

Neodecanoate esters as highly branched building blocks for radiation-curable reactive diluents and oligomers

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ABSTRACT

Esters of neodecanoic acid are highly branched structures that can impart specific properties and processabilities to the design of reactive diluents and oligomers used in radiation-curable systems. By way of example glycidyl neodecanoate can advantageously be combined with unsaturated building blocks like acrylic acid or more sustainable itaconate derivatives in a low temperature solvent-free and catalyst-free process without generating water by-product to design a variety of hydroxyesters suitable for high-performance radiation-curable systems.

INTRODUCTION

Over the years, reactive diluents and oligomers used as radiation-curable materials by the industry are moving together with the other formulative components towards more sustainable and toxicologically friendlier profiles, as illustrated by the continuous development of bio-based alternatives or the reduction of migration issues for low volatile reactive diluents. With an increased regulatory pressure, the toolbox available to develop new binders and formulate UV systems with a good cost/performance balance is however shrinking. The molecular structure of the raw materials used to design those binders have major influences on a series of properties including processability, reactivity upon curing and adhesion along with allergenic potentials, especially when the monomers used as reactive diluents have low molecular weight and low viscosity.

Neodecanoic acid (Versatic™ acid 10) is a branched tertiary monocarboxylic acid containing 10 carbon atoms. Its highly bulky aliphatic structure is known to provide superior properties to binder resins: high hydrophobicity, excellent outdoor durability, better viscosity control, improved pigment wetting, enhanced adhesion to apolar substrates and better overall flow and appearance are typical improvements that can be accordingly expected. To benefit from these properties, the industry can rely on two established esters derived from the acid and depicted in Figure 1: glycidyl neodecanoate (Cardura™ E10P) and vinyl neodecanoate (VeoVa™ 10).

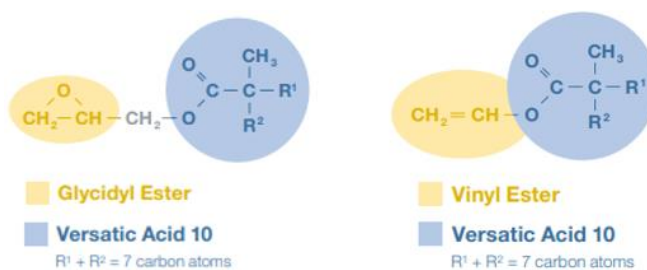


Figure 1: Glycidyl ester and vinyl ester of neodecanoic acid (Versatic acid 10)

The glycidyl ester of neodecanoic acid is mostly used in high performance polyesters and acrylic polyols for industrial and automotive coatings, whereas the vinyl ester of neodecanoic acid is widely used in combination with vinyl acetate and acrylates to prepare emulsions of premium performances. Additionally, the vinyl ester can be used as a vinyl reactive diluent in UV-curable coating formulations. On the other hand, the specificity of glycidyl neodecanoate can advantageously be used to design UV-curable reactive diluents or oligomers, with the most straightforward approach being the combination of its glycidyl (epoxy) group with acrylic acid to form a hydroxyester adduct, ACE.

ADDUCT OF ACRYLIC ACID WITH GLYCIDYL NEODECANOATE (ACE):

The commercially available ACE adduct¹ belongs to the family of monofunctional hydroxy acrylates. Its high molecular weight (284g/mol) and flash point (170°C) make it an attractive monomer for UV applications. Its low volatility and low residual acrylic acid level translate into a Draize value of 0.9², which is advantageously lower than most of the monofunctional acrylates³, limiting risk of irritancy and sensitization by skin contact. Typical properties of ACE are given in Table 1.

