Novel plant-based dialkyl hydroxylamine antioxidant

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Abstract

Dialkyl hydroxylamine antioxidant (AO) has received much attention from the polyolefin industry due to its super non-yellowing properties and resistance to gas fading. This AO has found wide acceptance as a standard in several high-end film and fiber applications based on polyolefins.

However, first generation hydroxylamine is based on tallow and this has raised concerns among vegetarians, some religion faiths, mad-cow disease watchers, and so on. To introduce this technology into more applications, a new type of hydroxylamine, not of animal origin, is available to the polyolefin industry.

Chitec now offers a novel plant-based hydroxylamine AO based on sustainable palm oil which has been registered with TSCA, REACH, NDSL, TCSI and FDA over the past five years.

In this presentation, the plant-based AO will be compared with the tallow-based product with respect to both composition and antioxidation efficiency.

In addition, its synergistic effect in combination with secondary AO and light stabilizer will be discussed using a melt strength model which is a critical aspect in film production.

Other experimental results will be discussed including gas fading, stretchability, retention and so forth, to show that the plant-based hydroxylamine is an ideal AO for both film and fiber production.

Introduction

Unlike commodity hindered phenolic AO, dialkyl hydroxylamine AO does not discolor when it comes in contact with NOx. In other words, it is strongly resistant to gas fading. This advantage makes dialkyl hydroxylamine AO popular in polyolefin-based fiber and film industries where gas fading is severe.

The structure of dialkyl hydroxylamine is hawk-shaped and is not an efficient processing stabilizer in protection of melt-flow, for example, which is critical for multiple passes testing. However, it is an excellent protector of melt-strength, which is one of the most critical properties for film and fiber processes, besides color.

In U.S. Patent No. 4,876,300, dialkyl hydroxylamine shows powerful protection of color in comparison to hindered phenolic AO or hindered amine light stabilizer (HALS). In example 29, PP that contained hindered phenolic AO + HALS went from YI=12.5 to 51.3 after five extrusions at 280°C while dialkyl hydroxylamine + HALS went merely from YI=7.4 to 9.7.

First generation hydroxylamine is a derivative of tallow amine, as described by its chemical name. The word “tallow” has raised concerns among customers especially vegetarians, some religious groups, and those concerned about mad-cow disease. A hydroxylamine antioxidant of non-animal origin has been long expected by the market.

The concept of tallow replacement has been adopted in other products, for example hydrotalcite DHT-4A was used extensively in the US five years ago. But it has been replaced by DHT-4V in almost every food contact polyolefin application, if not all, in the US nowadays. V stands for vegetable grade.

Chitec observed this opportunity and initiated a project to develop a dialkyl hydroxylamine with no animal origin in 2012. We replaced tallow amine with palm-oil amine which not only makes it non-tallow but also green in nature as the plant-derived feedstock is sustainable. Replacing the amine raw materials also changes the composition of dialkyl hydroxylamine, hence it requires a new chemical name and a new CAS Registry Number (RN). The first generation dialkyl hydroxylamine carried the name *Amines, bis(hydrogenated tallow alkyl), oxidized* and was listed with CAS RN 143925-92-2. The vegetable version of dialkyl hydroxylamine is named slightly different; *Amines, bis(hydrogenated palm-oil alkyl) hydroxy* with a CAS RN 1374859-51-4.

Dialkyl hydroxylamine is a UVCB substance comprising at least eight constituents. Even with similar raw material, i.e. dialkylamines, the composition of palm oil-based hydroxylamine AO is still slightly different from the tallow-based one. The three major constituents are hydroxylamines, nitrones, and the raw material dialkylamines. Palm oil-based dialkyl hydroxylamine contains 73% hydroxylamines vs. 67% in the tallow-based dialkyl hydroxylamine[1]. But palm oil-based dialkyl hydroxylamine has a higher content of nitrones at 14% vs. 5%. The analysis is completed by LC-MS.

