Poly(Vinyl Chloride) Nanocomposites Prepared in the Suspension Polymerization Process. Part I. PVC Filled with Hybrid Nanofiller

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Abstract: PVC syntheses were done by suspension polymerization in the presence of hybrid silicone/acrylic core-shell type nanofiller. The moldings made from PVC nanocomposites are fully homogeneous and of good transparency. SEM images show very good, uniform dispersion of nanofiller in PVC matrix. The blends made from nanocomposites show higher tensile strength (~10%) and tensile modulus (20% higher for nanofiller amount equal to 0.2 wt.%/VCM) than PVC homopolymer. The impact strength of all samples made from PVC nanocomposites are higher than of PVC. Blends of nanocomposites containing 0.5 or 1.0 wt.%/VCM of nanofiller show the best impact strength: 28 and 32% better than PVC, respectively. Nanocomposites containing 0.5 wt.%/VCM of core-shell nanofiller show the highest stiffness. The nanofiller used practically does not influence thermal properties of the polymer. The use of PVC nanocomposites in typical PVC applications gives possibility to obtain the novel PVC products with the properties better than the present ones as well as the possibility to reduce processing costs *via* reduction of processing aids amounts, especially impact modifiers, what additionally will lead to tensile properties improvement.

Key words: Core-shell nanofiller, VCM suspension polymerization, mechanical properties.

Nomenclature

G' : Storage modulus
 $tg\delta$: Loss tangent

1. Introduction

The demand for the research works on poly(vinyl chloride) (PVC) nanocomposites are going not long ago. The published papers and patents covers the last decade. Majority of them concerns the nanofiller introduction in polymer processing or *via* melt blending. At first mainly the clays: montmorillonite (MMT) or bentonite [1-4] were used as nanofillers but also precipitated calcium carbonate [5-6] were tested. The clays are concerned not only as modifiers of polymer mechanical properties but also their effect on

flame retardancy [7] and/or reduction of smoke evolution were studied. For example Awad et al. found a suppression of smoke generation as well as in the peak heat release rate for PVC composites with appropriately modified bentonite or hectorite [8]. Authors say it is true that “this finding of smoke reduction is not in agreement with the classic measurement of thermal stability” but independently on mechanism of this phenomenon it is of great importance in many PVC application as cables, wires and other insulations.

A bit later first papers on nanofillers introduction at the vinyl chloride monomer (VCM) polymerization were published. Several of them concerned emulsion VCM polymerization in the presence of MMT [9-11] while the others - the suspension polymerization in the presence of MMT [9, 12-14] or $CaCO_3$ [15-18] as well as wide investigations of the properties of

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nanocomposites obtained. Yong-zhong et al. [19] investigated both thermal stability and smoke emission of PVC/hydrotalcite composites produced in suspension polymerization. The hydrotalcite (HT) surface was earlier modified with alkylphosphonate. For the HT part equal to 2.5 and 5.3 wt.% per PVC smoke density decreased about 1/3 and 1/2, respectively. Thermal stability of composites (measured by Congo Red and TGA) was better than of pure PVC. Additionally, toughening and stiffening effects on PVC were observed for PVC/HT nanocomposites. The research works on PVC nanocomposites with clays have still carried out focused often on clays modification to improve the filler distribution in polymer matrix and to prevent polymer degradation (ammonium salts often used to intercalate MMT catalyze PVC dehydrochlorination [20-22]). So to maintain polymer thermal stability and to enhance mechanical, dielectrical or fire properties of composites special techniques are used to make clays more compatible with PVC and not deteriorating its thermal stability. For example, Yarahmadi et al. [23] used montmorillonite specially treated with chelating agents, i.e., propylene glycol monostearate, polyethylene glycol or palm oil, to prepare PVC nanocomposites with good thermal stability and good mechanical properties, though authors thought they did not reach the full potential of such composites. Also, Madaleno et al. [24] investigated the PVC composites with montmorillonite, their morphology, thermal stability and mechanical properties having found the different effects of natural sodium montmorillonite and organically modified MMT, as well as strong influence of preparation method (solution blending or solution blending + melt compounding) on the final composite properties. Generally, composites prepared via solution blending and melt compounding showed better thermal properties than those prepared by solution blending only. Vicat softening temperature of composites were significantly lower (worse) than of unfilled PVC while Young's modulus, tensile strength and elongation

especially of composites containing 2 or 5 wt.% of O-MMT were improved.

