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Controlling polypropylene rheological properties by promoting organic peroxide during extrusion with improved properties for automotive applications

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Controlling polypropylene rheological properties by promoting organic peroxide during extrusion with improved properties for automotive applications

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Abstract. Excellent stability and process-ability of Controlled-Rheology Polypropylene (CRPP) was mandatory parameters especially for automotive application. Selected organic peroxide which was used to control the rheology of PP should perform good stability in physical properties due to pre-process of compounding for automotive application. The common organic peroxide that widely used is 2,5-dimethyl-2,5-di-tert-butylperoxyhexane (DHBP). However, the problems that usually encountered are Melt Flow Index (MFI) stability, color stability, initial color, izod impact properties, and the odor which come from decomposition process. Research and Development (RND) team of PT Chandra Asri Petrochemical, Tbk (CAP) did the study to change the type of organic peroxide to 3,6,9-triethyl-3,6,9,-trimethyl-1,4,7-triperoxonane (TETMTPA) which was intended to improve these inferiorities when using DHBP. The results indicate similar MFI stability, similar color stability, better initial color, higher izod impact properties, and less odor when using TETMTPA than DHBP. This superiority is very applicable particularly for automotive application. Detailed analysis about volatile decomposition product from both peroxide indicated CRPP with TETMTPA has lower volatile compound which result lower odor level than CRPP with DHBP.

Keywords: rheology, Melt Flow Index, DHBP, TETMTPA, odor

1. Introduction

Polypropylene (PP) produced in conventional reactors by using fourth generation of Ziegler Natta (ZN) catalyst system presents relatively high Molecular Weight (MW) and broad Molecular Weight Distribution (MWD). These features generate high melt viscosity (low MFI) which makes them unsuitable for commercial end-use such as fiber spinning, blown film, and injection-molded thin walled product. The MWD largely determines the rheological properties of PP melts and many physical properties. Therefore, this parameter must be controlled to improve the material response during processing and to achieve the diversity in polymer grades suitable for the different applications of PP. Controlling MWD of PP can be done economically by post-reactor operation such as reactive extrusion. This technique incorporate peroxide to induce controllable degradation of PP chains which efficiently result in polymer with tailor-made properties [1].

Organic peroxide is widely used to control the rheological properties of PP as well as polyethylene (PE). PE is an easily crosslinking polymer when organic peroxide is promoted, contrary with isotactic polypropylene (iPP) which is considered until very recently as a non-crosslinking-able polymer due to fact that the β-scission degradation process predominated over the crosslinking mechanism [2]. Therefore, organic peroxide acts as cracking agent in this PP case. The modification of molecular structure of PP during reactive extrusion after polymerization by the action of peroxide-generated radicals is known as Controlled-Rheology Polypropylene (CRPP) [3-6]. When PP resin and peroxide is melt-extruded, the peroxide thermally decomposes to produce peroxy radicals that attack the polymeric chain then decrease the molecular weight. Statistically, the larger molecular weight chains are cleaved more than low molecular weight chains, resulting in the overall effect of a decrease in the average molecular weight and a narrowing of the MWD [6-7]. This process converts the low MFI commodity resin to polymer with higher MFI (up to 100 times the original value) [8].

CRPP has good process-ability because of less elasticity and less shear sensitivity. CRPP also has less part warpage and better physical properties such as heat deflection temperature, and accurate dimensional stability [9-10]. These all properties are required for automotive applications.

It is necessary to have sufficient stabilization in order that direct recycling PP –which is commonly occurs at pre-process of compounding at automotive application - presents no problem such as significant change in molar mass, alteration to the polymer chains or morphology [11]. To study this behavior, the PP rheological properties were determined by multiple extrusions.

Some attention should be addressed to the peroxide especially on decomposition substances and the performance of end product. The decomposition substance of organic peroxide is the item that needs to be considered especially related to the acceptance of end product especially for the application requiring stringent requirements such as for food contact, automotive application, etc. It is not advisable if the peroxide decompose to be high level of volatiles compound which remaining in the end product because it give rise to odor and taste problem or even worse if toxic. So, the present work aims to compare the odor level on the use of organic peroxide at PP production.

2. Methods

2.1. Materials

Commercial PP Trilene® BI9.0GA was used and supplied by our PP production of PT Chandra Asri Petrochemical at polymer plant site. The physical properties of the product are shown in table 1.