Typical properties of ACE	
Appearance	Clear liquid
Color (Hazen)	<100
Viscosity @20°C	<300 mPa.s
Flash Point	>170°C
Surface tension	32.3 mN/m
OH value	198 mgKOH/g
EINECS & TSCA	listed
Draize value	0.9

Table 1: Typical properties of ACE

In terms of performance features, a closer look at its chemical structure (Figure 2) helps to understand how this acrylate can benefit to UV formulators:

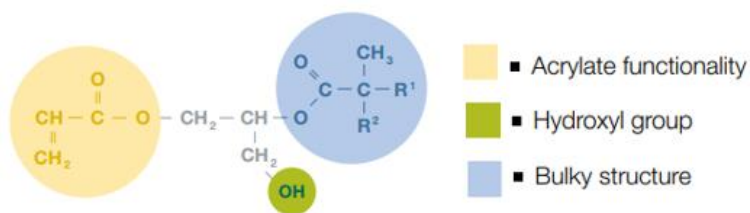


Figure 2: Adduct of acrylic acid with glycidyl neodecanoate (ACE)

- The bulkiness and dense methyl content of the aliphatic group provides superior hydrophobicity, UV stability and additional protection to the ester bonds which translates into higher outdoor durability as compared to typical acrylate building blocks. Additional features include a better viscosity-cutting power, an improved pigment wetting capability and a better adhesion to apolar substrates.
- The hydroxyl group provides polarity and compatibility with a wide range of products, but also capabilities for dual-cure systems (e.g. by reaction with isocyanates). Depending on the process parameters used to prepare ACE, the reactivity of the hydroxyls can be balanced between more reactive primary OH or more stable secondary OH.

- c) The reactivity of the acrylic group ensures high conversion and fast drying speed upon radiation curing.
- d) The relatively high molecular weight of ACE compared to other monofunctional acrylates translates into low level of shrinkage.
- e) By combining a bulky apolar group with a polar hydroxyl group, ACE can exhibit surfactant-like features with unique wetting abilities.

To illustrate the advantage of ACE on the adhesion to difficult substrates, two examples are given below on oriented polypropylene (OPP) for laminating adhesives and on polyethylene terephthalate (PET) for pressure sensitive adhesives (PSA).

BENEFITS OF ACE ON ADHESION TO OPP FOR LAMINATING ADHESIVES:

Polypropylene (PP) is notoriously difficult to wet and to coat because of its extremely low surface tension. A surface treatment is usually applied to improve its adhesive properties. We compared ACE and 2-ethyl hexyl acrylate (2EHA) as reactive diluents for urethane diacrylate systems on corona pre-treated OPP. Laminating adhesives were prepared by mixing a commercial aliphatic urethane diacrylate with various amounts of ACE (10 - 25 - 55wt%) and 2EHA (10 - 25%) in presence of a photoinitiator. Before application, a thin layer (<0.1 micron) of a 10% ACE solution in isopropanol is applied on the OPP sheets. An adhesive layer of 10 microns is subsequently applied and the coated OPP sheet is laminated with a second OPP sheet. The laminate passes twice under a UV lamp (120W/cm) at a speed of 6 m/min. The peel strength of the various samples is measured according to test method ASTM D3330; the results presented in Figure 3 shows that ACE outperforms 2EHA at all concentrations investigated and that the adhesive performance is directly related to the level of ACE.

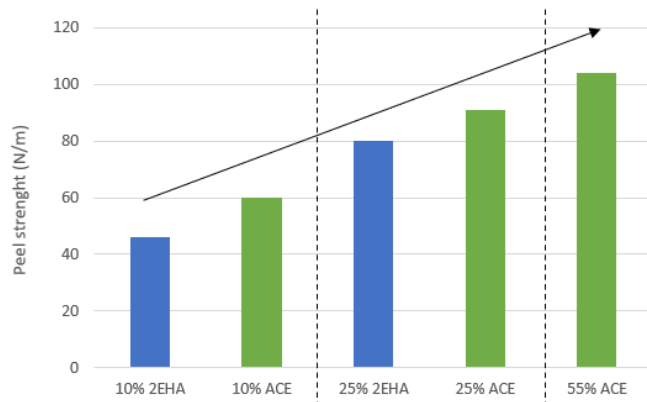


Figure 3: Peel strength of OPP/OPP laminate

BENEFITS OF ACE ON ADHESION TO PET AND OPP FOR PRESSURE SENSITIVE ADHESIVES:

A comparison is made by partially or totally replacing ethoxy-ethoxyethyl acrylate (EEEA) by ACE (@16wt% and 32%) and evaluating the adhesion properties to PET and OPP. The full composition details are presented in Table 2; the PSA investigated are based on a urethane diacrylate oligomer formulated with a tackifier, two acrylate monomers (EEEA + ethoxylated nonylphenol acrylate) and a photoinitiator.

