Radiation Curable Hyperbranched Polyester Acrylates

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Abstract

After many years of study dendritic and especially hyperbranched materials are becoming commercially viable raw materials for industrial applications. Structurally hyperbranched oligomers are quite different from the typical oligomers used in radiation cure applications having a "globular" rather than linear morphology. This 3-dimensional shape leads to unique structure/property relationships and new opportunities for design of products. Some of the attractive features of hyperbranched materials for radiation cure applications include low viscosity at a given MW, high end group (acrylate) concentration, fast cure and low shrinkage. The paper will discuss the structure/property relationships for a new series of hyperbranched polyester acrylates and highlight the usefulness of these products in applications such as ink jet and flexographic inks and hardcoats.

Introduction

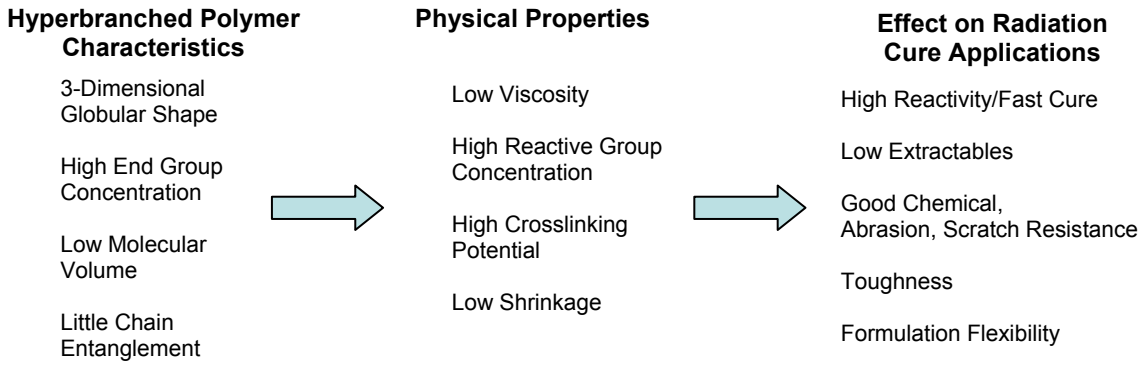
Dendritic polymers have been the subject of intense study in both academic and industrial labs for many years[1, 2]. However, the commercial success of dendritic polymers in general industrial applications has been limited by their high cost which is a direct result of the multi-step repetitive synthesis routes required to form the highly symmetrical dendritic structure. More recently, closely related hyperbranched polymers have been developed that can be made by more industrially attractive processes, and thus, bring many of the features of dendritic structures at a fraction of the cost. The difference between dendritic and hyperbranched polymers is shown schematically in Figure 1.

Figure 1

Dendritic Hyperbranched

Because of their approximately spherical or globular morphology the properties of hyperbranched polymers differ from traditional linear polymers in that they have relatively low molecular volume for a given molecular weight and have a high concentration of end groups. In addition, the end group concentration remains relatively constant as molecular weight increases. These unique structural features of hyperbranched polymers result in uncommon combinations of physical properties and opportunities for achieving interesting new properties in end-use applications. How the structural features of hyperbranched polymers might translate to physical properties and ultimately to end-use performance in radiation cured applications is described in Figure 2.

Figure 2



Use in Radiation Cured Systems

Materials with high acrylate functionality are used in radiation-cured systems because of the enhancements they can bring in properties such as cure speed, hardness, scratch resistance and chemical resistance. Use of traditional high functionality materials, such as dipentaerythritol hexaacrylate (DPHA) or high functionality urethane acrylates, require a trade off with less desirable properties, such as high viscosity, high film shrinkage on cure and brittleness. The unique structural features of hyperbranched polyester acrylates may make it possible to break these paradigms.

Sartomer Company has developed general methods to prepare hyperbranched polyester acrylates (abbreviated HB-PEA for the remainder of this paper) that are practical for industrial use. The products discussed in this paper have all been made using these techniques on commercial or semi-commercial scale. The five HB-PEAs that will be described were designed for different end-use applications by modification of the backbone structure and level of acrylate functionality: CN2300 – inkjet or flexographic inks, CN2301 – coatings, CN2302 – inks and coatings with improved flexibility, CN2303 – inkjet inks and hardcoats, CN2304 – hard- and scratch-resistant coatings. The products and their general descriptions and properties are shown in Table 1 along with DPHA, which was used for comparison in all studies.