Another possibility of mechanical properties of PVC/MMT nanocomposites improvement was described in Ref. [25]. The PVC/MMT films, containing up to 5 wt.% of MMT modified with dodecylamine were produced by solution-elution technique and then subjected to controlled uniaxial stretching at temperature 80 °C. The films stretched close to the PVC softening temperature showed higher crystallinity degree what positively affected tensile strength and Young's modulus of the films. However, some authors reported unacceptable decrease in impact properties of PVC/MMT composites (at 5 phr of clay) [26]. Dielectric properties of PVC and its nanocomposites are also subject of studies [27, 28]. Mobarak et al. [27] stated that the presence of nanofillers such as MMT and fumed silica in PVC could restrict the chain mobility and result in increasing electric insulation. MMT in amount 1-10 wt.% successfully decreased dielectric loss tangent constant (from 0.57 to 0.5 at 100 Hz). Fumed nanosilica enhanced PVC resistivity up to 1×10^{11} Ohm·m. Nanofillers such as silica, titania or alumina at the concentration of 5 wt.% were used for modification of PVC dielectric and thermal properties in plasticized blends [28]. The samples were γ -irradiated. Authors found that silica, probably due to its availability of hydroxides generation, caused higher permittivity of PVC material while titania showed an opposite action because of its acidic behavior. Alumina, having amphoteric character, did not influence permittivity and dielectric loss of PVC. The irradiation of these insulation materials should allow production of materials with good dielectric characteristics even for high frequency range. Nanosilica is investigated as possible filler for PVC not only as pure nanosilica, sometimes various its modifications give good results, e.g., nanosilica particles covered with PMMA looks to improve the silica dispersion in PVC matrix resulting in increased tensile strength, elongation at break and

heat resistance [29]. Similar results were obtained when hybrid PSBA-silica system (terpolymer styrene-*n*-butyl acrylate-acrylic acid grafted-nanosilica) was used [30]. Titania in nanodimensions was used as PVC filler unmodified or with modified surface. Olad et al. [31] modified TiO₂ surface with PANI and prepared PVC composites with unmodified or modified titania. They observed better adhesion between filler and polymer in PVC/PANI-TiO₂ nanocomposites which showed better thermal stability, tensile strength and Young's modulus than unfilled PVC and PVC/TiO₂ nanocomposites.

Even the application of carbon nanotubes in PVC composites was reported, among others, by Bokova et al. [32]. Carboxymethylcellulose was used to entail uniform dispersion of single-wall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (MWCNT) in polymer matrix. The films of optical and electrical quality have been obtained. The UV-VIS-NIR spectroscopy confirmed good distribution and of individual SWNT in polymer matrix and properties improvement with growing content of carbon nanotubes [33].

In the Industrial Chemistry Research Institute last few years, we enriched the VCM suspension polymerization mixture with spherical nanofillers including hybrid core-shell type filler according to ICRI elaboration [34-37].

In this paper, the effects of hybrid core-shell nanofiller on PVC morphology and physico-chemical, rheological, mechanical and thermal properties were investigated.

2. Experiments

2.1. Materials

The following materials were used in VCM polymerizations:

- Vinyl chloride monomer (Anwil SA, Poland);
- Suspension stabilizers:
methylhydroxypropylcellulose derivatives
(Metolose 60 SH50, Shin-Etsu Chemical Co. Ltd.,

Japan) and poly(vinyl alcohol) (Alcotex C74, Synthomer, UK) in weight ratio 1 : 1, 0.07 wt.%/VCM;

- Initiators:

1,1,3,3,-tetramethylbutyl peroxyneodecanoate and di(2-ethylhexyl) peroxydicarbonate (Triginox 423 and Triginox EHPC, respectively, both Akzo Nobel Polymer Chemicals bv, The Netherlands) in weight ratio 1:2, 0.1 wt.%/VCM in organic solvent;

- Silicone-methacrylic core-shell type nanofiller (core:shell ratio = 60:40) with average particle size ~100 nm, 0.2-2.0 wt.%/VCM; prepared in ICRI according to [34];

- Distilled water.

In processing step we used the additives as follows:

- PVC/core-shell nanocomposites, 100 phr;
- Stabilizers:

Tribasic lead sulfate (Grautz Dolau, Germany), 4.0 phr;

Lead stearate (Grautz Dolau, Germany), 1.0 phr.

- Lubricants;

Loxiol G 22 (Henkel, Germany), 0.5 phr;

Calcium stearate (Boryszew S.A, Poland), 0.3 phr.

- Flow modifier: Paraloid (TM) K 125 ER, (Rohm and Haas Company, United Kingdom), 1.0 phr

- Filler:

Calcium carbonate (Hydrocarb 95T, OMYA Poland, Poland), 10.0 phr;

Titanium dioxide (Kronos International, INC., Germany), 2.0 phr.