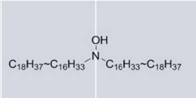
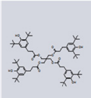
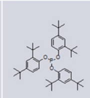
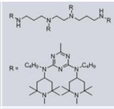
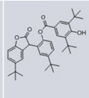
Because of the difference in composition and CAS RN/name, a complete new global registration is required for this palm oil-based hydroxylamine AO. The registration process was initiated in December 2012 by obtaining a CAS RN, and in following three years, REACH, TSCA, and NDSL were obtained in sequence. In July 2016, another milestone was achieved as this palm oil-based hydroxylamine AO acquired FDA clearance for food contact applications in PP and HDPE with a 0.1% maximum dosage. The last goal is to receive EFSA's food contact authorization in 2018 and this initiative is estimated will cost 0.5 million dollars to complete. Ever more complicated and expensive global chemical inventory registration has created a major hurdle for a small company like Chitec to innovate and invent.

Experimental section

Palm oil-based and tallow-based dialkyl hydroxylamine AOs were compared for protection of melt-strength and color. Other AO packages containing traditional phenolic AO, HALS and lactone-based AO respectively were also compared. The experiment was conducted using virgin PP (MI = 16.47) available from Formosa Plastics by using twin extruders under a nitrogen blanket.

The dosage of each AO package is 1,000 ppm. The respective composition is shown in Table 1. All of the formulations contain phosphite AO 168 as a secondary AO by varying the primary AO which is palm oil-based hydroxylamine as AO-1, tallow-based hydroxylamine as AO-2, hindered phenolic AO 1010 as AO-3, HALS-1 as AO-4, and the combination of 1010 plus a lactone-based AO as AO-5. The last two are also proprietary products of Chitec. Their chemical structures are attached. The last two were tested because they are known as AOs with high color stability. Beside the AO, all of the formulations contain 200 ppm hydrotalcide as an acid scavenger.

Table 1. Composition of AOs

	Palm-based hydroxylamine	Tallow-based hydroxylamine	1010	168	HALS-1	Lactone
						
AO-1	1			2		
AO-2		1		2		
AO-3			1	2		
AO-4				2	1	
AO-5			1	2		0.2

Melt-strength analysis

The melt-strength analysis was conducted by an elongation rheometer, the Rheotens 71.91 from Goettfert, at 180 °C. The result is shown in Figure 1. "Force" as indicated by the Y axis stands for melt-strength which is a function of velocity. Overlapping lines of AO-1, AO-2, and AO-3 indicates that palm oil-based dialkyl hydroxylamine AO, tallow-based dialkyl hydroxylamine AO, and hindered phenolic AO gave similar melt strength performance. In other words, even though they possess different structures they provide the same protection on PP's melt-strength.

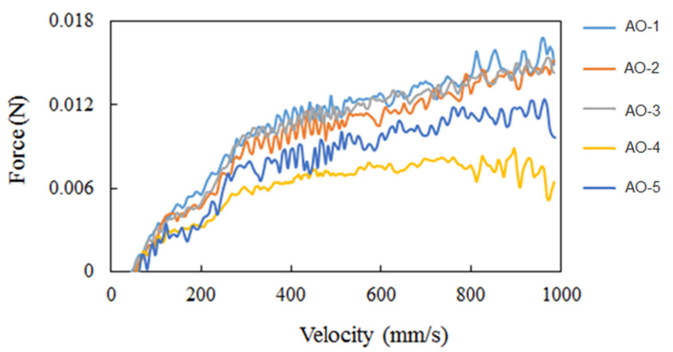


Figure 1. Results of melt-strength analysis

AO-4, where hydroxylamine AO and hindered phenolic AO were replaced by HALS, a known long-term heat stabilizer, shows a different curve which indicates inferior melt-strength performance. In other words, HALS is not efficient in protecting melt-strength at 180 °C.

