Biologically derived diacids and their use in UV/EB coatings and adhesives

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ABSTRACT:
Using genetically bioengineered yeast strains as bioreactors, a novel biochemical process was used to convert ordinary alkanes and fatty acids into corresponding dicarboxylic acids. A series of polyester acrylate oligomers using bio-derived dicarboxylic acids with varying chain lengths (C9 to C36) were developed. The synthesis and preliminary performance evaluations of these oligomers in EB cured adhesives and coatings are presented.

INTRODUCTION:

Short chain dicarboxylic acids (C4-C10) like adipic acid and aromatic diacids and their esters are key building blocks in the manufacture of polyesters and polyamides, polycarbonates produced in billions of pounds worldwide and used in film, fibers, coatings, adhesives and composites. However except for C-12 (Dodecandioic acid) made from petrochemical feedstock, butadiene, and C-36 (Dimer of oleic acid), there are few economically and commercially available long chain (>C10) diacids even though these diacids are expected to have significant market potential. For example, the increased hydrophobicity of these diacids could be used in many polymer coating applications. Further, these long chain diacids could be co-reacted to produce nylons and engineering polymers[1] or UV curable and/or traditional powder coatings that could be processed at lower melt temperatures. The main reasons for non-availability of long chain diacids is a) lack of right feed stock, b) lack of economically viable traditional chemical manufacturing processes.

In the last three years, a new commercial process harnessing biotechnology has been developed that allows the selective bioconversion of long chain alkanes and monocarboxylic acids to long chain diacarboxylic acids in high yields with few by products[2]. This has been made possible by first genetically modifying certain yeast strains to amplify the required bioreaction, suppress both side products and degradation of the species of interest. In this paper we first review the development of these bio-diacids and present initial studies on developing the first in a series of possible downstream products: UV curable polyester acrylate oligomers for use in adhesives and coatings.

EXPERIMENTAL:

Materials: Nonyl phenol (3PO) monoacrylate, acid functional adhesion promoter acrylate Photomer® 4703 (AV = 270 mg KOH/g), and all other starting materials unless otherwise noted were obtained from Cognis Corporation, Ambler PA. Photoinitiators used were from Ciba Specialty Chemicals. Alkanes used to make diacids were obtained from commercial sources.

Bioacid synthesis: The starting point for C18 diacid was the readily available oleic acid or stearic acid. Most other acids were made using the corresponding alkane feedstock. First, genetically bioengineered *Candida Tropicalis* yeast cells were allowed to grow and multiply in a fermentation broth rich in nutrients. In the induction and production phases, the starting materials were added under controlled conditions of pH, temperature and oxygen demand. After the bioreaction, the desired diacid was separated and isolated from fermentation broth, followed by special purification techniques to obtain highly purified dicarboxylic acids. Thus octadec-9-enedioic acid was obtained from oleic acid. A saturated C18-Diacid was obtained by hydrogenation of the C9 double bond of octadec-9-enedioic acid. In a similar manner a series of diacids from C12-C22 were made from the corresponding alkanes. Two products, C12 and C18-diacid were chosen for commercial scale-up. The details of the synthesis and purification of these novel diacids is presented elsewhere[1].

Polyester acrylate synthesis:
Polyester syntheses were performed by reacting two moles of propoxylated glycerol with one mole of dicarboxylic acid(s) using acid catalyst first to produce hydroxyl terminated polyester polyols. These were further reacted with acrylic acid to make polyester polyacrylates.

Surface tension: Contact angle measurements were done using a Rame-Hart Goniometer at 22 °C. All measurements were made by placing a single drop of material on a Teflon substrate. Products of known surface tension were measured for contact angle then a linear equation was extrapolated. They were water, butanol (two concentrations) and ethanol in one set. Regression line had $R^2 = 0.9916$). In a second set the contact angle of four commercial products of known surface tension, namely Neopentylglycol (2PO) monomethyl acrylate (Photomer® 8127), Neopentylglycol (2PO)diacrylate (Photomer® 4127), 1,6-Hexanediol (2EO) diacrylate (Photomer® 4361) and Bisphenol A (4EO) diacrylate (Photomer® 4028) was measured. Regression line had $R^2 = 0.9959$. The contact angle of the five bioacid based polyester acrylates was measured and the surface tension was determined using the extrapolated line generated in the previous step.

Viscosity: The viscosity of polyester acrylates was measured using a Brookfield Cone and Plate viscometer at 25 ^{o}C.

Curing conditions:

A. Coatings – All coatings were applied to a degreased (acetone), white pigmented epoxy primed cold rolled steel panel. All curing was performed under ambient condition (22 ^{o}C, air atmosphere) using a conveyorized LESCO EBS machine fitted with a medium pressure mercury bulb (Primarc UV). A total energy of 662 mJ was used to cure the coatings.

