

## Development of modified polypropylene with polyfunctional monomers by gamma irradiation

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One of the effective approaches to achieve high melt strength polymers (HMS) is to add chain branches onto backbone species using gamma radiation. Branching and grafting result from macroradicals combinations during the irradiation process. Nonetheless, crosslinking and main chain scission in the polymer structure are also obtained. Gamma irradiation technique was used to induce chemical changes in commercial polypropylene with two different monomers: ethyleneglycol dimethacrylate (EGDMA) and Tri-methylol-propane-trimethacrylate (TMPTMA) with concentration of 5.0 mmol/100g of polypropylene. These samples were irradiated with a <sup>60</sup>Co source at doses of 12,5 and 20kGy and two different routes of HMS-PP processing have been used. In this work we investigate how different methods of mixture can modify HMS-PP samples properties. Indeed the results from melt flow, gel fraction and rheology reveal that HMS-PP properties can be considerably influenced by mixture temperature of virgin PP with monomer.

### Introduction

The polypropylene (PP) has been applied to a wide range of production due to its various excellent properties such as high stiffness, chemical resistance, no environmental pollution when incinerated and low specific density. Therefore PP has been preferred to polyvinylchloride, polyurethane and polyethylene in a wide range of applications. However, PP is a linear polymer which exhibits low melt strength.

High melt strength polypropylene (HMS-PP) has been recently developed and introduced in the market by the major international polypropylene producers. As a consequence different methods have been applied to modify polypropylenes by chain branches. BRASKEM, the leading Brazilian PP producer, together with EMBRARAD, the leading Brazilian gamma-irradiator, and the Nuclear and Energy Research Institute (IPEN) polymer group jointed forces to develop a national technology for the production of HMS-PP. The technology obtained comprises chain branches added onto backbone species using gamma irradiation, which is generated from a Co<sup>60</sup> source. Such irradiation is very convenient in order to improve polymer materials by crosslinking, grafting and degradation. These reactions occur on account of the rearrangement of radicals formed in polymer materials.<sup>1-4</sup>

Radiation processing of polymers can be suggested as environmentally and energetically safe way with lower costs to modify molecular structures as alternative to research new materials.

The use of radiation does not require solvents or initiators at high temperature and the possibility of processing the polymer in the solid state in its final shape furnishes new stimulating applications to obtain materials with well-tailored properties.

It is well known that the main effect of gamma rays and polymers interactions is the creation of free radicals, which may further evolve into chain scission with molecular weight decrease, and chain branching

with molecular weight increase up to crosslinking. Generally, although all these phenomena coexist, the dominance of each one depends on many factors, such as the initial molecular structure, polymer morphology and experimental irradiation conditions. Polypropylene is degraded by oxidation in two stages, i.e. during irradiation and during storage after irradiation. Thus a larger dose is not desired for PP modification when using irradiation.

It is acknowledged that crosslinking with polyfunctional monomers improves physical properties of polymer materials at lower doses. In this work gamma radiation technique was used to induce chemical changes in commercial polypropylene with two different monomers, EGDMA and TMPTMA, with polypropylene concentration of 5.0 mmol/100g.<sup>1-4</sup>

### Experimental

#### Preparation of samples

Isotactic polypropylene (24 g/10 min) was modified by gamma irradiation with multifunctional monomers. Monomers at a concentration of 5.0 mmol/100g iPP were in the first case mixed with iPP at room temperature (Method 1) and in the second case submitted to higher temperature mixing followed by fast cooling (Method 2). Afterwards, all samples received gamma radiation (<sup>60</sup>Co) at dose of 20 kGy at nitrogen atmosphere. The polyfunctional monomers studied comprised a bifunctional monomer EGDMA as well as a trifunctional monomer TMPTMA.

#### Melt flow index

The melt flow rate of the modified polypropylenes in both process methods was measured in a Melt flow Junior equipment Mod 09237 in which the samples were flowed through an orifice of 2.00 mm diameter during 10 min under 1 2.16 Kg loading at 230°C (ASTM D 1238).