Table 1. Physical properties of PP Trilene® BI9.0GA

Physical Properties	Test Method	Unit	Value
Melt Flow Index (230 °C / 2.16 kg)	ASTM D 1238	g/10 min	9
Density	ASTM D 792	g/cm^3	0.9
Tensile Yield Strength (@50 mm/min)	ASTM D 638	MPa	27
Hardness, Rockwell	ASTM D 785	R-Scale	80
Melting Temperature	ASTM D 3418	°C	163

The organic peroxide is 2,5-dimethyl-2,5-di-tert-butylperoxyhexane (DHBP) and 3,6,9-triethyl-3,6,9,-trimethyl-1,4,7-triperoxonane (TETMTPA) were supplied from our additive vendor. DHBP is the organic peroxide which is commonly used in production of CRPP and polymer grafting. DHBP is our existing cracking agent in production of CRPP. TETMTPA is new generation of organic peroxide that claimed generates less volatile, improved safety and organoleptic profile, and food contact approved. The properties comparison of DHBP and TETMTPA are shown in table 2.

Table 2. Physical properties of DHBP vs. TETMTPA

Properties	Unit	DHBP	TETMTPA
Molecular weight	g/mol	290	264
Density, 20^{o}C	kg/m^3	870	875
Viscosity, 20^{o}C	MPa.s	6.4	5
Active oxygen	%	10.14	7.3
SADT*	$^\circ$C	80	110

*Self-Accelerating Decomposition Temperature

2.2. Reactive Extrusion Process
For extrusion, a twin screw extruder at PP production plant from Kobe Steel was used. The normal capacity is 20 ton/hour with screw speed was fixed at two fixed speed at 500 rpm and 375 rpm. During production, initial temperature of extruder is 100^{o}C and increase to peak point at 250^{o}C. Prior to extruder, feeding facility for the liquid peroxide consists of pump and tank. The liquid peroxide was diluted by mineral oil then fed to the feed zone of the extruder at the predetermined rate by the liquid additive feed pump which is diaphragm type. The concentration of peroxide was based on target of MFI at 33. Multiple extrusions test with single screw laboratory mini-extruder was done to analyze for the stability of CRPP's properties. Each polymer resin from virgin toward multiple extrusions (1st, 3rd, and 5th) has to be analyzed for some parameters like MFI, YI, izod impact, and odor level.

2.3. Melt Flow Index (MFI)
MFI values are measured based on the reference: ASTM D1238 using Tinius-Olsen Melt Indexer. This test method covers the determination of the rate of extrusion of molten thermoplastic resins using an extrusion plastometer. After a specified preheating time, resin is extruded through a die with a specified length and orifice diameter under prescribed condition of temperature, load, and piston position in the barrel. For PP, the temperature is at 230^{o}C and the load is 2.16 kg. MFI value is in grams per 10 min. Longer polymer backbone chain needs higher energy used to flow which indicates the material is more viscous (low MFI), and vice versa. The test is done to determine successfulness of peroxide to increase MFI.

2.4. Yellowness Index (YI)
Visually, yellowness is associated with scorching, soiling, and general product degradation by light, chemical exposure, and processing. Yellowness Index is a number calculated from spectrophotometric data that describes the change in color of a test sample from clear or white toward yellow. Higher value of YI indicates more yellow and lower value of YI indicates less yellow or whiter. We use Nippon Denshoku Colorimeter to calculate YI with ASTM E313 as reference. Higher YI indicates more yellow color.

2.5. Izod Impact
The test is done to determine the resistance of materials from impact load. The test uses "standardize" pendulum-type hammers, mounted in "standardize" machine, in breaking standard specimen with one pendulum swing. Automotive application will need higher izod impact due to resist impact load in case of collision. The unit of izod impact is in J/m or kg-cm/cm.

2.6. Odor Level
We use organoleptic test to determine odor level of sample. Organoleptic testing refers to subjective evaluations that need individual experience by their sensing (including taste, sight, smell, and touch). The odor level is determined by selected tester or panelist and can be helped by standard sample. The sensing of tester or panelist is reevaluated periodically to ensure the consistency of testing activity. The

standardize PP resin with specific odor level is used as reference to help the tester to determine the odor level of the sample. The standard consists of five level of odor with scale 5 is the highest and 1 is the lowest level of odor.

3. Results

In order to convert MFI from 9 to 33, based on our historical data, we used about 300 ppm concentration of DHBP as our existing organic peroxide. TETMTPA as new organic peroxide at first also use same dosage with DHBP but cannot achieve the MFI target. Then slowly increase the dosage till we can achieve the MFI target by 400 ppm of TETMTPA. TETMTPA need higher dosage since it has lower active oxygen which will lead to generate lower peroxy radicals. The result analysis as comparison of multiple extrusions of those two types of peroxides is shown in Figure 1.