Table 1

Product	Acrylates/ Molecule	Acrylate Equivalent Weight	Viscosity @ 25C, cPs	Surface Tension, dynes/cm @ 25C
CN2300	8	163	600	32.6
CN2301	9	153	3500	38.4
CN2302	16	122	350	37.8
CN2303	6	194	320	40.3
CN2304	18	96	750	32.6
DPHA	6	102	13,000	39.9

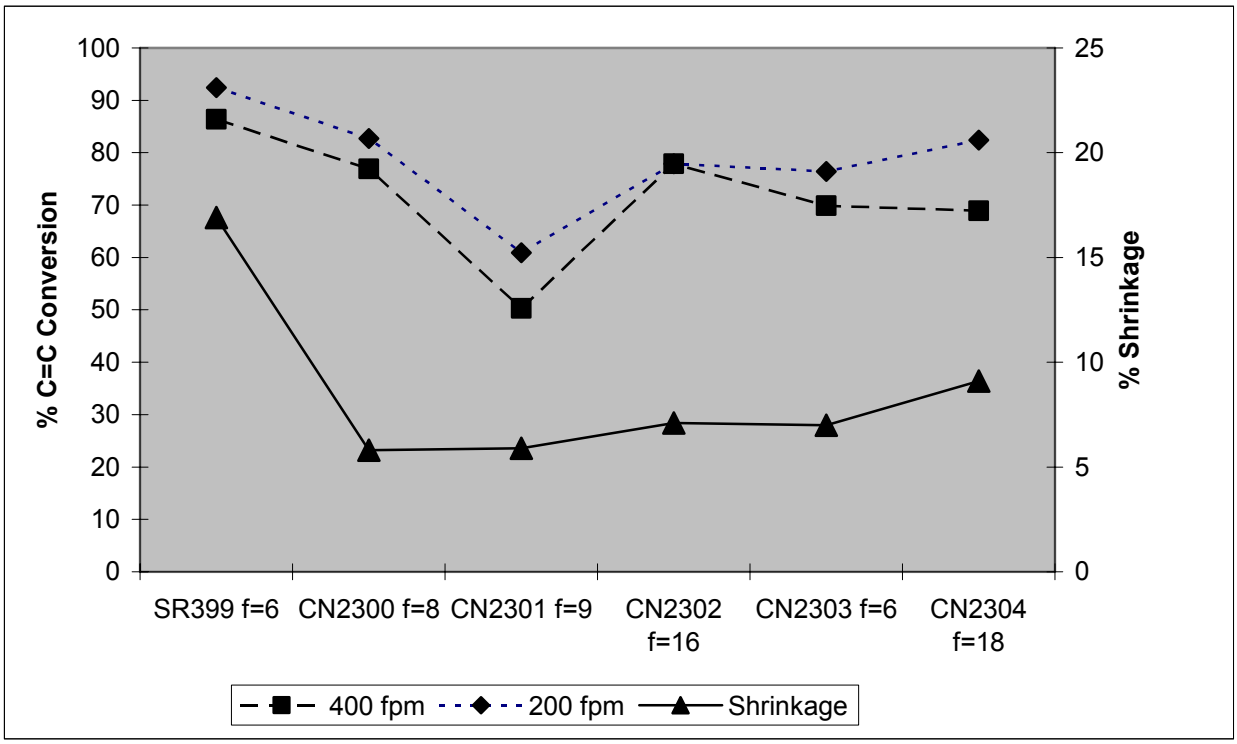
The purpose of the current study is to investigate the basic cure characteristics and physical properties of HB-PEAs to lay a groundwork for developing formulations around these unique materials. Cure studies were carried out to screen for photoinitiator effects and determine the effect of cure speed on properties. Curing was done with one Fusion F600 mercury lamp set on high (the measured integrated energy is 129 mJ/cm^2 @ 100 foot/min using an Illuminations Industry IL 390 radiometer). Extent of cure was judged by MEK double rubs and by FTIR measurement of the acrylate C=C band at 1630 nm. Four photoinitiators were screened for effectiveness at 5% concentration at various line speeds. The photoinitiators tested are shown in Table 2. Of these, the KTO46 gave the best results – highest C=C conversion – for all products and was used for the rest of the study.

