Specialty Low Molecular Weight Polyolefins for Digital Printing Applications

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Abstract

Low Molecular Weight Polyolefins (LMW Polyolefins) have been widely used in coatings, plastics and printing inks to provide low energy surface, abrasion/scratch resistance and release properties. Waxes, including LMW Polyolefins, are one of the key additives in digital printing such as electrophotographic printing, thermal and inkjet printing. Waxes provide release, lubrication and improve image sharpness. However, the dispersibility and stability of non-functionalized waxes with toner resins has long been a challenge. In this paper, a series of compositions consisting of polyester based resin, non-functional LMW Polyolefins (release agent/waxes) and specialty performance LMW Polyolefins have been prepared to better understand the dispersibility of LMW Polyolefins in the polyester toner resins. SEM, light microscope and DSC experimental results showed that several specialty performance LMW Polyolefins improved the dispersion of non-functional LMW Polyolefins (release wax) in the toner resins. Therefore, they can be used as compatibilizers for toner applications. They also have the potential to provide adhesion, abrasion resistance and improve gloss for electrophotographic printing, thermal and inkjet printings, as well as media coatings.

Introduction

Low Molecular Weight Polyolefins discussed in this paper are polyethylene, polypropylene and polyalphaolefin-based waxes. Waxes are mixtures of various long-chain, low-melting substances that are usually solid at ambient temperature but become low viscosity liquids at temperatures slightly above their melting temperatures. They are classified into two major categories: natural and synthetic waxes. Their classifications are indicated in Figure 1.

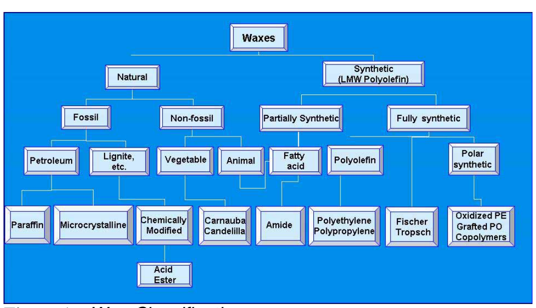


Figure 1. *Wax Classification*

Historically, conventional printing inks often incorporate waxes in letterpress, lithographic, screen, gravure and flexographic inks to impart mar-resistance and to improve slip and water repellency.

Because waxes, including non-functional LMW Polyolefins, normally have low surface energy and low viscosity properties, they are not only an important additive in conventional inks but also are an important component in digital printing. In electrophotographic printing, also called xerographic printing or xerography, wax serves as a key toner additive to improve fuser roll release and to improve toner fix. Waxes also have long been one of major components in thermal transfer ink ribbons. They provide lubrication to protect printheads, give100% ink transfer to the various printing substrates, and offer ink adhesion to both ink carrier and printing recording media. Additionally, wax is used in hot melt inkjet ink to improve image quality and rheological properties for office printing and 3D rapid-prototype application.

Xerographic printing is a process that generates and develops electrostatic toner images onto recording media. The basic steps for hot roll fusing xerographic engine are the following: 1) charging of the photoreceptor, 2) generating electrostatic images onto the photoreceptor 3) developing electrostatic images with toner (4) transferring toner onto the recording media (5) fusing toned images onto the recording media to form final images, and (6) releasing the recording media from the fuser roll. A typical toner consists of resins, colorants, charge-control agents, and functional additives. Wax, one of these functional additives, is a key component in a toner formulation. It provides release property to prevent toner offset onto the fuser roll in the fusing step. Specialty performance waxes can be used in conjunctions with release wax or alone to disperse pigment and charge-control agents into the toner resins, to improve toner charge stability, and to improve non-functional wax dispersibility in the toner resin. Furthermore, some high-performance functional waxes can be used to improve toner adhesion to substrate. Figure 2 illustrates the fusing step in xerography and the wax release function during the toner fusing step.