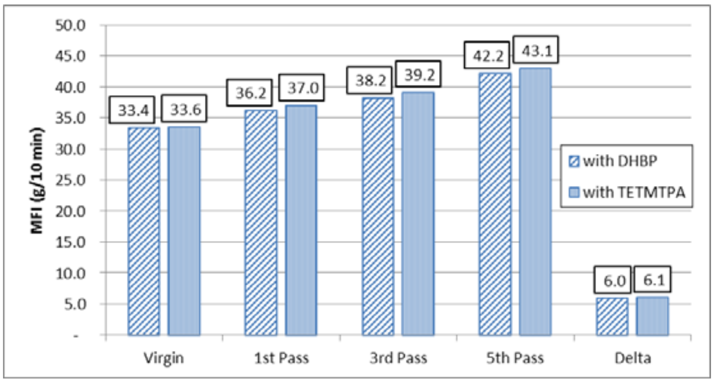

Figure 1. MFI properties of PP end-target with 33 MFI

We conduct multiple extrusions to see MFI stability. After done every pass, MFI value will increase since the polymer will slightly degrade due to heat in extrusion process. Degradation followed by chain scission that generates lower polymer chain length which cause higher MFI value. Good MFI stability will be indicated by smaller delta value of 1st pass and n-th pass, in this activity we multiple extrusion till 5th times (5th pass). Delta value of MFI for CRPP with TETMTPA and DHBP is similar which indicate that MFI stability of CRPP with new TETMTPA is similar than that of existing DHBP.

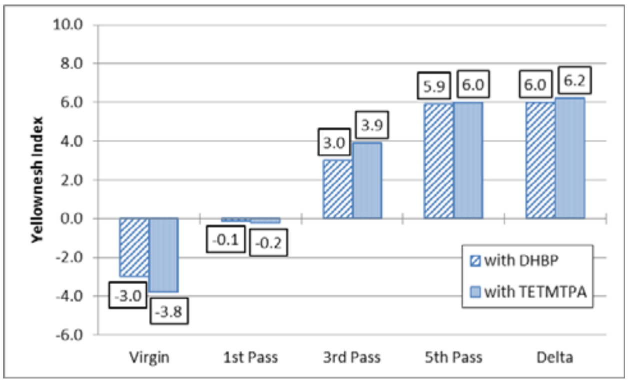

Figure 2. YI of PP end-target with 33 MFI

Initial color of CRPP as shown at virgin YI of figure 2 shows that CRPP with TETMTPA is whiter than CRPP with DHBP. It is caused by the degradation of polypropylene with cyclic ketone peroxides (TETMTPA) results in less yellowing than comparable processes employing their noncyclic ketone peroxides (DHBP) [13]. However, multiples extrusion test indicates those two TETMTPA and DHBP gave similar delta value meaning that they gave similar color stability.

Table 3. Odor test by Panel of PP end-target with 33 MFI

Person	**CRPP with DHBP**	**CRPP with TETMTPA**
Man-1	4	2
Man-2	4	3
Man-3	4	2
Man-4	4	2
Man-5	4	2

As shown at table 3, odor test by panel (5 panelists) is done and give the result that CRPP with TETMTPA was lower odor level than CRPP with DHBP. The statement was supported by result analysis of volatile decomposition from DHBP and TETMTPA (data not shown due to confidentiality). Apart from methane and ethane (C1 + C2), both peroxides produce different decomposition product. Volatile like t-butanol and acetone will partially remain in the final product and give rise to odor and taste problem [12]. This is undesirable, especially for certain end uses such as for the manufacture of articles or component part for the automotive industry [13].

According to decomposition mechanism of DHBP [14], DHBP will undergo homolytic reaction producing two molecules of tert-butyl and one alkoxy radical. The further reaction, radical chain continues by hydrogen abstraction (α-decomposition) from the substrate forming tert-butyl alcohol (tert-butanol) and alkyl radical. The other decomposition of tert-butyl by β-decomposition simultaneously forms acetone and methane radical, which decomposes further to form methane and alkyl radical [14]. The following compounds generated during decomposition of DHBP, such as t-butanol, acetone and methane, will give a strong odor level. Thus, CRPP with TETMTPA had significantly lower odor level than CRPP with DHBP.

TETMTPA also gives higher izod impact properties than DHBP, 406 vs 183 J/m. This higher value will give high resistance due to impact load when use for automotive application. Higher value of izod impact with balance with other properties is the desired requirement especially for automotive application.

4. Conclusions

With temperature profile at extruder from 100^{o}C to 250^{o}C as the operating condition, it was concluded that comparison using TETMTPA and DHBP as rheology controller to achieve similar MFI target for CRPP production resulting some points:

- TETMTPA gives similar MFI stability and color stability than DHBP
- TETMTPA gives better initial color to DHBP
- TETMTPA generate less odor than DHBP which was indicated by odor test and detailed analysis of volatile formation in CRPP.
- TETMTPA gives higher izod impact properties than DHBP

Therefore all those positive points are the improved properties required for automotive applications.

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