

## Modification of Nanoparticle Elasticity and Morphology: A Practical Approach to Improve the Efficiency of Purging Compounds

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### Abstract

In this research, the performance of polyethylene-based nanocomposites containing cross-linked styrenic nanoparticles was evaluated as purging compounds. By increasing the cross-linker content from 1 to 10 wt. %, the consumed purging mass was reduced compared to neat polyethylene. This improvement was ascribed to the increased melt viscosity of the compound as well as modification of scrubbing nanoparticle properties such as increased elasticity and surface roughness of aggregates. However, the increase in melt viscosity also resulted in higher purging time. To overcome this drawback, the viscosity of the compound, as well as characteristics of the scrubbing nanoparticle were tailored by adding 1 wt. % of the surface modifier of nanoparticle which resulted in a 40% increase in purging efficiency, regarding both purging time and material consumption compared to neat polyethylene.

**Keywords:** Purging efficiency, Nanoparticle elasticity, Dispersion state, Aggregation morphology, Melt viscosity

### Introduction

Purging of polymer processing machines is a vital procedure in the polymer industry. The competitive market has compelled compounders to use purging compounds, minimizing machine downtime and boosting productivity [1]. These compounds may consist of a polymer media containing abrasive organic/inorganic particles. Despite high efficiency of inorganic particles, their prolonged consumption can cause damages of the internal surface wall of the machine. Hence, using an all-polymer purging compound is preferential, provided that the properties of the organic particles are optimized [2]. For instance, polymer nanoparticle surface topology can be tailored by altering the cross-linker content, affecting polymer/nanoparticle interplay [3].

In this paper, we investigated the effect of cross-linker content of nanoparticles as well as the addition of a nanoparticle surface modifier on aggregation size and morphology by rheological analysis and scanning electron microscopy (SEM). These modified nanoparticles were added to polyethylene to optimize its purging performance.

### Experimental

Poly (styrene-co-methyl methacrylate) nanoparticles, containing 1 (X1) and 10 (X10) wt. % of

divinylbenzene (DVB) as the cross-linker, were synthesized through batch emulsion copolymerization. Three nanocomposites containing high density polyethylene (HDPE, 4005EA, received from Tabriz Petrochemical Co.), 10 wt. % of X1 and X10 nanoparticles, as well as 1 wt% of ethylene bis stearamide (EBS, Semnan energy Co.) as the surface modifier of X1 nanoparticles, were prepared by mixing in an internal mixer (Brabender, pl2200) at 190°C and 60 rpm for 15 minutes. The nanocomposites were coded as HX1, HX10 and HX1E1, respectively. The cross-section of fractured nanocomposite films in liquid nitrogen was coated with a thin layer of gold before their examination by SEM, AIS2100 model of Seron Technology. The melt flow index of samples was measured at 190 °C/5Kg by a MFI tester machine Utility model, Daventest. The rheological tests were performed by Antonppar 302 rheometric mechanical spectrometer (RMS) at 190°C utilizing a parallel plate fixture 25 mm in diameter and a constant gap of 1 mm in stain-sweep mode ( $\omega = 1$  rad/s). The purging test was performed by passing 6-gram batches of HDPE and nanocomposites through the MFI machine after machine contamination with 3 gram of carbon black masterbatch (received from Kavash Polymer Alborz Co.).