2.2. Preparation of Hybrid Silicone/Acrylic Nanofiller

Core-shell particles were prepared by emulsion method in two-stage process. In the first stage the synthesis of silicone "core" from functional silanes and cyclic siloxane monomers was carried out. Dodecylbenzenesulfonic acid, causing the opening of octamethylcyclotetrasiloxane ring, was the reaction catalyst and the same time emulsifier.

As a result of polysiloxane chain hydroxyl end groups bonding with hydrolyzing methoxy groups from trifunctional silanes, the partially crosslinked

silicone rubber is formed, being a core of core-shell nanoparticles in aqueous dispersion used for Stage 2, polymerization nucleation. In Stage 2, the polymerization of acrylic monomer in the presence of silicone rubber particles as nuclei was carried out. The reaction initiator was potassium persulfate and methyl methacrylate was used as acrylic monomer. The particles of reactive oligomers built the shell on silicone nuclei forming core-shell particles.

2.3. Preparation of Nanocomposites

2.3.1 VCM Polymerization

VCM suspension polymerizations with use of silicone-methacrylic core-shell type nanofiller were carried out in the glass laboratory autoclave 1.5 L of capacity (Büchi AG, Switzerland) equipped with water heating-cooling jacket, a stirrer with variable gear, temperature and pressure measurements, connections for reagents and gas as well as safety valve.

The process runs as follows: distilled water, aqueous solutions of suspension stabilizers, initiators in aqueous emulsions or organic solvents and nanofiller in dispersion were introduced to the reactor. Then the reactor was closed and air was evacuated. The reactor was blew through with nitrogen and the pressure test was carried out (at 0.9 MPa for 30 min). Then, after inert gas evacuation under vacuum a liquid vinyl chloride monomer was introduced through needle valve and the stirrer started. The chosen revolutions per minute were fixed. At the same time the polymerization mixture was heated to the polymerization temperature which was maintained with the precision ± 0.5 °C during the whole process. The polymerization was stopped by rapid cooling with simultaneous degassing of unreacted monomer. The polymer was separated from the aqueous phase using laboratory centrifuge (3,000 r.p.m.) and dried to a constant weight under the lamps (500 W) fixed about 30 cm over the powder layer. The temperature in the polymer layer was about 45 °C.

The nanofiller amounts used in VCM

polymerizations were in the range 0.2-2.0 wt.%/VCM. Nanofiller was used in the form of aqueous dispersion what prevented its grain agglomeration. Polymerization temperature was 53 °C, time: 4 hours (since the moment when polymerization temperature was reached), maximal pressure: 1 MPa. The stirrer worked with constant speed 600 r.p.m.

2.3.2 Processing

On the basis of PVC/core-shell products powders, the processing blends with stabilizers, lubricants and impact modifier were prepared. The blends obtained were then rolled (at temp. 160 °C for 6-7 min) and compression molded to plates (at temp. 180-190 °C, pressure 20 MPa), from which the test specimens were cut.

2.4. Characterization Methods

To characterize the PVC nanocomposites powders the following measurements were realized:

- The structure was characterized by scanning electron microscopy (SEM) using Hitachi S-3500N apparatus and high resolution scanning electron microscope Hitachi S5500;
- *K* value was calculated from viscosity number measurements using Ubbelohde viscometer, according to Ref. [38];
- Bulk density was determined according to Ref. [39];
- Sieve analysis was done using Alpine Augsburg sieve analyzer according to Ref. [40].

To characterize the PVC nanocomposites blends the following measurements were realized:

- Tensile strength was tested using Tira Test apparatus according to Ref. [41] (crosshead speed was 100 mm/min);
- Charpy notched impact strength was determined according to Ref. [42];
- Hardness was tested using Shore D scale according to Ref. [43];
- Melt Flow Rate (MFR) was measured using plastometer IIRT type equipped with a nozzle with

circular channel ϕ 2 mm and length 8 mm according to Ref. [44] (measurements carried out at temp. 180 °C and loading 200 N);

- Thermogravimetric (TGA) measurements were done using TGA/SDTA851E apparatus at linear temperature increase from room temperature (25 °C) up to 500-550 °C at heating rate 10 °C/min in an air atmosphere. The data analysis was carried out using Star 8.1. program;

- Dynamic Mechanical Thermal Analysis (DMTA) tests were done using RDS II apparatus (Rheometrics) at torsional strain 0.1%, linear temperature increase and constant strain frequency with constant amplitude. The measurements conditions were as follows: temperature range from -150 °C up to 150 °C, heating rate 3 °C/min, frequency 1 Hz. The storage modulus (G') and loss tangent ($\tan \delta$) versus temperature were determined.