B. Adhesives: Curing was performed under nitrogen atmosphere on a conveyorized AEB bench top curing machine. The operating voltage was 100 KeV. The adhesive formulation was laminated between two corona treated polypropylene films (AET Inc) using #3 Meyer bar and cured at 60 ft/min. The total energy incident on the sample was 30 kGy.

Moisture resistance tests: A UV curable formulation consisting of bio-diacid based polyester acrylate 60%, aliphatic urethane diacrylate (Photomer® 6230) 25%, HD(2EO)DA 6%, Benzildimethyl ketal 4%, Irgacure-184 3% (Ciba Specialty Chemicals) and an amine acrylate Photomer® 4967, 2%. 50 micron thick, top-coated metal panels as described above were placed in a humidity chamber at 38 °C and 100% relative humidity. Tests were done per ASTM D2247.

Crosshatch Adhesion test: 10 micron films were coated and cured directly on phosphated steel panels that had been degreased with acetone. After 24 hours, the panels were tested for cross hatch adhesion using ASTM method D3359.

Tensile tests and Glass transition temperature (T_g): A UV curable formulation consisting of the bio-diacid based polyester acrylate 90%, TRPGDA 5%, Benzildimethyl ketal 2%, Irgacure-184 2% (Ciba Specialty Chemicals) and an amine acrylate Photomer® 4967 1%, was made. Seven mil thick films were coated on polished aluminum panels, UV cured as above and tested on an Instron Tensile Tester using ASTM D882 test method. Glass transition temperature of EB cured polyester acrylates were measured using Perkin Elmer DSC-7 under nitrogen at a heating rate of 10 ^{o}C/min. The endotherm corresponding to the second heating cycle was used to determine T_g.

Peel Strength tests: 180^{o} peel test was performed on EB cured adhesive laminates using a Thwing-Albert Peel tester. Laminates were prepared by applying a 6 – 8 micron thick coating between two substrates. The adhesive was cured by electron beam as describe above. Laminates were peeled apart at 12 inches/min. The mean of triplicate tests was reported.

RESULTS AND DISCUSSION:

Development of Bioacids:

Candida Tropicalis is a commonly found yeast, was found to excrete diacids from alkanes and monoacids (Figure 1). To make bio-diacids in commercial quantities three important aspects of the manufacture need to be understood and optimized. A schematic of a yeast cell is presented in Scheme 2.

1. The sensitivity and activity of the organism to the desired bio-diacid has to be increased (i.e. more throughput per batch). Biochemically, this requires increasing the amount of the enzyme/protein which transforms the monoacid to the diacid. This in turn requires over expression of the genes that code for the protein. The process requires complex biomolecular techniques like gene

cloning, sequence amplification, insertion into host DNA to produce the enzyme complex and is described in detail elsewhere[3, 4].

2. The desired products should be selectively produced, for example, branched alkanes with branches in the middle should not produce polycarboxylic acids. Fortunately, the enzyme is selective and only terminal methyl groups at the longest chain length is oxidized. Next, it is necessary to block the degradation of the newly formed diacid. Again, this was done by genetically blocking the β-oxidation pathway[5].
3. Lastly, the products so produced from the biochemical process should be isolable in a pure form so that they can be used in polymer applications. Using a patented extraction method the diacids could be isolated and purified to high purity needed for polymer applications[6,7].

