

Method for the suspension polymerization of vinyl chloride in the presence of a nanofiller

This invention comprises a method for the suspension polymerization of vinyl chloride in the presence of a nanofiller with nanometer-size granulation.

Typical suspension polymerization of vinyl chloride produces poly(vinyl chloride) (PVC) with specific mechanical properties, largely depending on the molecular weight (expressed for commercial purposes with Fikentscher value, i.e. the so-called *K-value*). During PVC processing, additives are used to secure the required product properties. To improve mechanical properties, different modifiers are added during the processing.

At the processing stage, it is possible to improve mechanical properties of PVC by adding a nanofiller, i.e. montmorillonite or precipitated calcium carbonate, when the nanofiller-to-PVC weight ratio exceeds 5 weight % or even more than 10%, with significant improvement observed for the weight ratio of 6-10 weight %. According to literature, the application of clay, i.e. layered silicates, e.g. montmorillonite, causes difficulties with PVC thermal resistance, as ammonium salts used for clay pretreatment cause PVC degradation (Trlica J., Kaledova A., Malac Z., Simonik J., Pospisil L., ANTEC 2001 conference materials, Dallas, May 6-10 2001, communiqué No 415)

There is few reports on PVC nanocomposite preparation straight at the polymerization stage. A significant difference between these methods consists in the fact that at the processing stage it is relatively easy to add different materials to PVC (resulting in either product property improvement or deterioration), while in the polymerization process many additives cause reaction inhibiting, excessive grain agglomeration (blocking polymerization mixture) and other adverse effects, including deterioration of properties.

The first literature reports on PVC nanocomposites achieved at the polymerization stage concerned adding of a specially pretreated montmorillonite. {2,2-azobis [2-amidinopropane dihydroxychloride, trimethylammonium ([2-methacryloyloxy) ethyl chloride or α -alkenyltrimethylammonium bromide} as a component of the reaction mixture in emulsion or suspension polymerization of vinyl chloride [1. Aguilar-Solis C., Xu Y., Brittain W. J.: „PVC Nanocomposites via Emulsion and Suspension Polymerization” Polymer Preprints, No. 2, Vol. 43, 2002, s. 1019 – 1020; 2. Xu Y., Malaba D., Huang X.,

Aguilar-Solis C., Brittain W. J.: Polymer layered silicate nanocomposites by suspension and emulsion polymerizations: PVC - MMT nanocomposites. *Polymer Preprints* 43(2), 2002, s.1312 –1313]. The authors of works 1 and 2 produced PVC nanocomposites on a laboratory scale by adding appropriate amounts of clay to the polymerization mixture - in the case of suspension polymerization, and to the polymerized PVC latex in the case of emulsion - and examined the degree of dispersion nanofiller by X-ray diffraction. The mechanical properties have not been tested due to the very small amounts of the products obtained. Chinese publications on emulsion polymerization of vinyl chloride [3. Pan M., Shi X., Li X., Hu H., Hang L. : “Morphology and properties of PVC/clay nanocomposites via in situ emulsion polymerization”, *Journal of Applied polymer Science* (2004), 94(1), s. 277 – 286; 4. Shi X., Pan M., Li X., Hang L., Ding H.: “Study on the morphology and properties of PVC/Na + - MMT nanocomposites prepared by in situ emulsion polymerization”, *Gaofenzi Xuebao* (2004), (1), 149 – 152] report on obtaining composites with clays such as montmorillonite (layered aluminosilicate) directly in the process of emulsion polymerization. The publications contain information on the improvement of the mechanical properties of PVC, - addition of 5 wt. montmorillonite / vinyl chloride increases the tensile strength of the polymer by 31% and increases Young's modulus by 54%, while the addition of 1% montmorillonite / vinyl chloride causes only a slight increase, by 4%, in elongation at break [5. Gong F., Feng M., Zhao Ch., Hang S., Yang M.: „Particie configuration and mechanical properties of poly(vinyl chloride)/montmorillonite nanocomposites via in situ suspension polymerization”, *Polimer Testing* (2004), 23(7), 847-853].