Table 2

Photoinitiator Name	Description
Esacure KTO46	blend of: 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2-hydroxy-2-methyl-1-phenylpropanone, oligo(2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl)propanone), and 2,4,6-trimethylbenzophenone)
Esacure KIP150	oligo(2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl) propanone)
Esacure KIP LE	(oligo(2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl) propanone) in TMPTA)
Esacure KT55	blend of: oligo(2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl)propanone), 2,4,6-trimethylbenzophenone and 4-methylbenzophenone)

Studies of the effect of acrylate double bond conversion on shrinkage and physical properties were carried out at 200 and 400 ft/min. Results for acrylate double bond conversion at the two line speeds and for shrinkage are shown in Figure 3. Surface cure for all samples was good at both line speeds as all passed 200 MEK double rubs. As expected, conversion increased at lower line speed for all products except CN2302, which reached a relatively high conversion (78%) even at the faster speed. DHPA reached the highest conversion under both conditions.

Figure 3



What stand out from this data are the shrinkage results. Shrinkage was measured by comparing the density of the liquid materials and their cured films and using the equation: % Shrinkage = 100 x $(d_p - d_l)/d_p$, where d_p is the density of the polymer film and d_l is the density of the liquid. Despite their high functionalities the HB-PEAs all had shrinkages of less than 10% compared to the 17% measured for DHPA under these cure conditions. Except for CN2304 all the HB-PEAs had shrinkage in the 5-7% range. Measured shrinkages at 200 and 400 fpm line speeds were within the estimated 10% error of the method for all samples.

Shrinkage of radiation-cured acrylate systems is generally accepted to depend on the molecular weight and functionality of the materials being cured[3] and typically falls into the range of 10-15%. Based on the molecular weight/functionality relationship, the shrinkage of the HB-PEAs should be similar to other acrylate monomers or oligomers. Currently, the feeling is that the low shrinkage of the HB-PEAs can be explained by a combination of two factors that would both tend to limit the "pulling together" of the film as it cures: 1) a relatively high level of intramolecular polymerization and 2) the fact that while acrylate equivalent weight is quite low, the average distance between crosslinks is large. For example, in DPHA there is an average of 6.8 atoms between acrylate groups, while in CN2300 there is an average of 16 atoms, resulting in a more loosely crosslinked system.

Pencil hardness was also measured on the films cured at both 200 and 400 fpm to judge the effect of higher double bond conversion on properties. The data is summarized in Table 3. While not as hard as DPHA, even those products not designed for hardness (CN2300, CN2301, and CN2302) gave acceptable results. CN2303 cured to a film that is nearly as hard as DPHA, but is much less brittle.

Table 3

Product	Pencil Hardness	
	@ 200 fpm	@ 400 fpm
CN2300	3H	HB
CN2301	4H	1H
CN2302	2H	2H
CN2303	8H	6H
CN2304	5H	2H
DPHA	9H	8H

To measure ultimate physical properties the HB-PEAs were cured with a 1500 mJ/cm^2 integrated energy to give films as fully cured as possible. Properties are shown in Table 4. Data is not included for DPHA as it was too brittle to test. In all cases films with good integrity are formed. This is in contrast to DPHA which was too brittle to test when cured under these conditions. CN2302 in particular has high tensile, elongation and modulus indicating a very tough cured film.

Table 4

	CN2300	CN2301	CN2302	CN2303	CN2404
Functionality	8	9	16	6	18
Tensile Strength, psi	5360	4880	7400	7675	8750
Tensile elongation, %	4.5	3.8	9.1	1.9	1.1
1% Modulus, psi	98,800	194,950	162,800	237,423	204,356
Tg by DMA, ^{o}C	96	77	87	60	181

Conclusions

Because of their unique structure hyperbranched polyester acrylates offer an unusual combination of features and properties in radiation cured systems: high functionality, low viscosity, fast cure, low shrinkage and good physical properties. In contrast to other high functionality acrylates, such as DPHA or some urethane acrylates, they cure to films that are non-brittle and tough. Ongoing work in our laboratories shows that these combinations of properties are useful in formulating new products for uses such as inkjet inks, flexographic inks, specialty coatings and various high tech applications. In addition, the hyperbranched structure offers many opportunities for further tailoring of properties by modification of the backbone structure or type and number of end groups.

References

1. Newkome, G. R.; Moorefield, C. N. ; Vogtle, F.; "*Dendritic Molecules",* VCH Verlagsgellschaft mbH, 1996

2. Newkome, G. R.; Moorefield, C. N.; Vogtle, F.; "*Dendrimers and Dendrons",* Wiley-VCH Verlag GmbH, 2001

3. Pezron, E.; Magny, B.; *European Coatings Journal,* 9, 602 (1996)