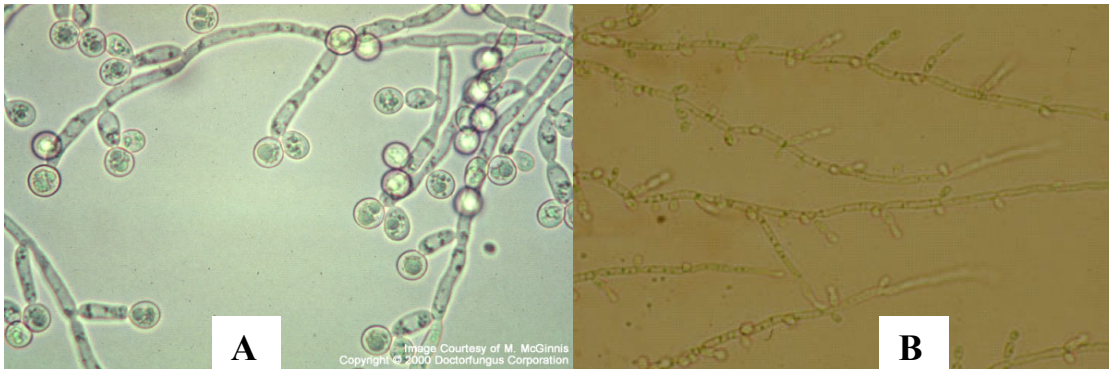
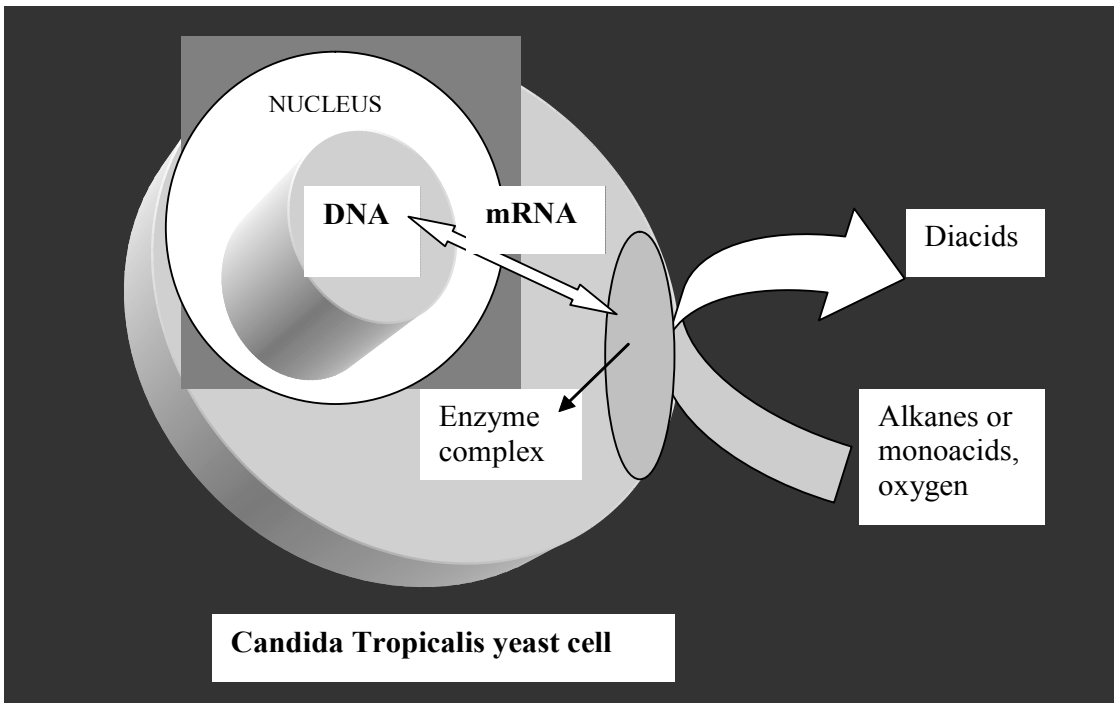


Figure 1 Photomicrograph of A) Candida yeast and Candida Tropicalis strain
Source: http://www.doctorfungus.org/thefungi/Candida_spp.htm



Scheme 1: *Candida Tropicalis* yeast cell: A dispensable bioreactor for making diacids

The general pathway for converting an alkane, paraffin or a monocarboxylic acid is given in Figure 2. The yeast cells, present in the fermentation broth take up an alkane or a monoacids, oxidize the α -methyl group to the alcohol using a hydroxylase enzyme redox complex to the α,ω-hydroxycarboxylic acid and then to the monocarboxylic or α,ω-diacid via the carboxaldehyde. For an alkane converting to a monocarboxylic acid, the process is then repeated at the ω–methyl end to get the dicarboxylic acid. A competitive reaction that reduces the yield of the desired diacid is the conversion of the monoacid or the diacid via a β-oxidative step to CO_2, water and energy using a coenzyme-A ester complex. This pathway was blocked allowing high yield production of the diacids[5].

Figure 3 shows the 13C NMR spectrum for the α,ω-octadecanedioic acid[8] and Figure 4 the melting point of a series of purified bio-diacids. The figure shows a general decreasing trend in melting point with increasing carbon numbers. Odd carbon lengths have lower melting points than the neighboring even counterparts and the difference in melt points is reduced as the carbon lengths increase from C9 through C21. The main advantage of lower melt points is the possibility to manufacture and process powder coatings and engineering polymers at lower temperatures. For the study of UV cured adhesives and coatings based on these bio-diacids, we chose, C6 (Adipic) which is of course from petrochemical sources, C9 (Azelaic) obtained by ozonolysis of oleic acid. C12 was made from dodecane and C36 diacid was obtained by dimerization and hydrogenation of oleic acid.