Components	Parts per 100		
Urethane acrylate	16	16	16
Tackifier (hydrogenated rosin)	32	32	32
Ethoxylated nonylphenol acrylate	12	12	12
Ethoxy-ethoxyethyl acrylate	32	16	0
ACE	0	16	32
Photoinitiator	8	8	8

Table 2: Composition of PSA formulation (parts per 100)

Corona pretreated OPP and PET sheets are coated with a thin layer of formulated PSA and cured by passing once (PET) or twice (OPP) under a UV lamp (120W/cm) at the speed of 6m/min. The curing took place in atmospheric conditions. After being cured, the samples are laminated with a second sheet of OPP or PET. The peel strength of the various samples is measured according to test method ASTM D3330. Results presented in Figure 4 shows that replacing EEEA by ACE in standard UV PSA formulations considerably improves the adhesion performance to OPP and PET substrates, the best results being obtained when all EEEA is replaced by ACE.

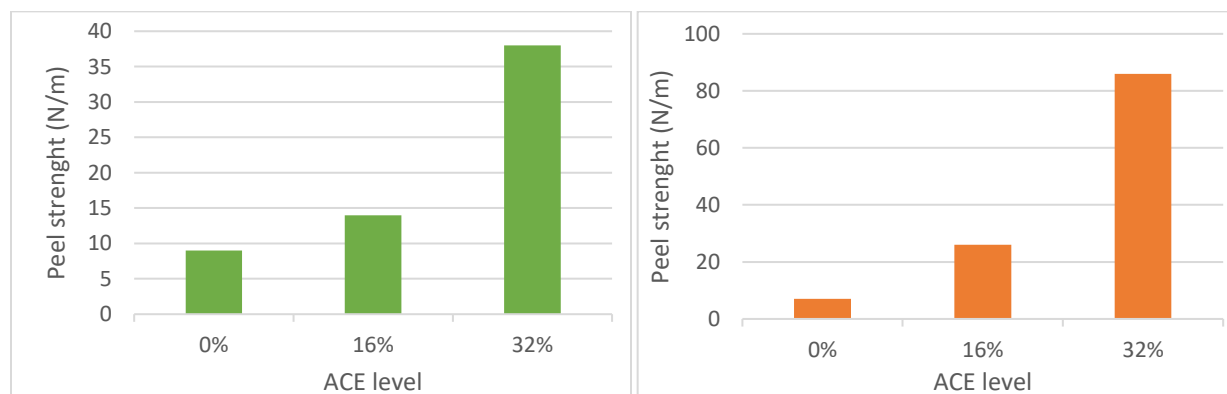


Figure 4: Peel strength of PSA on PET (left) and OPP (right)

To illustrate further the advantage of glycidyl neodecanoate as a building block for UV-curable materials, we synthesized and tested several hydroxyester itaconates based on a simple esterification process.

HYDROXYESTER ITACONATES BASED ON GLYCIDYL NEODECANOATE:

Most of the oligomers and monomers used in UV-curable materials are acrylic acid esters that exhibit relatively poor sustainability and HS&E profiles. More interesting alternatives with higher bio-based contents and lower allergenic potentials can be found in itaconate derivatives. Itaconic acid and its anhydride are bio-based raw materials with a radically polymerizable double bond that can be used to produce UV-curable polyesters. In combination with glycidyl neodecanoate, a seamless process can be developed to design hydroxyesters suitable as diluents or oligomers and polymers for formulated UV systems.

