Palm Oil-Based Bio-Resin for Toner

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Abstract

Recently, research on innovative approach that enables sustainable printing for the well-being of the environment has garnered a lot of attention and development, including non-impact printing industry. Energy conservation and sustainable printing have prompted the industry to explore new technologies or materials for the printing devices and its consumables. This paper will focus on the bio-based toner resin which derived from palm oil-based derivative and the preparation of bio-based toner for electrophotographic printing. Two different alkyd polyester macromers derived from palm oil were used to co-polymerize with petroleum-based monomers to produce the hybrid bio-resins, with bio-based content up to 21% or more. Bio-toners were formulated using these resins followed by evaluation of the printing results from a laser printer. The properties analysis of the bio-resins showed promising and desirable results in comparison to the commercially available, petroleum-based toner resin. The printing quality and performance of the bio-toners did achieve the overall targeted specifications. The outcome of this study has proven that this unique proprietary technology was feasible for toner resin making, in terms of processes, cost advantage, the significance of bio-content incorporated and the printing performance of the bio-toner.

Introduction

The sustainability agenda is nothing new to the non-impact printing industry. It has plagued a myriad of other industries so long as they have an irreversible impact on the environment and the Earth as a whole. This global movement towards sustainable industrialization mainly arises from regulatory pressure from more developed nations, rising consumer demand due to heightened awareness in the area of environmental conservation, and intense rivalry among competing firms to pioneer and lead the pack in providing greener products to consumers.

Several initiatives in the area of sustainable printing include the introduction of new printing/copying devices, which consume much less power than their predecessors through the use of lower temperature fuser units. The lower fuser temperatures of these new devices are further accompanied by new designs of toners made from resins with significantly reduced viscosity, thus exhibiting a more stringent fusing performance than before. This poses a new challenge to industry players as the technical sophistication of toner is pushed to the limits where a new balance between fusing and offset must be achieved. While these devices are designed to conserve energy as a critical natural resource to support life, there are others who focused on the use of more bio-degradable materials as sustainable alternatives to replace limited and non-renewable derivatives from fossil fuel sources. For instance, non-critical plastic components in printing/ copying devices, which were formally made from petroleum-based raw materials, are now manufactured using poly-lactic acid (PLA) derived from renewable resources [1].

Despite numerous efforts implemented to reduce environmental impact arising from electrophotographic printing, there is still very little research work being done to address one of the main global issues as compared to other areas in this field – development of alternative consumables such as sustainable toners which are able to deliver equivalent print performance as toners made from resins derived from fossil fuel sources. Several attempts on bio-based toners have been introduced in the market but due to commercial unviability, high costing and complicated technology which is still at its infancy, limited success has been achieved thus far to really encourage the use of bio-based resins in making toners and to internalize this as a norm among industry players and consumers.

This paper focuses on addressing the technological complication of developing a bio-based Palmotone® toner resin. More specifically, it will present a study on the use of modified palm oil derivative, an alkyd polyester, to replace petroleum-based monomers to prepare a bio-based resin for use in melt pulverized or conventional toner production. Palmotone® is a registered trademark of Jadi Imaging Technologies Sdn Bhd, Malaysia, which includes bio-based products of melt pulverized toner, toner resin and chemically prepared toner (CPT) [2].

Experimental

The bio-based alkyd polyester macromers with alkenyl group were prepared by polycondensing polycarboxylic acids, polyols and free fatty acids from palm oil derivatives [3]. These macromers are enriched with unsaturated alkenyl (C==C) groups on either main chains or side chains, which can be copolymerized and crosslinked by free radical reactions with various vinyl monomers. By proper selection of free fatty acids and varying the processing conditions, various types of macromer can be prepared with different physical and chemical properties. These properties are important in the characteristic design of bio-based toner resin, and then the final bio-toner. In this paper, two types of alkyd polyester macromer were prepared and labeled as APM1 and APM2.

Hybrid bio-based toner resins with different bio-content were synthesized by incorporating macromer APM1 and APM2 in different amount. Two different toner resins, HR1 and HR2 were prepared using APM1 and having estimated bio-content of 5 and 12 percent, respectively. Another toner resin, HR3 was incorporated with around 21 percent of bio-content by using APM2.

The preparation started with bulk polymerization process where styrene, butyl-acrylate and methyl methacrylate acid monomers were reacted under 130 to 140^oC for 60 minutes. Optionally, initiator and cross linking agents could be added to move forward the reaction. After certain conversion of reaction was achieved, it was then followed by a solution polymerization process where the resultant solution was reacted with the APM mixture, which had been prepared separately using the macromer,

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initiator, cross-linker and solvent. This mixture was added slowly across 180 to 300 minutes at a controlled process temperature of around 110°C. The reaction was allowed to age for a period of time to complete the reaction before it was dried in a laboratory-grade vacuum oven to produce the dried resin samples. Upon completion of the drying stage, the solidified resins were then crushed with a pilot-grade mechanical grinder to give irregular granulates of 1.0 to 5.0mm in diameter. The simplified process flow diagram is showed in Figure 1 below.