3. Results and Discussion

3.1 Nanofiller Dispersion in Polymer Matrix

The shape of typical suspension PVC grain being an agglomerate of primary particles is rather irregular and its surface is wrinkled because the contraction of monomer drop volume during polymerization (VCM density ~ 0.9 g/cm³ while PVC density ~ 1.3 g/cm³). Fig. 1 presents the SEM images of samples at magnification 1,000 times.

The presence of 0.2-0.5 wt.% of core-shell type nanofiller does not influence significantly the morphology of PVC nanocomposite obtained. However, the bigger amount (≥ 1 wt.%) of this nanofiller cause the change of particle shape-PVC grain is more spherical. The bigger concentration of nanofiller the more regular spherical shape of polymer grain. Its surface is not so corrugated as of PVC, it is more smooth though porous. The analysis of microphotographs let state that the filler used in vinyl chloride suspension polymerization is uniformly dispersed in PVC grain and the filler itself influence advantageously the regularity of polymer grain

structure.

3.2 Physico-Chemical Properties

The selected physicochemical properties of PVC and PVC nanocomposites powders obtained are shown in Table 1.

The use of core-shell type silicone-acrylic nanofiller in VCM suspension polymerization does not influence the polymer molecular weight - K -value keeps the level ± 1 . However, a decrease in bulk density was observed in the whole range of nanofiller concentration tested what can mean the grains of nanocomposites obtained were more porous than of PVC one. Also the effect of the filler on the size of polymer grain was observed: the amount of undersized grain ($\phi < 0.063$ mm) was increasing with growing part of nanofiller used what means the average diameter of the grain became smaller.

3.3 Rheological and Mechanical Properties

The nanocomposites obtained were used to prepare the blends of compositions similar to those used in the industry to produce rigid profiles. They contained 4 weight parts of thermal stabilizer, 1 part of lubricant, 10 parts of chalk - often used filler and no impact modifier. The blends were rolled and compression molded. Table 2 illustrates their properties. It has been found that increasing content of nanofiller caused decrease in MFR indices. The samples containing 0.5 or 1 wt.% of nanofiller showed improved tensile strength (7% and 12%, respectively). Hardness of all nanocomposites samples was practically the same as of PVC. The rigid blends of nanocomposites show also increase in tensile modulus just at the very small amount of a nanofiller (0.2 wt.%).

Then with growing nanofiller content the tensile modulus slightly decrease but in the whole range tested (up to 2 wt.% of nanofiller) is bigger (11% to 21%) than of control sample (PVC). Rigid materials are usually more brittle. So, higher tensile modulus proves the advantageous effect of nanofiller on rigid blends properties.

Fig. 1 SEM images of PVC (a) and its nanocomposites containing 0.2 (b), 0.5 (c), 1.0 (d), 1.5 (e) or 2.0 (f) wt.%/VCM of core-shell nanofiller.

Table 1 Properties of polymers powders obtained.

Filler content wt.%/VCM	<i>K</i> value	Bulk density (g/cm ³)	Grain size > 0.250 mm (%)	Grain size < 0.063 mm (%)
0	67.70	0.50	0.10	0.40
0.2	68.60	0.42	2.50	0.90
0.5	67.90	0.39	1.00	4.00
1.0	66.30	0.39	0.60	7.20
1.5	67.70	0.41	1.10	13.80
2.0	67.20	0.43	0.70	14.60

Table 2 Processing and tensile properties of rigid PVC and PVC nanocomposites blends.

Filler content (wt.% /VCM)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)	Charpy notched impact strength (kJ/m ²)	MFR (g/10 min)
0	50 ± 0.2	45 ± 3	1,750 ± 25	16 ± 0.4	9.2
0.2	51 ± 0.3	53 ± 1	2,110 ± 20	18 ± 0.2	6.1
0.5	54 ± 0.5	36 ± 3	2,010 ± 23	21 ± 0.4	5.6
1.0	57 ± 0.6	37 ± 2	1,960 ± 28	22 ± 0.4	5.7
1.5	53 ± 0.2	44 ± 2	2,010 ± 12	18 ± 0.2	5.6
2.0	49 ± 0.1	37 ± 1	1,940 ± 15	18 ± 0.3	4.9

Charpy notched impact strength depends significantly on nanofiller content. Unnotched samples did not break. All samples made from nanocomposites have better impact strength than control PVC samples. The samples containing 0.5 or 1.0 wt.% of nanofiller show the best impact strength: 31% and 37% better, respectively, than of standard PVC. It means the impact strength of PVC nanocomposites is much better than that characterizing PVC itself.

