

## 가지화된 폴리프로필렌의 유변학적 특성

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### **Melt Rheology of Graft Modified Polypropylene**

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#### **Introduction**

Polypropylene(PP) is one of the most widely used thermoplastics today. When compared with other polyolefin, such as polyethylene, PP has higher melting temperature, higher tensile modulus, lower density, and better chemical resistance. Generally, commercial PP produced in polymerization system that employ Ziegler-Natta catalysts is a linear architecture polymer. The absence of side branches leads to a deficiency in melt strength. As a result, its use has been limited in such applications as extrusion coating, blow molding, thermoforming, and foaming.

So, there have been many approaches to overcome this advantage and it is clear that the introduction of long-chain branching onto PP backbone is one of the alternatives to improve the melt strength. Some types of post-reactor modifications have been tried to increase the melt strength of PP by introducing long-chain branching. Scheve et al. (Scheve et al., 1990) tried to achieve this objective by irradiating a solid PP with high energy radiation. Many researchers including Wang et al. (Wang et al., 1996) have shown that branching can be introduced through the radical reaction in which PP reacts with polyfunctional monomers, having more than two double bonds, in the presence of peroxide. And another try is using reaction between a randomly functionalized PP and polyfunctional monomers (Halldenabberton, 1991).

In this work, two approaches were carried out to increase melt strength of polypropylene. The first one is introducing long-chain branches by the reaction of PP with peroxide and coagent. The second approach is to carry out reactions between maleated PP and diamine.

#### **Experimental**

The polypropylene modified in the presence of peroxide and coagent was PP homopolymer with melt flow index of 3.0(230<sup>0</sup>C, 2.16kg) supplied by Samsung General Chemicals. Dicumyl peroxide(DCP, from Aldrich) as an initiator, and pentaerythritol triacrylate(PETA, from Aldrich) as an coagent were used. An internal mixer was used to prepare the grafted modified PP. Determined amounts of polymer, initiator, and coagent were premixed, before being charged into the mixing chamber. The mixing temperature, time, and rotor speed were held constant at 200<sup>0</sup>C, 4minutes, 50 rpm.

Maleated polypropylene, supplied by Crompton, used in this study was Polybond

3002, Polybond 3150, and Polybond 3200 containing 0.2 wt%, 0.5 wt%, and 1.0 wt% of maleic anhydride respectively. As chain extenders two primary amines, hexamethylene diamine(HMDA, from Aldrich), and poly(propylene glycol)-bis-(2-propyl amine)(Jeffamine D-400, from Huntsman) were used. Polybond was first introduced into chamber. After passing 1 or 2 minutes of melting time, diamine was added. This moment was considered to be the start of the reaction and the reaction was continued to 5 minutes with the reaction condition of set temperature of 185°C and rotor speed of 50 rpm.

## Results and Discussion

### Reaction of PP with Peroxide and Coagent

During modification process of PP using peroxide and coagent, in addition to degradation PP chains may be extended, branched or even crosslinked simultaneously. Figure 1 and Figure 2 show the frequency dependency of  $G'$  of PETA/DCP modified PPs. Generally,  $G'$  and  $G''$  increase with increasing PETA concentration and decrease with increasing DCP concentration. Very similar values of  $G'$  with that of virgin PP are observed at high frequencies. It has been known that relatively short chain segments are involved in the relaxation at high frequency and the effect of local chain structure may become important in this region. So, it can be said that the structure of short chain segments of PP are not altered greatly. But,  $G'$  at low frequencies effected by large-scale molecular structures (molecular weight, molecular weight distribution and extent of long chain branching) are higher than that of virgin PP. this is certainly existence of long chain branch in these PETA/DCP modified PPs since they all have molecular weights lower than that of virgin PP and many of their MWD are not significantly different.

### Chain Extension of Maleated PP with Diamine

The resulting polymer can be chain-extended through the formation of amide and imide linkage, and even crosslinked with some insoluble gels. The amount of reacted MA in Polybond was measured by titration (Kim et al., 1995), and the results said that the reactivity of HMDA to maleic anhydride is higher than that of D-400. When equimolar ratio of

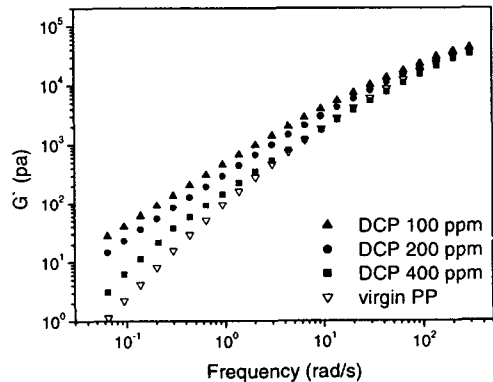


Figure 1. Effect of DCP concentration on storage modulus at initial PETA concentration of 1 wt% at 250°C

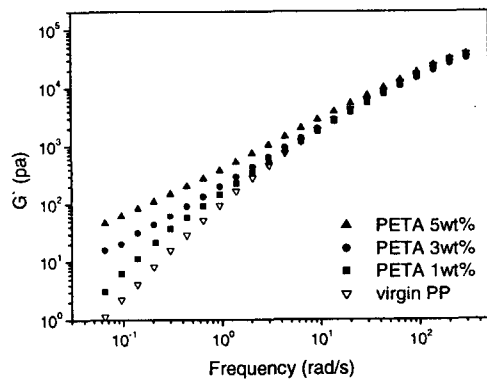


Figure 2. Effect of PETA concentration on storage modulus at initial DCP concentration of 400 ppm at 250°C

$[\text{NH}_2]/[\text{MA}]$  was used, 0.75 wt% of MA in Polybond 3200 was reacted with HMDA, but 0.52 wt% of MA reacted with D-400. Figure 3 and Figure 4 shows storage modulus of Polybond 3200 reacted with HMDA and D-400. For Polybond 3002 and 3150 with low MA content, increases in  $G'$  of reacted polymer were not observed, but there were considerable increases, when Polybond 3200 was reacted with diamine.

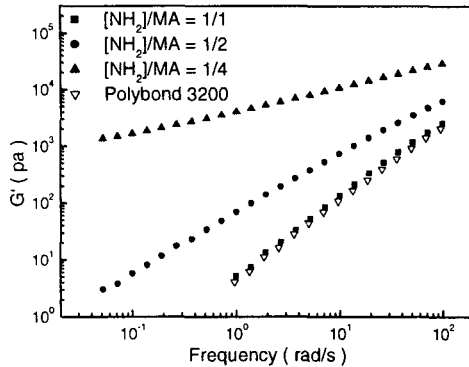


Figure 3. Storage modulus of Polybond 3200 reacted with HMDA at 180°C

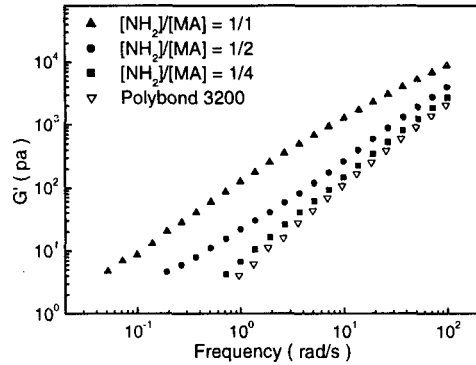


Figure 4. Storage modulus of Polybond 3200 reacted with D-400 at 180°C

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