The properties of the bio-based resin samples were measured and compared to commercially available petroleum-based resins. Some of the resin properties measured include the glass transition temperature (T_g) by Differential Scanning Calorimetry (DSC) instrument, molecular weight distribution (MWD) by Gel Permeation Chromatography (GPC) instrument, melt flow index (MFI) with 2.16 kg load, viscosity against temperature profile from Capillary Flow Tester, acid number (AN) by KOH titration and THF insoluble fraction percentage.

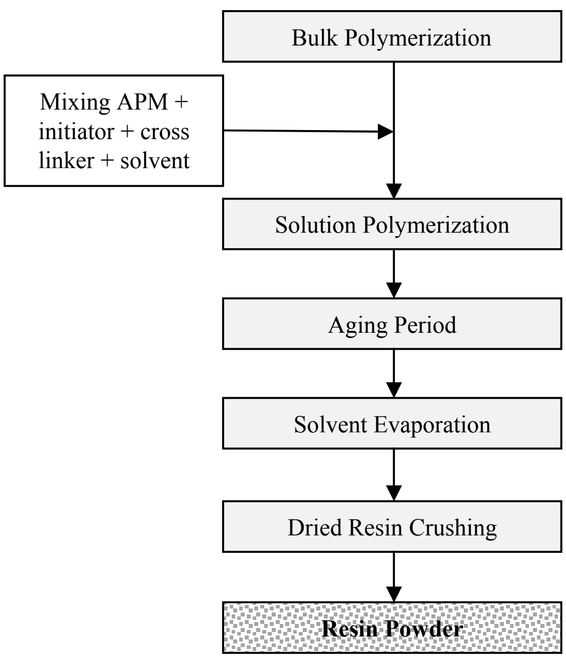

Figure 1. *Simplified process flow diagram for the hybrid bio-resin preparation*

In the subsequent stage of toner-making, bio-resin sample HR1, HR2 and HR3 were processed into toner T1, T2 and T3, respectively with the same processing parameters using pilot-scale equipment. As per melt-pulverized toner production method, the bio-based resin samples were pre-mixed in a Brabender mixer with other raw materials such as charge control agent to impart tribo-charge and wax for releasing effect. If magnetic property is required for controlling toner transfer, reasonable quantity of magnetite or iron oxide may be included in the pre-mix. Since this study was carried out on a magnetic mono-component system, an appropriate amount of iron oxide was also added in the pre-mixing step. The pre-mixed materials were melt-mixed in a Buss kneader at specific temperatures, feed rate and screw speed, followed by ambient cooling. The brittle output material was then broken down into flakes and grinded before being classified into the desired particle size. Lastly, the classified base products were blended in a pilot blender at specified blending speed and duration, together with other external additives such as silica to improve toner flow, charge stability and anti-blocking effect, as well as appropriate metal oxides or stearates for charge stability and drum cleaning properties.

The properties of toner samples were measured and compared against the properties of a commercial petroleum-based toner that was used as a benchmark. Properties measured include particle size distribution, sharpness index, tribocharge, melt flow index and apparent density. In addition to properties comparison, the toner samples were subjected to full cycle printing test and the results were evaluated against the benchmarked petroleum-based toner on a magnetic mono-component printer, HP® 1022 laser printer with print speed of 18 pages per minute (ppm). Print quality attributes such as image density, grayscale, background, fusing performance, offset properties were analyzed and compared to the benchmarked toner.

The bio-based content of the toner resins and its toner products were analyzed and estimated based on the international standard of ASTM D6866-10. This standard derives a ratio of the amount of radiocarbon (14C) in the sample analyzed to that of a modern reference standard, which defines pMC (percent modern carbon) [4].

Results and Discussion

Table 1 below summarizes the estimated bio-content for all toners, hybrid resins and alkyd polyester macromers discussed in this paper. The bio-content percentage has met the minimum of at least 20% requirement as bio-product, which was defined by some of the international standards. For examples, the BioPreferred® Program by the United States Department of Agriculture (USDA) [5] and DIN CERTO by the German Institute of Standardization [6].

Table 1. Summary of the estimated bio-content

Toner (~bio-content %)	Hybrid resin (~bio-content %)	Alkyd polyester macromer (~bio-content %)
T1 (~ 3 – 5)	HR1 (~ 5)	APM1 (~ 81)
T2 (~ 10 – 12)	HR2 (~ 12)	
T3 (~ 19 – 20)	HR3 (~ 21)	APM2 (~ 77)

The properties of APM1 and APM 2 are shown in Table 2. APM1 was synthesized using a combination of free fatty acids with about 30% of unsaturated type, whereas APM2 was having a nearly 100% unsaturated type fatty acid. Due to higher reactivity and more active sites available for grafting, APM2 shows much higher of molecular weight distribution (MWD) than APM1. In addition, APM2 appears semi solid but APM1 is able to flow under room condition.