### Gel content measurements

It was used the standard method ASTM D2765 to measure gel content. Samples modified iPP were weighed, placed in bags and extracted with xylene as solvent (i.e. refluxing) for 12 hours at temperature of 135°C. Latter, the extracts were removed, dried under vacuum for 1 hour at 150°C and the samples weighed again.

### Rheological characterization in shear flow

Rheological measurements in shear were performed at a temperature of 200°C using rotational Physica rheometer (MCR 300) with plate-plate geometry of 25mm in diameter and a 1.0mm gap. Samples of 1.2 thick and 25mm wide were prepared from the irradiated and stabilized pellets in hot press at a temperature of 190°C.

## Results and Discussion

**Table 1** – Results of melt flow index and gel fraction

iPP		Melt Flow (g/10 min)	Gel Fraction (%)
A	Pure	24,0	1,3
B	Mixed with EGDMA and irradiated	12,5 kGy 20 kGy	25,6 34,8
C			0,9
D	Mixed with TMPTMA and irradiated	12,5 kGy 20 kGy	23,6 31,3
E			1,5
F	Mixed with EGDMA, cooled and irradiated	12,5 kGy 20 kGy	1,2 2,3
G			17,8 17,0
H	Mixed with TMPTMA, cooled and irradiated	12,5 kGy 20 kGy	3,3 6,1
I			5,8 3,8

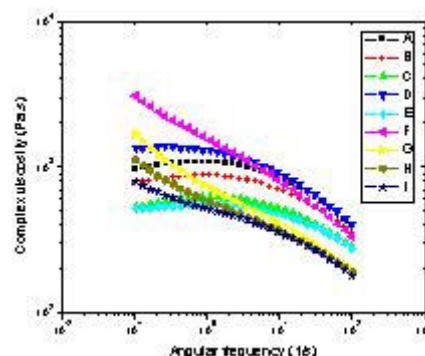
It can be seen in Table 1 that a melt flow index increase was observed for samples obtained by Method 1. Here the chain scissions occur preferentially over the other reactions. In Method 2 the decrease of melt flow index was significant. On the one hand no change in the gel fraction of the samples produced by the Method 1 in comparison with the pure iPP was noticed. On the other hand, however, the gel fraction increased for samples produced by Method 2 especially for the PP mixed with EGDMA.

**Table 2** – Results of tension and deformation at break

	Tension at break (MPa)	Deformation at break (%)
A	20,6 ± 4,6	592,8 ± 21,1
B	19,1 ± 2,1	624,9 ± 24,5
C	15,1 ± 1,9	652,8 ± 26,5
D	24,4 ± 0,8	9,4 ± 2,8
E	23,7 ± 1,9	4,6 ± 0,9
F	25,3 ± 1,5	6,9 ± 0,8
G	22,3 ± 1,8	14,9 ± 2,5
H	27,8 ± 2,5	6,7 ± 1,5
I	25,9 ± 2,9	5,9 ± 1,0

The samples with EGDMA processed by Method 1 showed a decrease in rupture strength and increase in deformation at break (Fig. 1), whereas the samples with TMPTMA obtained by Method 1 as well as all the

samples processed by Method 2 showed, on the contrary, an increase in strength and significant decrease in deformation at break.



**Figure 1** – Complex viscosity as a function of angular frequency.

The samples F, G, H and I presented lower viscosity at high frequencies and higher viscosity at lower frequencies in comparison with the pure PP, which demonstrates that samples obtained by Method 2 had their structure modified.

## Conclusion

In the samples mixed with EGDMA (B and C) and irradiated with 12,5 kGy dose (Method 1) the main present effect is degradation, which can be confirmed by increase of melt flow index, decrease of rupture strength and slight decrease of complex viscosity. In contrast, sample D had the rupture strength increase, even though melt flow index and complex viscosity decreased. Sample E evidenced increase of rupture strength and viscosity with increase of melt flow index. Finally the samples F, G, H and I showed a remarkable decrease of melt flow index and increase of gel fraction and viscosity at low frequencies. In this case, the experimental conditions favored chain branching and crosslinking phenomena. Based on these results, it may be concluded that polyfunctional monomers improve iPP mechanical properties at lower doses.

## References

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