Most surprisingly, with the addition of a small amount of a novel lactone based-AO, the melt-strength of AO-5 greatly deteriorated. This is the opposite of our prediction as lactone-based AO is known to be superior as a melt-flow property protector to hindered phenolic AO. In AO-3, hindered phenolic AO shows good performance.

Shear experiments

Another way to compare these five AO packages is to run shear experiments by using high pressure capillary rheometer, Rheograph 2003 from Goettfert, at 180 °C, 190 °C and 200 °C. The results are shown in Figure 2. No meaningful differences were found among these five spectra which indicates a similar polymer structure.

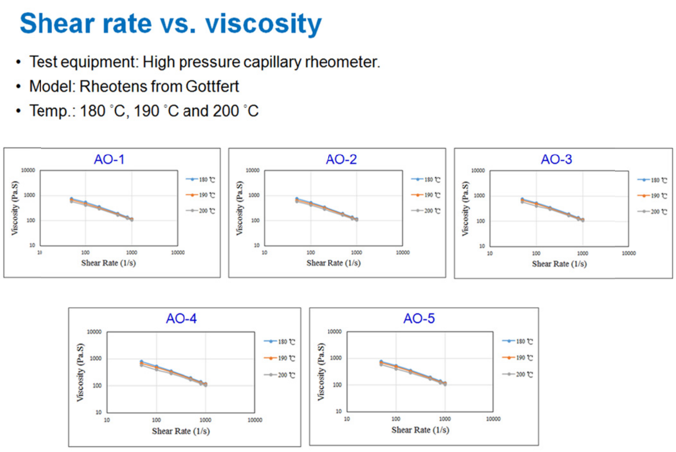


Figure 2. Result of shear experiment

Gas fading experiment

These five specimens were placed in a gas-fading reactor in which nitrogen oxides were generated by sodium nitrate reacting with sulfuric acid. The experiment ran for 24 hours at room temperature. The results are shown in Figure 3. Only the specimen containing AO-3 showed severe yellowing in contrast to the other four AO packages. This result is predictable as hindered phenolic AO is known to turn yellow on exposure to nitrogen oxide. Specimens containing AO-1 and AO-2 again are shown to be resistant to gas-fading without any visual differences. That means the byproducts of palm oil-based dialkyl hydroxylamine and tallow-based amine do not affect the performance of gas-fading resistance.

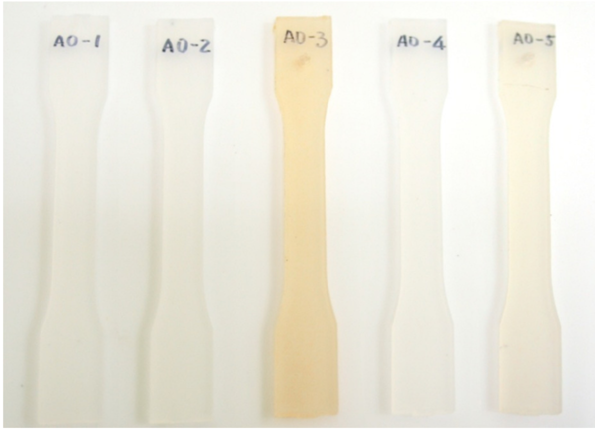


Figure 3. Results of the gas-fading experiment

Conclusion

1. A new palm oil-based dialkyl hydroxylamine AO is commercially available which is slightly different from the tallow-based predecessor in terms of composition.

2. The difference in composition between them does not affect AO efficiency in protecting melt-strength of polypropylene in combination with a secondary phosphite AO, as demonstrated by the rheometer.

3. Both palm oil-based and tallow-based dialkyl hydroxylamine AOs are highly resistant to gas fading in contrast to hindered phenolic AOs.

Reference

1. NICNAS, File No. NA/592, Full Public Report “Amines, bis(hydrogenated tallow alkyl), oxidised” , May 1998.