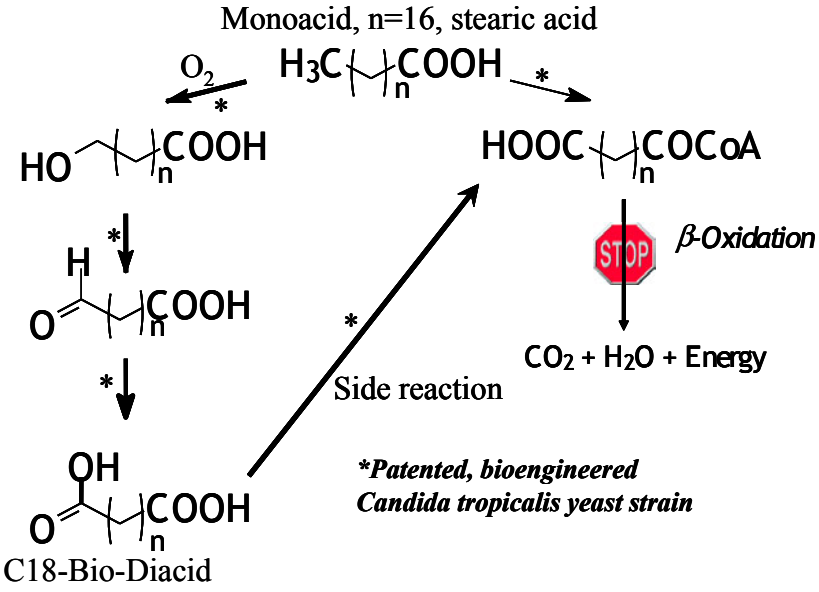


Figure 2: Biochemical pathway for conversion of alkanes and mono-carboxylic acids to α,ω-diacids using Candida Tropicalis

