Technology of PVC nanocomposites

1. **Polish Patent No. 213918** „Method for the suspension polymerization of vinyl chloride in the presence of a nanofiller". Owner: Łukasiewicz - Industrial Chemistry Institute in Warsaw

This invention comprises an application of spherical nanofiller in vinyl chloride (VC) suspension polymerization. The nanofiller is sol-gel silica with narrow particle size distribution. Resulted PVC nanocomposites, containing < 0.5 wt. %/VC of nanofiller, show much better impact strength of rigid goods prepared of them, than of PVC ones. This let decrease the level of impact modifiers in PVC blends processing (up to ~50 % of initial amount). Even at such lowered amount of impact modifier, the impact strength as well as corner strength of profiles made from PVC nanocomposites are better than made from commercial PVC containing higher amounts of impact modifiers.

2. General description of innovation

The solution is innovative in the world. There is no commercial PVC nanocomposites on the market up to now. The innovation consists in use of special spherical filler as additive in the process of suspension polymerization of vinyl chloride. It means **the composite is formed during the polymerization process and final product contains perfectly distributed nanofiller** – practically in each PVC grain. The nanofiller is silica produced by sol-gel method. In this one-step production of composite just very small amount of nanofiller (≤ 0.5 wt. %/VCM, *i.e.* much lower than needed in processing step) gives improvement in mechanical properties of the material – especially in impact strength. The solution according to the patent can be applied in any typical PVC production plants. The process can be used to obtain PVC nanocomposites of any molecular weight (the full range of Kvalue).

The solution has been checked in PVC pilot plant (4000 kg obtained) and in PVC production lines (nearly 100 tons obtained).
PVC nanocomposites production can be realized in standard PVC units.

3. Effects

The samples of PVC nanocomposites from pilot and production trials were investigated in rigid applications by several Polish and foreign companies especially for profiles, in tests to reduce the amount of the impact modifier in the product.

The results obtained show excellent impact strength of PVC nanocomposites, not possible to be reached for PVC:

- either one can reach impact strength up to 25 % better - when standard amount of an impact modifier is used in the given blend
- or impact strength can be kept or be slightly better (up to 10 %) and corner strength of profiles better up to 15 % when impact modifier amount is lowered to 50 % of its standard amount.

For all the goods tested (mainly profiles, but also semi-rigid films - constructional and of big industrial importance) there was possible to lower the amounts of impact modifiers in the blends of about minimum 25 – 50 %.

Even with the reduction of the modifier amount by 75%, it was observed that the proper impact properties were maintained, but it depends on the composition of the blend.

It means the following possibilities:

- the use of nanocomposites according to the invention instead of the standard PVC allows to achieve the level of impact resistance of a given product that is unattainable at the stage of standard PVC processing
- the use of nanocomposites instead of standard PVC let produce the new products with special properties, up to now not made from PVC
- the use of nanocomposites instead of the standard PVC gives significant **savings** of additives in PVC processing, even taking into account the cost of nanocomposite is higher than PVC
- the use of nanocomposites instead of the standard PVC means wider availability of long-term constructional products with excellent properties.

It is worth emphasizing that obtaining a nanocomposite directly in the polymerization process is more advantageous than adding nanofillers to PVC in the processing process, because it ensures excellent dispersion of nanofillers in the PVC grain and allows the use of smaller amounts to obtain the same improvement in properties.

The impact modifiers used in processing are very fine powders with a risk of explosion. To increase the safety of the processing installation, the smallest possible amounts should be used. The use of nanocomposites according to the invention in place of the standard PVC should significantly reduce the risk of explosion.

4. Comparison with the present state

There is no comparison as there is no production of suspension PVC nanocomposites in the world at all, neither in polymerization step nor in processing one. VCM polymerization process is very sensitive to all parameters changes so introduction of the new component usually causes problems. According to our solution PVC nanocomposites can be one-step produced in the polymerization process. The amount of nanofiller needed to improve the mechanical properties is in polymerization several times lower than in processing step.

5. Copy of patent – enclosed

6. References, prizes

We have got the reports of investigations done by Polish and foreign companies. They lowered the content of impact modifier even to -25 %, -50 % or even -75% in comparison to standard amount for their profile formulations. The results show that there is possible to lower the impact modifier content in the blend of about 50 wt.% with good results when PVC is replaced with PVC nanocomposite.

Prizes and awards

Invention Fair "Brussels Innova", Brussels 2011: Gold medal with Distinction; and Distinction by the University of Medicine and Pharmacy "Nicolae Testemitanu" from Moldova

International Chemical Industry Fair - Invention and Innovation Exhibition EXPOCHEM Katowice 2012: Silver Medal

Award of the Minister of Science and Higher Education for International Inventive Achievements, Warsaw 2012

7. Know-how

The production of PVC nanocomposites is carried out in a typical PVC production plant, using typical process initiators and suspension stabilizers. The difference is the addition of nanosilica with appropriate properties and in an appropriately selected amount at the appropriate stage, as well as the correction of the amount of suspension stabilizers, which may be needed.

Properly selected nanosilica does not disturb the polymerization process, does not prolong it, and does not interact with initiators and other auxiliary agents. It should have an average grain

size of about 40 - 80 nm and a narrow grain size distribution. It should be in a dispersed form (sol) in an alkaline aqueous phase (pH ~9). Silica concentration should be 25 – 50 wt. %.

This dispersion may be stabilized with protective colloids typically used in vinyl chloride polymerization: poly(vinyl alcohol)s, methylcellulose derivatives. This form of the filler prevents agglomeration and is suitable for feeding into a VC polymerization reactor.

The nanofiller dispersion should be transported and stored at the temperature range from + 5 to + 35 °C (40 ÷ 95 °F). The tanks with nanofiller should be sealed and constructed of plastic, reinforced plastic or stainless steel. The tanks should be stored out of direct sunlight or bright light.

To the VC polymerization reactor the nanofiller should be introduced from an intermediate tank equipped with an agitator, using pump, at the stage of loading water and / or suspension stabilizers into the reactor.

Small corrections of the amounts of protective colloids used in VC polymerization mixture could be needed – dependently on the polymerization mixture composition used. Usually they should be slightly decreased.