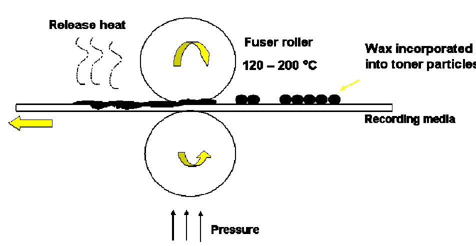
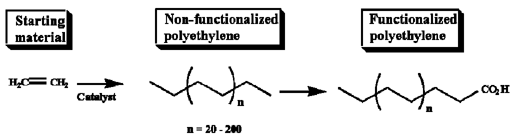


Figure 2. *LMW Polyolefin release function in toner fusing*

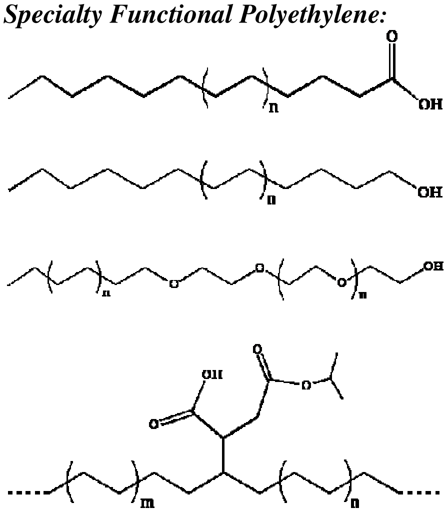
Non-functional waxes, including non-functional LMW Polyolefins (release wax), have low surface energy and low melt viscosity, making them ideally suited as release agent. However, the mixing and dispersing of non-functional waxes in the toner resin is often a great challenge. In order to obtain uniform wax dispersion in the toner resin, a compatibilizer is often required and preferred. Since polyester resin experiences much higher growth than styrene acrylic resin in current conventional toner design, this paper focuses on the use of specialty performance LMW Polyolefins as compatibilizers for toner polyester resins.

Chemistry

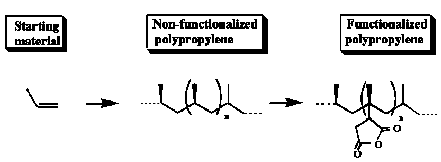
Polyethylene:



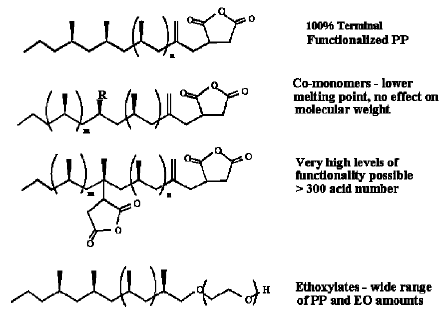
Specialty Functional Polyethylene:



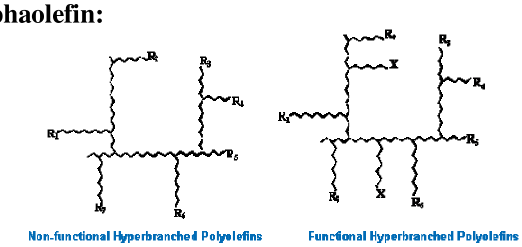
Polypropylene:



Specialty Functional Polypropylene Chemical Structures:



Polyalphaolefin:



(X is functional group such as OH, COOH, epoxide, ethoxylates etc.)

Experimental

Toner resin specimens were prepared by compounding polyester resin, wax (non-functional LMW Polyolefins), and specialty performance LMW Polyolefins in a Brabender batch mixer. Fracture surfaces of the compounded specimen were generated and inspected under a Scanning Electron Microscope or light microscope to reveal the size of dispersed wax domains and uniformity. The specimens' thermal behavior has been studied by Differential Scanning Calorimetry to understand the effect of compatibilizers on toner resin glass transition temperature.