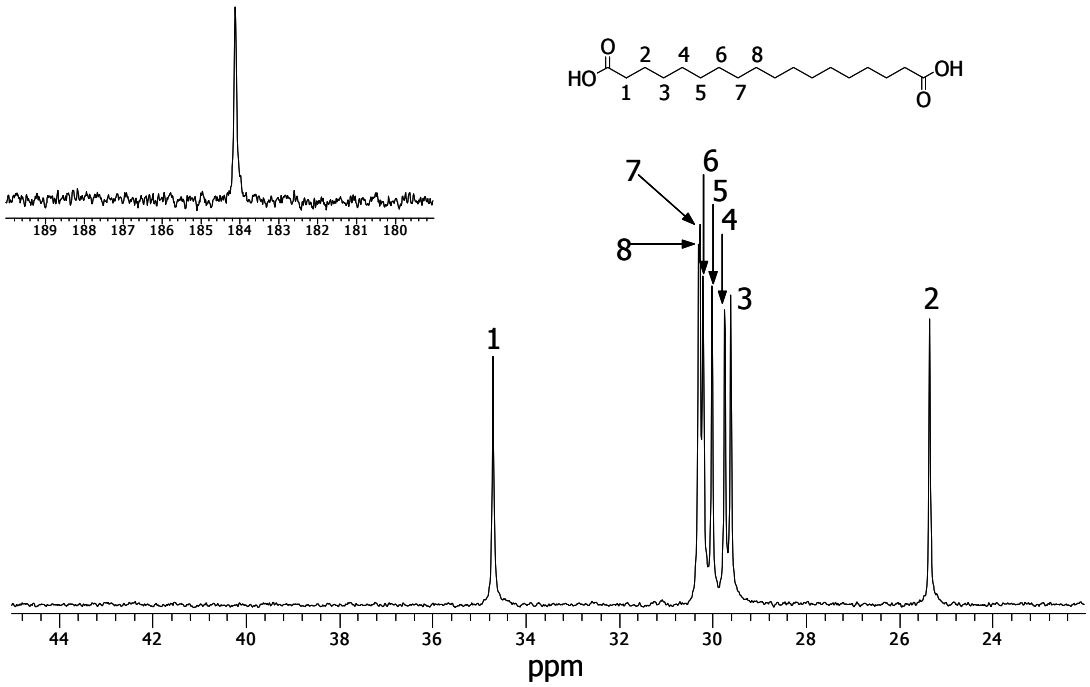


Figure 3 ^{13}C NMR spectrum of α,ω-Octadecanedioic acid

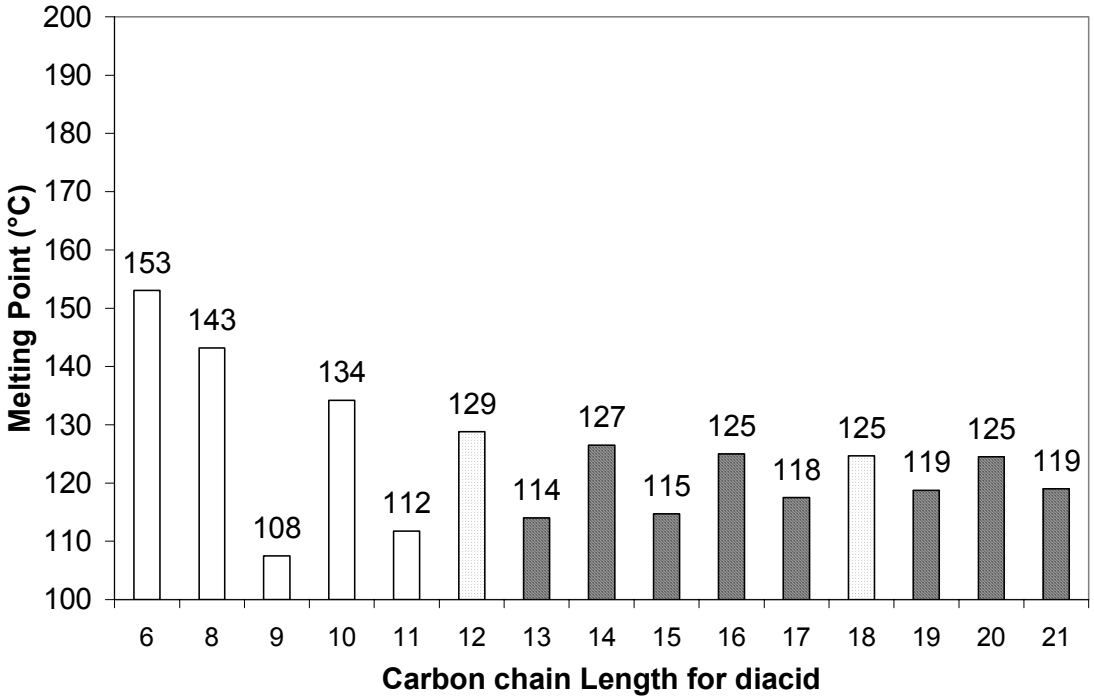


Figure 4 Melting point of purified dicarboxylic acids as a function of carbon chain length

Polyester acrylate: Synthesis and characterization:

Figure 5 shows a typical synthesis scheme for bio-diacid based polyester acrylate oligomers. By varying the molar ratio of the polyol to dicarboxylic acid one can produce highly branched structures with higher or lower molecular weight and acrylate functionality. For this study however, we prepared polyester tetraacylates *only* by varying the structure of dicarboxylic acid. Table 1 shows the viscosity and molecular weights of polyester tetraacrylates based on C6, C9, C12, C18 and C36 dicarboxylic acids. While the former three acids gave low viscosity oligomers, the dimer acid gave much higher viscosity oligomer due to an increase in higher molecular weight species (higher polydispersity index) from small amounts of trimer acid contaminants.

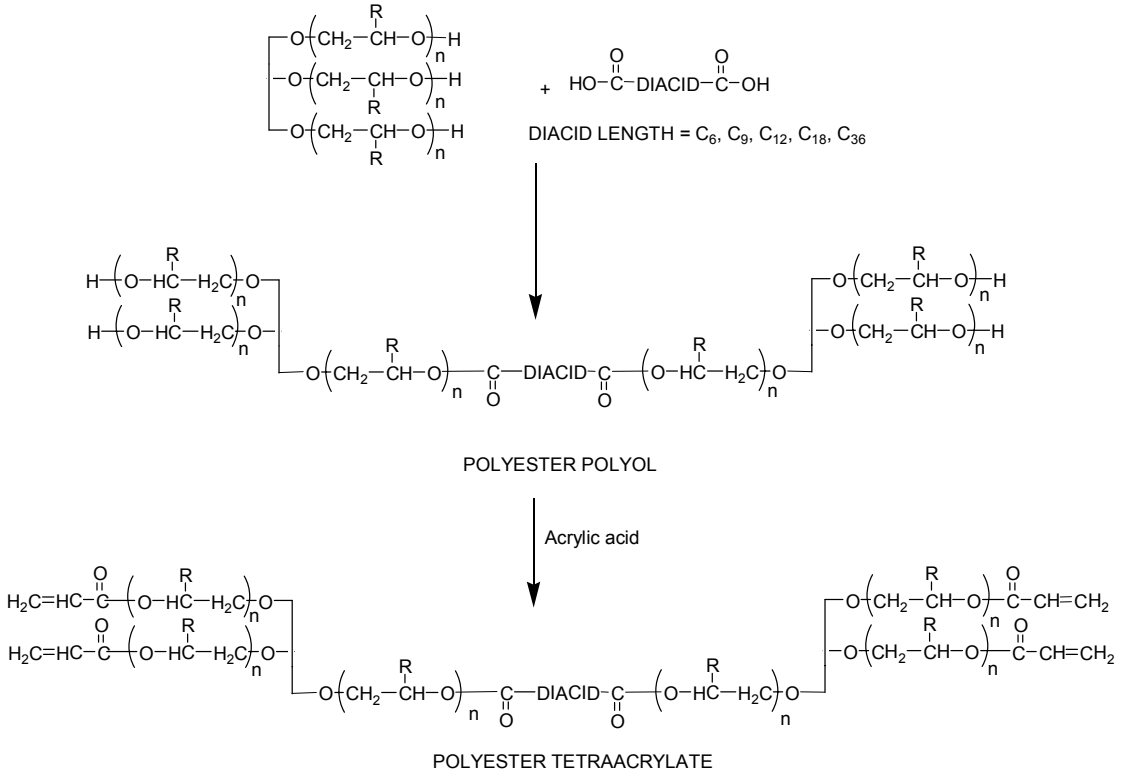


Figure5 : General synthesis scheme for bioacid based polyester tetraacrylate oligomers