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## Results and discussion

The SEM images of nanocomposites illustrated different aggregation morphology of X1 and X10 nanoparticles in HDPE, Fig 1. Due to high elasticity and low interpenetration ability of X10 nanoparticles they formed aggregates with high surface roughness, containing separated nanoparticles. Conversely, the mutual interpenetration of soft X1 nanoparticles made it almost impossible to distinguish the individual nanoparticles in each aggregate, causing reduced surface roughness of aggregates. Furthermore, the size of nanoparticle aggregates in the solid state decreased by increasing DVB content. The nanoparticle dispersion state in melt was scrutinized by critical strain ( $\gamma_C = \gamma$  at  $G' = 0.9G'_{\text{plateau}}$ ), obtained from the linear to nonlinear transition point in storage modulus ( $G'$ ) vs. strain plots, Fig 2. The lower  $\gamma_C$  value of HX10 than HX1 was attributed to improved dispersion of X10 nanoparticles [4] which was consistent with SEM results. Moreover, MFI of HDPE declined in the presence of X1 and X10 nanoparticles that was ascribed to the hindered chains motion and imposed local friction at the nanoparticle-chain interface, Table 1. Lower MFI of HX10 than HX1 was suggested to be due to the slower dynamic of matrix chains in the presence of X10 nanoparticles [3]. The purging process with 6-g batches of purging compounds was continued until no sign of carbon black masterbatch was remained and the consumed purging mass was measured Table 1. The decrease in purging mass in the presence of nanoparticles was ascribed to the higher melt viscosity of the compounds and scrubbing effect of nanoparticles, both enhanced by increasing DVB content and resulted in lower purging mass consumption. The nanoparticle scrubbing action was dependent on its elasticity and the surface roughness of aggregates. Although purging mass consumption decreased by increasing DVB content, the increase in melt viscosity resulted in higher purging time compared to HX1. In order to optimize both purging mass and time, 1wt% EBS was added to HX1 nanocomposite. According to SEM images, the mutual interpenetration of X1 nanoparticles was suppressed due to the localization of EBS on their surface, resulted in the formation of aggregates with higher surface roughness than HX1. Furthermore, poor entanglement between ethylene segments of EBS and matrix chains led to higher aggregation size than HX1, according to both SEM and rheology results. Although slippage of matrix chains on short ethylene segments of EBS resulted in lower melt viscosity of HX1E1 than the other nanocomposites, it was compensated by the increase in the size and surface roughness of aggregates. This revealed that scrubbing particle's size and morphology had a significant effect on purging

efficiency provided that melt viscosity was not below a critical point.

## Conclusions

Increasing the content of nanoparticle cross-linker enhanced its scrubbing action and increased the nanocomposite melt viscosity, resulting in lower purging mass consumption compared to the neat polyethylene. Despite this, purging time increased by increasing the melt viscosity of the nanocomposite. To optimize both purging criteria, EBS was added to the nanocomposite, leading to 40% improvement in purging efficiency (according to multiplication of purging mass and time) in comparison to polyethylene.

## References

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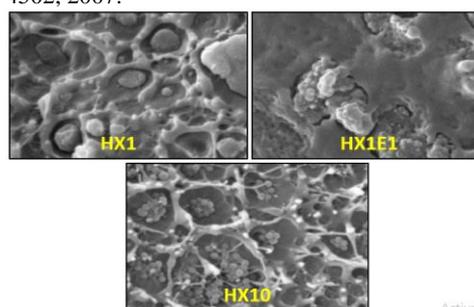


Fig 1. SEM images of the nanocomposites with the magnification of 30K.

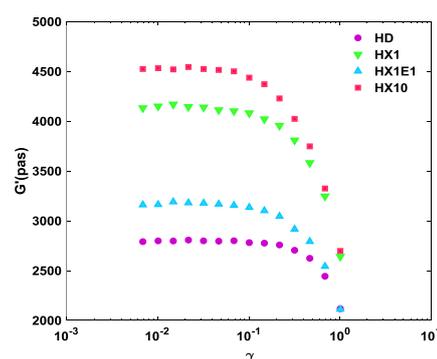


Fig 2. Storage modulus vs. shear strain curves

Table 1. Aggregate size,  $\gamma_C$ , MFI, purging mass and time

Sample	Aggregate size ( $\mu\text{m}$ )	$\gamma_C$	MFI (g/10min)	Purging mass (g)	Purging time (min)
HD	-	0.592	1.97	39	258
HX1	1.91	0.366	1.75	36	246
HX1E1	1.97	0.395	2.02	30	195
HX10	1.19	0.291	1.50	33	270