Compositions:
Materials:

LMW Polyethylene: POLYWAX® 850 polyethylene (PW850 in short) as non-functional LMW Polyethylene (release wax) from Baker Petrolite.

Polyester resin: Crosslinked polyester ER508 from Dianal America and Linear polyester (proprietary material).

Specialty performance LMW Polyolefins studied as compatibilizers: all from Baker Petrolite.

Table 1: Specialty performance LMW Polyolefins as compatibilizers studied in this paper:

Chemistry Category	Product Name	Abbreviation	Function Level
Polyethylene Ethoxylate	UNITHOX® 720 Ethoxylate	U720	Low (HLB*=4)
	UNITHOX® 750 Ethoxylate	U750	High (HLB=10)
Maleic grafted polyolefin	CERAMER® 67 Maleic grafted polyethylene	C67	Low (Sap#*=77)
	CERAMER® 1608 Maleic grafted polymer	C1608	High (Sap#=190)
Polyalphaolefin	VYBAR® 103 Polyalphaolefin	V103	Highly branched

**HLB is the hydrophilic-lipophilic balance. The HLB value of 0 corresponds to a completely hydrophobic molecule, and a value of 20 would correspond to a molecule made up completely of hydrophilic components.*

**SAP# refers to saponification value or saponification number and it represents the number of milligrams of potassium hydroxide or sodium hydroxide required to saponify 1g of material under the conditions specified.*

Base formulations:

Specimens consist of polyester resin 90-95%, non-functional wax 0-5%, and specialty performance LMW Polyolefins 0-5%. Control specimens were prepared by mixing crosslinked polyester and 5% non-functional polyethylene POLYWAX® 850 polyethylenes.

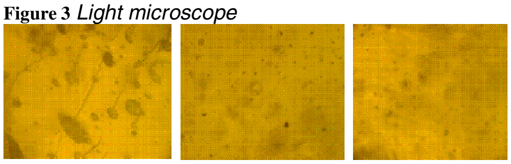
Results and Discussion

Comparison of various specialty performance LMW Polyolefin's' chemistry and their ability to compatibilize release wax in cross-linked polyester

UNITHOX ® Ethoxylate:

Figure 3 shows the comparison of wax dispersion in polyester resin with different levels of HLB polyethylene ethoxylates by light microscope.

Figure 3 *Light microscope*



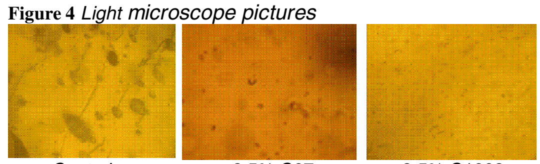
Control ***2.5% U720*** ***2.5% U750***

Light microscope demonstrates that both UNITHOX 750 and UNITHOX 720 Ethoxylates appear to improve the wax dispersion in polyester toner resin. However, higher functionality U750 ethoxylate improves the wax dispersibility more than low functionality U720 ethoxylate. It is clearly shown that non-functional polyethylene can be dispersed uniformly in the base resin and its domain size can be reduced by incorporating UNITHOX Ethoxylates. The results reveal that polyethylene with ethylene oxide functional groups appears to create a bridge between the polar polyester resin and the non-functional LMW polyethylene that improves dispersibility of release wax in the polyester resin.

CERAMER® Maleic grafted polyethylene

Figure 4 illustrates the dispersibility of non-functional polyethylene in the base resin by incorporating maleic grafted polyethylene by light microscopy.

Figure 4 *Light microscope pictures*



Control *2.5% C67* *2.5% C1608*

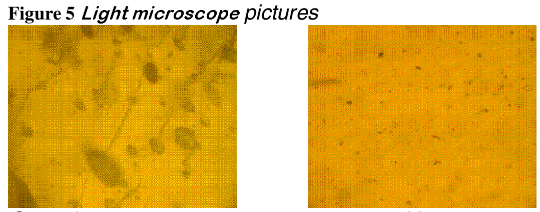
Light microscope results indicate that both high functional polymer C1608 and low functionality C67 polyethylenes improve the wax dispersion in the polyester resin. The acid functionality in the polyethylene seems to improve compatibility between non-functional polyethylene and polyester resin to assist dispersion of the release wax.