Table 1: Physical Properties of Bio-Diacid based polyester acrylate oligomers

Polyester acrylate	SEC Mol. Wt.			
Diacid Chain Length	Mw	Mn	PDI	Viscosity, cP (25°C)
C6-PE	1370	810	1.69	530
C9-PE	1600	870	1.84	580
C12-PE	1760	930	1.89	584
C18-PE	3910	1360	2.88	1460
C36-PE	5060	1750	2.89	2460

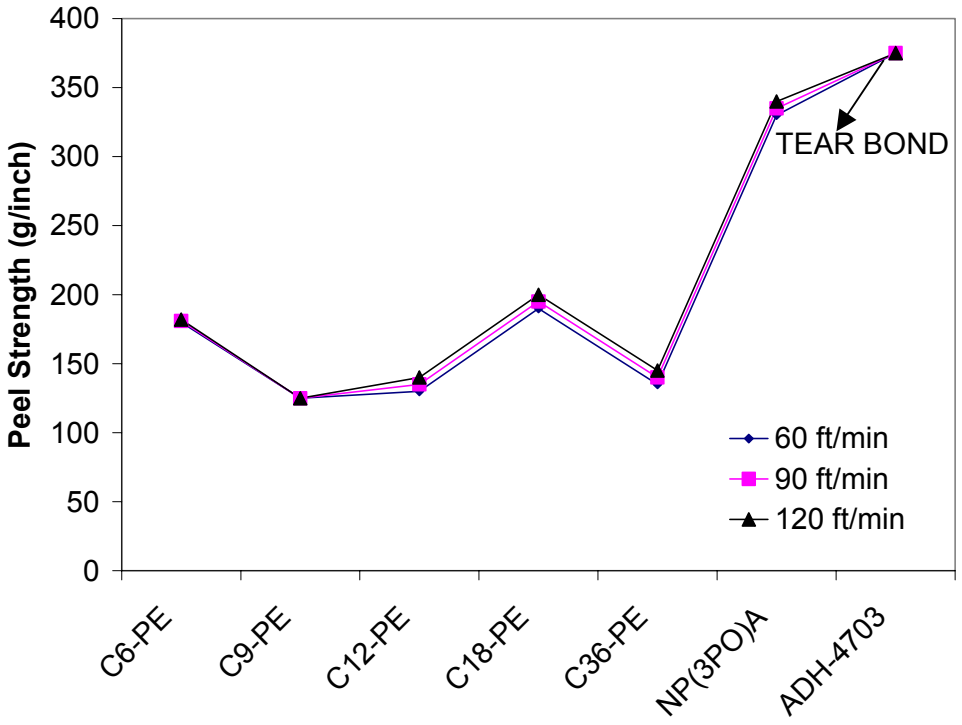


Figure 6: Peel strength of EB cured laminating adhesives incorporating bioacid polyester acrylate oligomers. Each formulation except for pure ADH-4703 had 80% oligomer and 20% adhesion promoter ADH-4703.

All formulations containing polyester acrylate oligomers showed peel values in a modest range (125-200 g/inch). Presumably, the high functionality of the oligomers produced higher shrinkage and tightly cross linked laminates. This was verified by testing peel strength of a 80:20 mixture of Nonylphenol (4PO)

monoacrylate and ADH-4703, also a monoacrylate. This formulation gave much higher bond strength value of 335 g/inch. EB cured laminate of pure adhesion promoter resulting in tear failure of the film. Of the tested polyesters, the one based on C18 bio-diacid gave the highest peel adhesion value of 190 g/inch. The peel adhesion values are independent of the conveyor speed in the tested range of 60-120 ft/min, indicating that the potential exists to cure these laminates at lower electron beam doses.

UV cured coatings based on bio-diacid based polyester acrylates

Table 2 shows the tensile strength of a series of UV cured films of polyester acrylates oligomers where the only difference was the chain length of the diacid. Despite an approximately 4x factor difference in the molecular weight of the adipic (C6) and dimer acid (C36) and a 2x factor difference in the molecular of the polyester acrylates, the tensile properties of UV cured films of all these oligomers falls within in a narrow range: tensile strength , 400-560 psi and elongation 9-12%. This shows that the functionality (nominally 4) of these oligomers and not the diacid spacer chain length plays a determining role in tensile properties. One would expect the glass transition temperatures (T_g) of these films to also exhibit a narrow temperature range. Interestingly, the T_g films with C18 and C36 polyester acrylates is the lowest (-30 °C). Higher T_g was obtained for the lower carbon chain length polyester oligomers. The reason for this dichotomy is not apparent.

