

Formation and Control of Nanoparticles

In- Situ During Melt Extrusion of Polyolefins

The subject of submicron particles in solution has been termed using a new provocative word “Nanotechnology”. The term has evolved from Colloidal Chemistry to Nano Technology. The chemistry continues in practice in solution to avoid agglomeration of the particles in the solid state.

In order to take advantage of the physical chemical properties of nanoparticles from a solution to a solid matrix economically requires control of the particle size distribution and prevent agglomeration of the particles producing macro particles.

In addition, it has been illustrated over time that nanoparticles are more catalytic (Hammett Acidity Function H_0), than comparable particles in the macro scale around 1 to 10 microns. This catalytic effect reduces the performance of all hindered amine light stabilizers and a similar effect on thermo-oxidative stability of the matrix containing a primary phenolic antioxidant.

Understanding the problem and having control of the catalytic process has been a challenge with little resolution until now.

A solution to this problem was discovered during a study of Argentinum (or silabar) organic compounds. During these studies we found that nanoparticles of 4-8 nm in diameter were formed in-situ during melt extrusion of polyolefins above 230C.

The key was control of the structural chemistry of the organic compound and characterization of the compounds produced prior to integration into the polymer. Thermal Analysis (DSC) and Thermo-gravimetric analysis was used to determine melting and decomposition temperatures while GCMS and ICP: AES was used to characterize the distribution of organic derivatives initially and after thermal conversion and the metal content of each organic compound.

Control of the in-situ conversion process to either the oxide or metal was controlled by both the process chemistry and the residence time in the extruder at a preferred temperature. Temperatures as low as 163C allowed oxide conversion in-situ to the metallic form as 4-8 nanoparticles depending on the chemistry of the metal.

Furthermore, conversion of the organic compounds provided a broad range of outcomes in the system depending on the metal in the compound. Argentum conversion led to permanent selective UV absorbance, in other cases synergisms between hindered amines and better buffer systems that seen from macro particles of similar chemistries.

Transition metal organic compounds from the d-block elements such as period 5 group 11 shows great promise as both a UV Absorber at very low concentrations and permanence for long term protection but also a selective blue blocker for packaging with antimicrobial activity.

D-block Period 4 Group 12 nanoparticles provide synergisms between phenolic antioxidant and stronger amphoteric control of phenolic antioxidant transformation products over time in dark storage.

Period 5, Group 10 d-block nanoparticles provide for strong ethylene scavenging activity at high relative humidity and show permanence over time. Levels as low as 50 ppm in the polyolefin are strong inhibitors exogenous ethylene species. Period 5, Group 11 nanoparticles in combination with this group also controls senescence of plant organs and is synergistic in endogenous ethylene production.

Period 4, Group 8 nanoparticles show a very interesting challenge to achieve reproducible results observed due to changes in in-situ valence of the oxide and metal formed.

Studies to date indicate the valence of the iron organic compound determines the final in-situ conversion of oxide formed and its synergisms as a Spectral Enhancer with organic ultraviolet absorbers and hindered amine light stabilizers.

As noted in previous reports a Spectral Enhancer is a substance that alters both the hyperchromic absorptivity of the organic UV absorber and control of bathochromic red shifts of the organic UVA. Alone Spectral Enhancers provide for low absorptivity but broad permanent UVA in the system.

Finally, period 2 elements have been investigated in our studies and found to provide colorless and active nanoparticles which act as good acid acceptors and synergists for phenolic antioxidants depending on their chemistries. For example period 2 group 4 element gives a basic nanoparticle with a specific pKa value while period 2 group 3 element provides for a strong basic nanoparticle and different pKa value. In one case severe yellowing occurs with select phenolic antioxidants and in the other a colorless non-yellowing phenolic antioxidant with far different performance characteristics than without the strong basic nanoparticle.

In conclusion in-situ conversion of transition d-block elements as organic compounds with select decomposition temperature form nanoparticles in the polymer matrix that do not agglomerate and function as nanoparticles with a broad range of specific end use utilities for challenges being faced globally in the plastic industry including but not limiting control of degradation mechanisms and for long term thermo-oxidative protection of the polymer matrix.

The process described here is both economical and practical and requires no solution chemistries. This is a solid state process and suitable for masterbatch or direct addition at the manufacturing site of the polymer.

For masterbatch operations or toll compounders producing a final polymer

product of known composition reading for conversion this is an ideal solution to existing problems of permanence and discoloration and antagonisms from traditional nanoparticles formed outside the polymer and then integrated into the polymer as post polymerization additions.

Instead in-situ melt processing conversion takes place under controlled conditions of temperature, concentration, residence time to provide a predictable outcome each time. In our opinion the Hammett Acidity Function no longer applies once the particle has formed in-situ in the polymer matrix. Other physical chemical factors are now in control of the function of the nanoparticles. This conclusion is based on the results of years of study.

Further studies in this field are on-going at both the academic level and at the industrial level for practical solutions i.e. solutions to problems that exist not solutions to problems that do not exist.

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