Polyalphaolefins

VYBAR ® Polyalphaolefin

Figure 5 demonstrates the effect of hyperbranched polymer VYBAR 103 Polyalphaolefin to compatibilize wax in cross-linked polyester base resin.

Figure 5 ***Light microscope*** *pictures*



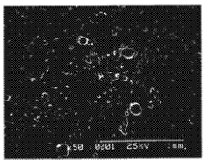
Control *2.5% V103*

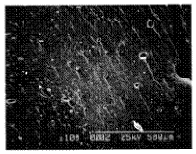
Highly branched polymer with wide polydispersity (V103 polyalphaolefin) appears to improve wax dispersion and change wax domain size in the polyester resin.

Polyester chemistry effect

Figure 6 demonstrates polyester resin chemistry effect on dispersing non-functional LMW Polyolefin (POLYWAX® 850 polyethylene)

Figure 6 *SEM micrographs comparison of wax domains in two types of polyester*





With *cross-linked polyester resin*   *With linear polyester resin*

In this study, we observed that wax dispersibility in linear polyester resin is better than that in cross-linked polyester resin. It appears that wax dispersion in polyester resin strongly depends on resin chemistry.

DSC Data

Specimens prepared with cross-linked polyester resin.

In this study, DSC is used as a tool to understand the effect of LMW Polyolefins on toner polymer glass transition temperature, which may have an impact on toner formulation and performance.

Table 2: Compatibilizer effect on polyester resin's Tg

Compound	Tg (°C)
Polyester resin	66.0
With 5% PW850	63.7
With 5% PW850/C67 (1:1)	63.7
With 5% PW850/U720 (1;1)	63.7
With 5% PW850/U750 (1:1)	63.4
With 5% PW850/Vybar103 (1:1)	63.5

DSC shows that the Tg of the polyester resin has a small down shift by adding LMW non-functional release wax. However, incorporating specialty performance LMW Polyolefins with compatibilizers in the formula does not further shift the polyester resins' Tg.

Specialty performance Low Molecular Weight Polyolefins as compatibilizers for dispersing polypropylene (PP) wax with polyester resin

In the above discussion, we observed that specialty performance LMW Polyolefins improved non-functional polyethylene dispersibility in polyester resin. In this study, we will discuss the effect of specialty performance LMW Polyolefins on dispersing PP wax in polyester resin. Samples were prepared by mixing cross-linked polyester resin, PP wax, and specialty performance LMW Polyolefins.

Table 3. Compatibilizer effect on PP wax in polyester resin

Compatibilizer	DSC(J/g)		
	Before pulverizing	After pulverizing	
		Classified	Fine powder
Control (polyester resin+ 4% PP wax)	1.19	0.88	3.84
Replace 2%PP with 2%U720	1.19	1.13	1.63
Replace 2%PP with 2%U750	1.19	1.34	1.4
Replace 2%PP with 2% C67	0.99	0.8	2.67
Replace 2%PP with 2% VYBAR 103	1.15	1.18	2.37

DSC data compared ΔH before pulverizing and after pulverizing to understand wax dispersion in polyester resin. The data indicated that wax remained in the polymer composition after classifying and ΔH did not change much between classified and fine for compositions containing specialty performance LMW Polyolefins. Clearly, UNITHOX ® 750 Ethoxylate and UNITHOX ® 720 Ethoxylate showed the most benefit for compatibilizing PP wax among all the materials studied here. Unithox 750 Ethoxylate proved to be the most effective compatibilizer in compatibilizing PP wax in polyester resin. This study illustrates that a compatibilizer assists wax incorporation and dispersion thereby reducing free wax. With reduced likelihood of free wax and a better dispersion of wax within the toner particle, more wax is available to improve release function during the toner fusing step.