Another nanofiller used directly in the suspension polymerization of vinyl chloride is CaCO₃, prepared e.g. with esters [6. Ye L., Chen D., Liu J., Mao L., Bing J., Xie J., Li X.: “Influence of surface treatment on in-situ suspension polymerization of PVC/nano CaCO₃ composite”, *Zhongguo Suliao* (2002), 16 (6), 39-43; 7. Sheng S., Xu Y., Jia Y.: “Preparation of nanoparticle - modified polyvinyl chloride resin”, the patent CN 1392177 – 2003 r. or stearic acid [8. Han H.: “In – situ preparation of polyvinyl chloride composite containing nano-CaCO₃”, the patent CN 1353121 – 2002 r. CaCO₃ may be added in the vinyl chloride polymerization step as a suspension or as an aqueous microemulsion [8. i 9: Zhang X., Zhou J., An Z., Song X., Huang D. “In situ polymerization and comprehensive dispersion technology for preparing nanometer calcium carbonate – modified PVC resins” the patent CN 1468901 – 2004 r.

The Chinese patent description [10. Li Ch., Hang L., Sun S.: “ Inorganic nanoparticle containing poly(vinyl chloride) nanocomposite material” CN 1618865 (2005) presents PVC nanocomposite production during polymerization. Polymerization of vinyl chloride was performed at a temperature of 50°C and a pressure of 1 MPa in the presence of modified nanofillers, namely CaCO₃ modified with stearates or SiO₂ functionalized with silanes or TiO₂ functionalized with titanates. PVC composites produced in the above manner were mixed with PVC, thermal stabilizers, modifiers and additionally nanofillers, and processed at 140–180 °C, obtaining new PVC nanocomposites. Their properties were not defined in detail.

It turned out unexpectedly that the application in the polymerization process an addition of a nanofiller with spherical construction and narrow particle size distribution (up to 200 nm) in the form of a non-functionalized silica, significantly improves PVC mechanical properties, with the nanofiller amount substantially below that used in the processing. Thus, there is no need to use modifying additives at the processing stage to the final product, or their amounts can be significantly limited.

The application of these nanofillers in the polymerization process, with temperature ranges typical of suspension polymerization of vinyl chloride, i.e. 50-70°C, substantially increases PVC tensile strength about 40 % and relative elongation at break about 30% – for plasticized products – and increase about 60% impact strength – for rigid products, compared with PVC with no nanofiller added.

According to the invention, suspension polymerization of vinyl chloride, at temperature of 50-70°C, with the application of suspension stabilizers and free radical initiators as well as with nanometer-size fillers, consists in the fact that polymerization is performed in a mixture containing a nanofiller in the form of nanospheres with an average size of primary particles of up to 200 nm, i.e. non-functionalized silica , with 0.001 – 5 % weight ratio to vinyl chloride, with nanofiller used in the form of a sol, gel, powder or in the form of aqueous dispersion of a powder, added once, in portions or continuously.

It is a good solution to use 0.01 – 3 % of the nanofiller, ideally in the 0.1 –2 % weight ratio to vinyl chloride.

It is a good solution to stabilize aqueous dispersion of a nanosilica with a suspension stabilizer from the methylcellulose derivatives or poly(vinyl alcohol)s group.

According to the invention, polymerization with a spherical nanosilica is performed using popular suspension stabilizers, e.g. methylhydroxypropylcellulose derivatives or

poly(vinyl alcohols), first- or second-order, or their mixtures, and popular free radical initiators, e.g. from peroxides, peroxyesters and peroxydicarbonates groups.

Polymerization products, obtained according to the invention, with different K-values depending on the process temperature, satisfy all PVC standards requirements and their mechanical properties are much better than those of standard PVC types.

The invention-based process and results are illustrated in examples and tables.

Examples.

To eliminate the influence of other factors on the process, all polymerization examples illustrating the invention method and comparative examples (without a nanofiller) were conducted in the same reactor and under the same conditions, with the only changes in the polymerization temperature, dosing method and the quantity and form of the applied nanofiller.

The polymerization reactor with the capacity of 1.5 l was filled with demineralized water (540 mL), aqueous solutions of suspension stabilizers: first-order poly(vinyl alcohol) and methylhydroxypropylcellulose 1:1 (in total, dry mass equivalent of 0.28 g), a mixture of initiators: 1,1,3,3-tetramethylbutyl peroxyneodecanoate and di-(2-ethylhexyl) peroxydicarbonate (1:2), with the total value of 0.1% (weight/VC) and a spherical nanosilica. The air was removed from the reactor and 410 g of vinyl chloride was added. The reaction mixture was heated and the required polymerization temperature was maintained. After 4 hours, the reaction was stopped and properties of the polymer obtained were studied in the processing, on blends prepared based on the following description.

The nanosilica was added either once, at the beginning of polymerization (method I), in two (method II) or three portions (method III) (the first portion during reactor loading, together with other polymerization mixture components, the second portion after 1 hour, the third portion after 2 hours after reaching polymerization temperature) or continuously (method IV), with the speed allowing for total nanofiller to be added during the first 3 hours of polymerization.