Glycidyl neodecanoate (CE10P) is a mono-epoxy molecule known for its excellent reactivity under low process heat, and for its high boiling point and excellent solvent ability, which makes it a raw material of choice to ease polyesterification processes. A schematic view of such approach is given on Figure 5. When anhydrides are combined with CE10P, the polymerization process can even be further simplified via a polyaddition mechanism at relatively low reaction temperature without the need for additional catalyst or solvent, and without generating water by-product. A practical example of such process is illustrated below in the making of a simple dihydroxyester adduct by reacting 1 mole of itaconic acid with 2 moles of CE10P in absence of solvent:

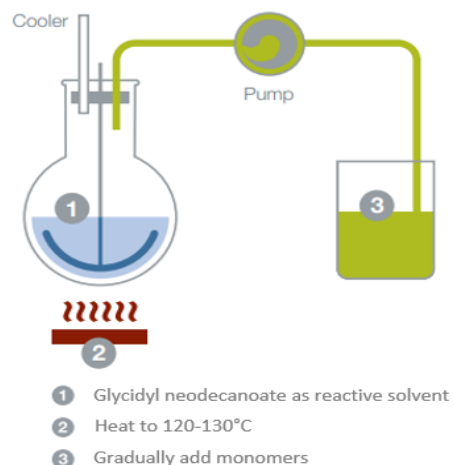


Figure 5: Schematic process view

In a glass reactor equipped with an anchor stirrer, a reflux condenser and nitrogen inlet; itaconic acid is dissolved in a small quantity of CE10P at a temperature of 120°C. Once dissolved, additional quantities of CE10P are added during one hour in a molar ratio 1:2 to form a dihydroxyester adduct. The acid-epoxy conversion is followed by Epoxy Group Content (EGC) and Acid Value (AV) titrations. The excess of acid is scavenged by adding to the reactor the corresponding molar amount of glycidyl neodecanoate to complete the conversion.

Different reactive diluents and oligomers have been prepared following the same approach; the recipes are given in Table 3 below together with the resulting viscosity and molecular weight measured by Gel Permeation Chromatography (GPC) against polystyrene standards.

Adduct/oligomer	HydroxyEster Itaconate (HEI)	DiHydroxyEster Itaconate (DHEI)	Linear Itaconate PolyEster (LIPE)	Star Itaconate PolyEster (SIPE)
Initial reactor charge	<i>wt%</i>	<i>wt%</i>	<i>wt%</i>	<i>wt%</i>
CycloHexanol	22.0	-	-	-
Trimethylol propane	-	-	-	11.4
Itaconic Acid	-	21.4	9.9	-
Itaconic Anhydride	24.9	-	-	28.6
CE10P	-	15.5	15.5	20.0
CE10P addition*	<i>wt%</i>	<i>wt%</i>	<i>wt%</i>	<i>wt%</i>
CE10P	53.1	63.1	57.2	40.0
Itaconic Anhydride addition	<i>wt%</i>	<i>wt%</i>	<i>wt%</i>	<i>wt%</i>
Itaconic Anhydride	-	-	17.4	-

(*): additional CE10P is added to convert remaining acid towards the end of reaction

Viscosity @22°C (Pa.s)	6	19	47	365
Mw (Da)	570	770	1300	2230

Table 3: Recipe of different reactive diluents and oligomers based on glycidyl neodecanoate (CE10P)

The respective glass transition temperatures (T_g) of the different homopolymer adducts are determined by Differential Scanning Calorimetry (DSC) and compared to ACE and vinyl neodecanoate homopolymers.

	T _g (°C)
ACE	-1
Vinyl neodecanoate	-3
HEI	28
DHEI	14
LIPE	-7
DIPE	13

Table 4: Glass transition temperatures obtained by DSC analysis of the homopolymers

The performances of those hydroxyester itaconates are evaluated into basic UV formulations containing an oligomer (~50wt% of LIPE or SIPE), one or more reactive diluents (~50wt% HEI or DHEI), a photoinitiator (3% of Omnirad 4265 supplied by IGM) and an inhibitor (0.5%). For the comparative study, trimethylol propane triacrylate (TMPTA) and hexanediol diacrylate (HDDA) are used as commercial acrylate reactive diluent benchmarks. After application on metal plates, irradiation with an UV-LED lamp (385nm) under nitrogen flow is performed for 10 seconds. The hardness is measured with a Koenig pendulum (Table 5), the adhesion is determined by a cross-cut test (Table 6) and the gel content is evaluated on Table 7 by immersing a cured specimen in methyl ethyl ketone (MEK).