Table 2: Tensile properties of UV cured polyester acrylate oligomers

Polyester acrylate	Tensile Strength[1], psi	Elongation[1], %	Tg[2] (°C)	Crosshatch adhesion[3]	Surface Tension dynes/cm
C6-PE	485	10	-11	2B	40.20
C9-PE	400	11	-19	2B	41.80
C12-PE	560	12	-10	5B	28.30
C18-PE	425	12	-30	1B	35.20
C36-PE	467	9	-30	0B	23.20

1: ASTM D882
2: By Differential scanning calorimetry
3: ASTM 3359

The cross hatch adhesion (ASTM 3359) test done on degreased phosphated steel panels showed that the C12-polyester acrylate had excellent adhesion as a direct to metal coating. Both the longer and shorter chain diacids gave inferior results in cross hatch adhesion tests.

With the exception of C-18 polyester acrylate, there is a general downward trend in surface tension as a function of increasing diacid chain length. Substrate wetting is a necessary (but not sufficient) condition for adhesion to low energy

surfaces. The oligomers with low surface tension values are interesting screening candidates for testing coating adhesion in plastics. Initial tests on untreated thermoplastic polyolefin panels did not show any significant adhesion improvement for any of the oligomers.

It is well known that polyesters have inferior hydrolytic stability and moisture resistance than polyethers. Since we used diacids with increasing hydrophobicity in making the polyester acrylates, we hypothesized that the UV cured films should have good moisture resistance. To test this, we top coated steel panels with white pigmented epoxy basecoat, with different polyester acrylate oligomers (see methods section) and placed the panels in a humidity chamber (5 Days, 100% relative humidity, 38 °C). The color and gloss change after this test is shown in Figures 7 and 8.

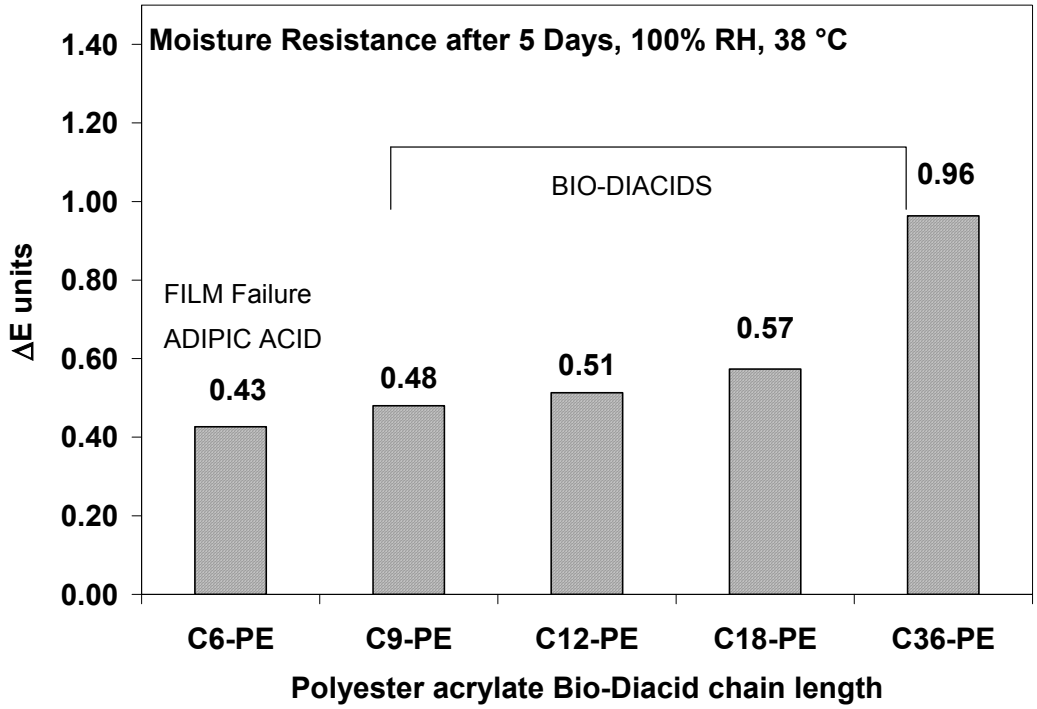


Figure 7: Color change as a function of humidity exposure for polyester acrylate oligomers based on bio-diacids

Except for C-36 dimer acid based coating, Figure 7 shows comparable ΔE values for bio-diacid based polyester acrylates and adipic (film failed after 3 days). The bioacid based topcoats, however, did not delaminate from the basecoat. Dimer acid is a mixture of aliphatic linear, branched and small amounts of aromatic diacid. With the limited available time data, we speculate that color bodies carried over from the isolation and processing of oleic acid to dimer and then to the polyester acrylate are responsible for higher ΔE in C36 based coating. The gloss change shows a similar response to color change. In both tests the C9, C12 and

C18 gave better performance than adipic based coating which failed in less than three days of testing. In future we will further develop novel urethane, epoxy, polyester acrylates and methacrylates. We will investigate the physical, chemical, thermal, rheological and corrosion resistance properties of these novel bi-diacids with an aim to expanding their use in coatings, adhesives, inks and composites.

