons (such as in automotive and display rack applications) and development continues in applications which require excellent mechanical durability, toughness, and superior adhesion.

Summary

Polyhydroxyether thermoplastics possess a unique property profile which includes excellent adhesion to a variety of substrates, mechanical stiffness and durability, optical clarity, and ease in thermal processing. A new type of epoxy-based plastic, PHAE, has recently been added to this family, one that exhibits superior gas barrier performance. Through reactive extrusion technology, this versatile collection of polymers are now commercially available with a significantly more attractive pricing structure, which should spur their use in a variety of new applications.

Acknowledgements

References

(1) McAdams, L. V.; Gannon, JA. In Encyclopedia for Polymer Science; Kroschwitz, J. L., Ed.; Wiley: New York, 1986, Vol. 6; 322.

(2) Heinemeyer, B. W.; Tatum, S. D. (The Dow Chemical Company). U.S. Patent 4 612 156, 1986.

(3) Flory, P.J.; Chem. Rev. 1946, 39, 137.

(4) White, J.E.; Brennan, D.J.; Silvis, H.C.; Mang, M.N. Specialty Monomers and Polymers. ACS Symposium Series), in press.

(5) White, J.E.; Silvis, H.C.; Mang, M.N.; Brennan, D.J.; Schomaker; J.A.; Haag, A.P.; Kram, S.L.; Brown, C. N. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 1993, 34 (1), 904.

(6) a) Silvis, H.C.; White, J.E.; Polymer News 1998, 23, 6.
     b) Silvis, H. C.; White, J. E.; (The Dow Chemical Company). U.S. Patent 5 275 853, 1994.

(7) Salame, M.J. Plast. Film Sheeting 1986, 2, 321.

(8) DeLassus, P. Barrier Polymers. Encyclopedia of Chemical Technology, 4th ed.; Wiley: New York, 1992; Vol. 3, pp 931-962.

(9) Wright, C.D.; Muggee, J.M. In Structural Adhesives: Chemistry and Technology; Hartshorn, S. R., Ed.; Plenum : New York, 1986, pp 113.

(10) Kanninen, M. F. International Journal of Adhesion, 1973, 9, 83

(11) Brennan, D.J.; White, J.E.; Barger, M.A.; Silvis, H.C. (The Dow Chemical Company). U.S. Patent 5 731 094, 1998.