Reactive diluent : oligomer Ratio 50:50	Koenig Hardness (in sec)	
	LIPE	SIPE
TMPTA	81	69
HDDA	77	54
ACE	13	10
Mix TMPTA:HDDA 50:50	65	65
Mix ACE:TMPTA 65:35	20	16
Mix DHEI:TMPTA 55:45	31	27
Mix HEI:TMPTA 55:45	33	38

Table 5: Koenig hardness of 50:50 mixtures between oligomers (LIPE or SIPE) and reactive diluents

The hardness results show that all systems containing itaconate unsaturation have cured in a satisfactory manner, and that the final hardness values are significantly influenced by the respective T_g of the reactive diluents used in the mixture.

Ratio 50:50	LIPE	SIPE	TMPTA
HEI	2	1	5
DHEI	2	1	5
TMPTA	5	5	5
HDDA	5	5	5

Table 6: Cross-cut adhesion test on metal plate (ISO classification: 1=best, 5=worst)

The best adhesion results on metal are obtained with the formulations containing HEI and DHEI reactive diluents. The significant difference of adhesion measured between acrylate-based and itaconate-based diluents, 1 being scored as full adhesion and 5 being scored as no adhesion at all, can be explained by the presence of glycidyl neodecanoate and its hydroxyl group in combination with the better flexibility of itaconate adducts.

Formulation ratios	% Itaconate	% Acrylate	% Gel Content
ACE : TMPTA 50:50	0	100	97
LIPE : ACE : TMPTA 63:23:14	63	37	83
DHEI : SIPE : TMPTA 37:32:31	69	31	79
HEI : TMPTA 77:23	77	23	79
DHEI : LIPE 55:45	100	0	89

Table 7: Gel content analysis after immersion in MEK (10sec irradiation time)

Satisfying results are obtained for all cured films including those with very high itaconate content, which is not a given considering the higher reactivity of acrylate unsaturation compared to itaconate one. An indication of the relative percentage of acrylate or itaconate double bonds are given in Table 7 for each mixture. We can see that the system based solely on itaconate derivatives (DHEI + LIPE) performs better than formulations based on mixtures of acrylate and itaconate derivatives, probably because of the better reactive compatibility when mixtures are prepared with similar molecular structure. In addition, the presence of glycidyl neodecanoate could be beneficial to the itaconate reactivity. As we know that the itaconate double bonds are slower to react than their acrylate counterparts, we tested further the crosslink density by adapting the curing process; with longer irradiation time (1min instead of 10sec) the gel content of 100%-based itaconate derivatives are comparable to all-acrylate systems as suggested by the results in Table 8 below.

Formulation ratios	% Itaconate	% Acrylate	% Gel Content
TMPTA (100%)	0	100	98
ACE : TMPTA 50:50	0	100	97
DHEI : SIPE 50:50	100	0	96

Table 8: Gel content analysis after immersion in MEK (1min irradiation time)

CONCLUSIONS

Reactive diluents and oligomers based on the neodecanoate bulky aliphatic group are found to develop interesting UV-curable properties and to be suitable approaches for the design of hydroxyester materials via a seamless polyesterification process. The adduct of acrylic acid with glycidyl neodecanoate is found to improve adhesion performances on difficult apolar substrates as compared to other acrylate-based reactive diluents while exhibiting an advantageous HS&E profile. Various itaconate derivatives based on neodecanoate hydroxyesters are prepared and compared to acrylate benchmarks; encouraging performances are found even for 100% itaconate-based solutions that are typically considered less reactive than their acrylate counterparts. The toolbox available to develop binders and formulate UV systems with good cost/performance balance can benefit from the unique molecular structure of neodecanoate esters.

Footnotes:

1 – The adduct of acrylic acid and glycidyl neodecanoate is commercially available from various companies under the following tradenames: PolySurf ACE (Adapt), Ebecryl 113 (allnex), CN152 (Sartomer)

2 – Acute Dermal Irritation Study in rabbits, laboratory study 9560-05 conducted by Stillmeadow Inc. for Hexion

3 – Reference Radtech.org “Safety and Handling of UV/EB curing materials” by UCB Chemicals Corporation, pg.5: typical Draize score values for acrylate monomers are ranked from 1.5 (glycerol propoxylate triacrylate, minimal irritation) to 6.2 (hexane diol diacrylate, severe irritation)