Plasticized (table 1) and rigid (table 2) processing blends were prepared using the obtained PVC powders.

The plasticized blends contained: PVC – 100 weight parts, plasticizer di-isononyl phthalate DINP – 40 weight parts, liquid tinorganic stabilizer (MARK MOK 17, Akros) – 4 weight parts. A laboratory device called Brabender plastographometer, type Plasti-Corder 2200-3, was used for plastographometric studies, the mixer chamber had a capacity of 50 cm³, the batch was 54 g. The chamber temperature was 150 °C, rotors rotation was 20 min⁻¹. Gelated

plastificates taken off the chamber were rolled into patches (without cooling) and pressed into 1.5 mm thick plates used to cut moulds to examine tensile properties.

Non-plasticized (rigid) blends contained : PVC – 100 weight parts, tinorganic stabilizer (MARK MOK 17, Akros) – 4 weight parts, Loxiol G60 lubricant – 1 weight part. The chamber temperature was 175 °C, rotors rotation was 30 min⁻¹. Gelated plastificates taken off the chamber were rolled into patches (without cooling) and pressed into 3 mm thick plates used to cut moulds to examine impact strength.

Table 1. Properties of plasticized PVC blends without and with a nanosilica.

Polymerization temp. [°C]	Nano-filler	Filler form	Filler concentration [%]	Filler addition method	Tensile strength		Relative elongation at break	
					[MPa]	% of increase	[%]	% of increase
50	-	-	-	-	19,3	-	175,7	-
57	-	-	-	-	18,0	-	174,7	-
65	-	-	-	-	15,6	-	158,5	-
50	SiO ₂	Sol	0,001	I	19,8	2,6	180,2	2,6
			2	II	24,1	24,9	228,3	29,9
			10	III	22,3	15,5	207,8	18,3
57	SiO ₂	Sol	0,1	I	22,8	26,7	189,0	8,2
			3	I	23,6	31,1	218,2	24,9
			10	IV	22,1	22,8	206,1	18,0
57	SiO ₂	Powder	0,001	I	18,9	5,0	181,0	3,6
			3	III	23,4	30,0	216,7	24,0
			10	II	22,1	22,8	205,9	17,9
65	SiO ₂	Dispersion	0,01	II	17,1	9,6	170,0	7,3
			3	IV	22,1	41,7	205,3	29,5
			9	III	18,6	19,2	176,2	11,2

Table 2. Properties of non-plasticized (rigid) PVC blends without and with a nanosilica (polymerization temperature of 57 °C)

Nanofiller	Filler form	Filler concentration [%]	Filler addition method	Notched impact strength [kJ/m ²]	% of impact strength increase	Shore hardness [D]
-	-	-	-	6,8		89
SiO ₂	Sol	0,1	I	7,1	4,4	88
SiO ₂	Dispersion	1	II	9,6	41,0	89
SiO ₂	Powder	3	III	11,1	63,2	88

It was found that the obtained results of improving the mechanical properties of PVC in the case of using nanofiller in the polymerization process depended primarily on the type of filler used and its amount in the mixture, to a lesser extent on the form which it was introduced, and not on the method of introducing it into the polymerization mixture.

Patent claims

1. Method for the suspension polymerization of vinyl chloride, at a temperature of 50-70°C, using suspension stabilizers and free radical initiators and a nanometer-size filler, **characterized in that** the polymerization is performed in a mixture containing a nanofiller in the form of nanospheres with an average size of primary particle of up to 200 nm, with the nanofiller being a non-functionalized silica, with 0.001 – 5 % weight ratio to vinyl chloride, with nanofiller used in the form of a sol, gel, powder or in the form of aqueous dispersion of powder, added once, in portions or continuously.
2. Method according to claim 1 **characterized in that** 0.01 – 3 % of the nanofiller is used, ideally in the 0.1 – 2 % weight ratio to vinyl chloride.
3. Method according to claim 1, **characterized in that** water nanosilica dispersion is stabilized with a suspension stabilizer from methylcellulose derivatives and/or poly(vinyl alcohol)s.

Summary

Suspension polymerization of vinyl chloride is carried out at a temperature of 50-70°C, with the use of suspension stabilizers and free radical initiators, and with the addition of a nanometre size filler in the form of non-functionalized silica used in the amount of 0.001-5% by weight in relation to vinyl chloride, with the nanofiller being added to a polymerization mixture in the form of a sol, gel, powder or in the form of an aqueous powder dispersion, optionally stabilized with a protective colloid

(3 claims)