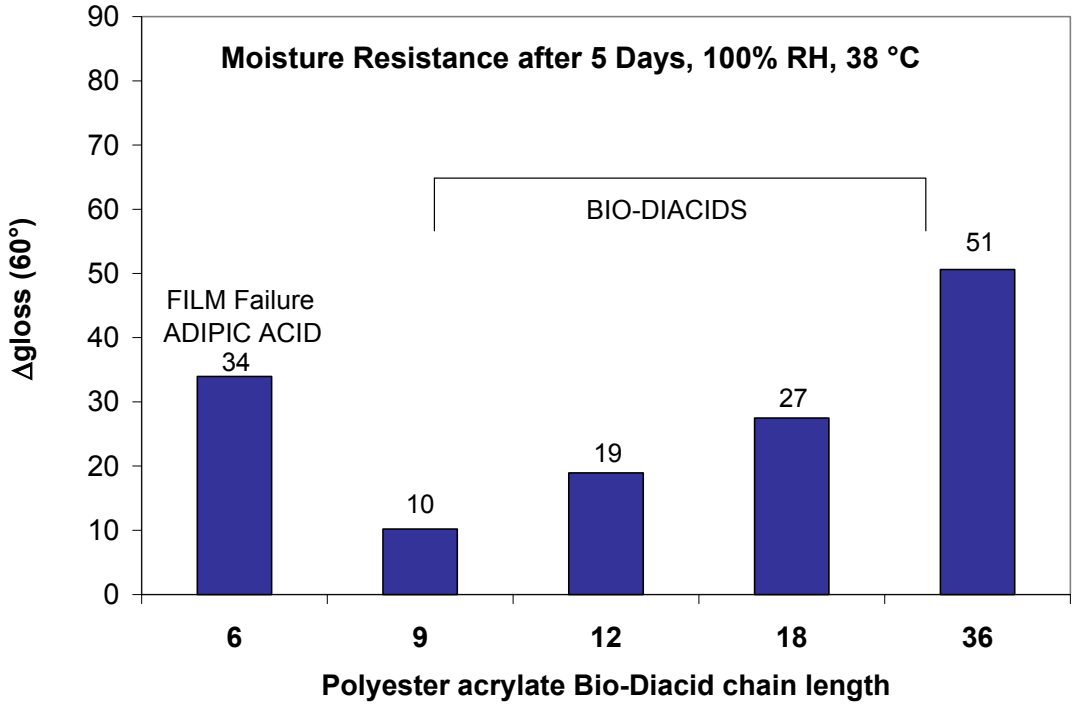


Figure 7: Color change as a function of humidity exposure for polyester acrylate oligomers based on bio-diacids

CONCLUSIONS:

A new series of bio-diacids was obtained from alkanes and readily available plant sources (oleic and stearic acid). These were used, along with a C6 (adipic acid) control , to make polyester acrylate oligomers. EB cured adhesives based on these oligomers had medium to low peel strength in polypropylene laminates. UV cured coating based on C12 diacid gave excellent direct to metal adhesion to steel panels. Coatings based on adipate polyester acrylates failed in humidity testing while those based on bio-diacids C9, C12 and C18 polyesters gave comparable gloss retention as adipates without film failure.

REFERENCES:

[1] Ehrenstein et al; *Polymer* 2000 Vol. *41 page* 3531.

[2] K. Anderson, D. Wenzel, R. Fayter, K. McVay; Henkel Research Corporation, 1999 US patent 5,962,285.

[3] S. Picataggio, K. Deanda, D. Erich; Henkel Research Corporation; 1993 US patent 5,254,466.

[4] J. Cregg, M. Gleeson, L. Haas, S. Picataggio; Henkel Research Corporation; 1993 US patent 5,204,252.

[5] D. Craft, R. Wilson, D. Eirich, Y. Zhang; Yeyan; Cognis Corporation; 2004 US patent 6,637,613.

[6] M. Staley; Cognis Corporation; 2004 US patent 6,660,505.

[7] M. Staley; Cognis Corporation; 2004 US patent 6,376,223.

[8] Private Communication to Cognis Corporation; Lon Mathias; University of Southern Mississippi.

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