Conclusion

Specialty performance LMW Polyolefins including UNITHOX ® 750 Ethoxylate, UNITHOX ® 720 Ethoxylate, CERAMER® 67 maleic grafted polyethylene and VYBAR ® 103 Polyalphaolefin improve both non- functional LMW polyolefin and polypropylene-based LMW polyolefin dispersion and domain size in polyester resin.

UNITHOX ® 750 Ethoxylate proved to be the best congruent agent among the materials studied for both polyethylene wax and polypropylene wax in polyester resin.

Resin chemistry has a strong effect on wax dispersion. LMW Polyolefins can be dispersed into special linear polyester resin more uniformly than into the cross-linked polyester.

Specialty performance LMW Polyolefins have a minor Tg shift when they displace non-functional release wax in a composition formulation.

Remarks

Light microscope and SEM images indicated that functional LMW Polyolefins improved POLYWAX® 850 polyethylene wax dispersion into the polyester resins. UNITHOX ® 750 Ethoxylate, CERAMER® 67 maleic grafted polyethylene, and VYBAR ® 103 Polyalphaolefin all show improvement in dispersing wax POLYWAX® 850 polyethylene, which is a very narrow melting range polyethylene.

Functional LMW Polyolefins appear to provide a bridge and interactions between non-functional LMW Polyolefins and polar resins such as polyester resins. UNITHOX ® 750 Ethoxylate and CERAMER® 67 maleic grafted polyethylene help to establish intermolecular forces between POLYWAX® 850 polyethylene wax and polyester resins. This hypothesis appears to be verified by light microscope, SEM, and DSC results in our study. The data shows that the non-functional release wax will not easily become free wax during toner processing and the printing process by incorporating specialty performance wax; therefore, it reduces photoreceptor contamination caused by wax and improves fusing release.

During our study, we found that processing with high mixing torque exhibited improved wax dispersion in polyester resins. Therefore, process conditions and equipment settings play an important role in wax incorporation. Optimized process conditions will help to disperse wax in the polyester resin.

Author Biography

Elizabeth Yuan *is a senior research chemist for Imaging and Industrial Coatings at Baker Petrolite Corporation in Sugar Land, Texas, USA , who is responsible for providing strategic advice for imaging and industrial coatings markets, identifying new applications, and developing new technology and materials. She joined the company after holding research positions at Xerox's Wilson Research Center in Webster NY and at Zeneca Specialty Ink Division. She received an MS from Eastern Michigan University in the area of polymer and coating technology, and a BS in polymer material from Beijing University of Chemical Technology. She has more than 25 patents and publications in electrophotographic printing, inkjet/thermal printing, and coatings.*

Sharon Hiergesell *is currently the Industry Manager for Imaging at Baker Petrolite Corporation in Sugar Land, Texas, USA. Before joining Baker Petrolite she was the Marketing Manager for Imaging Specialties at Reichhold, Inc., Research Triangle Park, in North Carolina. She has held various positions in Paper and Specialty Media, Print Quality Management, Color Program Development, and Chemical Analysis during her nearly twenty years of service at Xerox Corporation, in Webster, NY. Dr. Hiergesell has a PhD from Virginia Tech in Blacksburg, VA in the area of rotational spectroscopy of sulfur- nitrogen - fluoride molecules and holds several publications and patent in the areas of rotational spectra and electrophotography.*

Baker Petrolite is a division *of Baker Hughes Incorporated. The company is headquartered in Sugar Land, Texas and is noted for the specialty chemicals for oilfield services and many other diverse industries. Baker Petrolite's Polymers group is known for its specialty low molecular weight polyethylene, polypropylene, and polyalphaolefins.*