Table 2. Properties of the alkyd polyester macromers

Properties	APM1	APM2
Molecular weight distribution (MWD), Daltons		
$Mw \times 10^{-3}$	1.8 – 2.2	12 – 40
$Mn \times 10^{-3}$	0.70 – 0.85	1.1 – 1.4
$Mp \times 10^{-3}$	0.80 – 1.1	1.3 – 1.5
Acid number (AN), mgKOH/g	30 – 40	50 – 60
Appearance (~ 25°C)	Liquid	Semi-solid

In the hybrid resin synthesis, the characteristics of HR1 and HR2 were compared based on the same APM used. The resin properties results showed that higher amount of APM1 incorporated resulted in a tougher character of the resin. This is proven by the higher viscosity, molecular weight distribution, THF insoluble fraction and lower melt flow index of HR2 compared to HR1. This observation could be caused by stronger cross-linking effect between the bio-macromer and the monomers, which the bio-macromer has shown the ability to intensify the grafting process. Because of this, the cross-linker amount added for HR2 was reduced compared to HR1 to fine-tune its properties towards the commercial reference sample. The basic properties of the hybrid resin samples are shown in Table 3.

Hybrid resin HR3 was prepared using a different APM with much higher molecular weight distribution and with higher loading of the bio-macromer. This example demonstrates the viability of having high bio-content in bio-resin formulation by using this unique technology. The incorporation of APM2 was able to maintain or improve the overall desirable toner resin properties. In addition, APM1 and APM2 are miscible in solvent and hence, the processing is made easy. Since the commercial resin reference is a mixture of high and low molecular weight components (bi-modal), it shows a different distribution compared to the single modal distribution of the hybrid resins. The bi-modal distribution has also contributed to the high poly-dispersity.

In the toner making processes, similar raw materials, formulation and processing conditions were applied to make T1, T2 and T3 samples. The toner particle size, D_{50} was well-controlled between 10 to 11µm with good sharpness index in order for reasonable quality comparison. Noticeably, the rheology of the toner samples has changed significantly from its original resins after processing. The melt flow indexes were reduced and the toner needed a higher temperature to melt-flow than its resins. This phenomenon could be explained from the use of the chromium based azo complex charge control agent (CCA) in the toner formulation. Due to the heat assisting chemical reaction during extruding process, certain degree of cross-linking happened on the functional groups between resin and CCA. All other toner properties were similar and close to the reference. Furthermore, the samples were easily crushable during pulverizing and classifying processes.

The prepared toner samples were further evaluated in printing tests. The monochrome image density measured by densitometer was 1.45 to 1.60 and background of 0.09 to 0.10, fusing and fixing

Table 3. Properties of the hybrid resin and reference samples

Properties	Reference	HR1	HR2	HR3
Molecular weight distribution (MWD), Daltons				
$Mw \times 10^{-3}$	130	187	203	115
$Mn \times 10^{-3}$	3.2	20.4	12.9	8.3
$Mp \times 10^{-3}$	4.4	132	133	141
Mw/Mn	40	9.2	18	16
Glass transition temperature (Tg, mid-point), °C	61.7	63.6	68.5	65.0
Melt flow index (MFI), g/10min	8.5 @ 145°C	12.0 @ 160°C	6.6 @ 160°C	7.5 @ 180°C
Acid number (AN), mgKOH/g	8.3	10.4	12.4	8.5
THF insoluble fraction, %	5.1	2.2	17.6	30.0
Viscosity (flow tester)				
Tfb, °C	102.4	103.5	104.1	107.6
$T_{1/2}$, °C	129.1	137.0	138.5	137.2

Table 4. Summary of the toner properties

Properties	Reference	T1	T2	T3
Particle size distribution (PSD)				
D_{50}, µm	9.3	10.9	10.8	10.5
5 µm, %	8.2	4.8	3.3	4.3
Sharpness index, D_{95}/D_5, µm	4.3	3.3	2.7	3.5
Tribocharge, µC/g	-22	-21	-17	-20
Apparent density, g/cm³	0.53	0.52	0.55	0.54
Melt flow index (MFI), g/10min	15.4 @ 150°C	7.4 @ 190°C	21.8 @ 200°C	6.3 @ 210°C

tests by adhesion tape testing were moderate around 60 to 70% and good grayscale density. The quality of toner fixing can be improved by using a sub-binder with lower viscosity or creating a bi-modal system by mixing the hybrid resins with another lower molecular weight portion. No offset problem was observed during the printing tests.

Conclusions

This paper reveals the feasibility of using a bio-based alkyd polyester macromer derived from palm oil to prepare the bio-resin for toner applications. The proprietary and relatively cost advantage technology is capable to produce good quality of toner products and yet, it is flexible enough to alter the resin and toner properties to suit various printing requirements in the market. Based on the current research findings, the bio-content can be further increased to a significant level and this will enhance the value of the products towards sustainable environment.

Jadi has successfully scale-up and commercialized Palmotone® range of products, including chemical toners and toner resins. The intellectual properties of this invented technology have been patented.

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Author Biography

Jaan Soon Tan is the Senior R&D Manager in Jadi Imaging Technologies Malaysia. He has his Bachelor's degree in Chemical Engineering and received his Master's Degree in Mechanical Engineering in 2001. He has been involved in various toner research activities in the past 7 years.