The dynamic mechanical properties of of PVC and PVC/core-shell nanocomposites are represented in Figs. 2 and 3 and Tables 3 and 4.

Fig. 2 and Table 3 show the dynamic storage modulus (G') as a function of temperature for PVC and its nanocomposites. Storage modulus of PVC increases for core-shell filler content equal to 0.5 wt.%/VCM. Storage modulus of PVC increases due to the reinforcement effect and restrictions in the chain

mobility; increasing stiffness.

At temp. 80 °C the nanofiller content ≥ 1 wt.%/VCM caused decrease in storage modulus so the stiffness was significantly smaller what could prove the formation of nanofiller agglomerates.

Fig. 3 and Table 4 illustrate the effect of core-shell

Fig. 2 Temperature dependence of storage modulus G' of PVC and PVC/core-shell nanocomposites.**Table 3** Storage modulus of PVC/core-shell nanocomposites at temp.: -40, 25, 50 or 80 °C.

Filler content (wt.% /VCM)	G' (-40 °C) (MPa)	G' (25 °C) (MPa)	G' (50 °C) (MPa)	G' (80 °C) (MPa)
0	2,230	2,090	1,600	947
0.5	2,540	2,000	1,890	1,050
1.0	2,010	1,620	1,480	887
1.5	1,970	1,540	1,400	197
2.0	2,300	1,770	1,630	100

Table 4 Glass transition temperature of PVC and PVC/core-shell nanocomposites.

Filler content wt.% /VCM	T_g (°C)	$tg\delta$ at peak
0	95.0	1.30799
0.5	97.0	1.23741
1.0	96.5	1.29551
1.5	96.2	1.26672
2.0	96.5	1.26879

Fig. 3 Temperature dependence of loss tangent ($tg\delta$) of PVC and PVC/core-shell nanocomposites.

nanofiller on the loss tangent ($tg\delta$) of PVC nanocomposites. It can be seen the one relaxation transition α (a distinct sharp peak $tg\delta$) denoted as glass transition T_g .

The peak of relaxation transition α relates to change in polymer macromolecular segments mobility. Introduction of core-shell filler to PVC slightly increases T_g , maximally 2 °C for 0.5 wt.%/VCM filler content. Therefore thermal stability of such nanocomposite is better.

It is well known glass transition temperature (T_g) depends on polymer chains mobility. If this mobility is limited, T_g will increase and this increase can be related to uniform distribution of nanofiller in polymer matrix and polymer-filler interactions [45].

3.4 Thermal Properties

Thermal properties of PVC/core-shell nanocomposites were evaluated on the basis of thermogravimetric measurements. PVC homopolymer shows two-stage degradation: in first step the dehydrochlorination occurs and in the other one the breakdown of polymer chains runs. Also PVC nanocomposites containing layered aluminosilicates degrade this way [17].

In our work, we determined the characteristic values of degradation temperature: T_{10} , T_{50} , i.e., the temperature of 10 and 50% weight loss, respectively, similarly as it was reported in Ref. [1], as well as T_{max1} and T_{max2} describing maximal temperatures of particular degradation steps. The total weight loss was determined at 550 °C. Thermal properties of the composites obtained are presented in Table 5.

The T_{10} temperature for PVC nanocomposites is nearly the same as of PVC homopolymer while T_{50} is slightly higher for the composites containing 1.5-2 wt.%/VCM of nanofiller (3 °C). Nearly linear decrease in maximal temperature of the second degradation step T_{max2} with increasing content of the nanofiller has been observed (maximal decrease of 14 °C for nanocomposite containing 2 wt.%/VCM of a filler).

Table 5 Thermal properties of PVC and PVC/core-shell nanocomposites.

Filler content wt.% /VCM	T_{10} (°C)	T_{50} (°C)	T_{max1} (°C)	T_{max2} (°C)	Total weight loss at 550 °C
0	289	343	306	453	73.4
0.2	288	339	299	453	77.3
0.5	289	345	305	450	78.0
1.0	287	343	304	452	75.1
1.5	287	346	306	449	75.0
2.0	287	345	306	439	75.4

4. Conclusions

The vinyl chloride suspension polymerization conditions, allowing avoiding process disturbances by introduction to polymerization mixture of up to 2 wt.%/VCM of core-shell type silicone-methacrylic nanofiller, have been elaborated. SEM images show the nanofiller used advantageously influences the regularity (sphericalness) of PVC grain structure (especially for filler content 0.5-2.0 wt.%/VCM) and it is uniformly dispersed in PVC matrix. The blends made from nanocomposites obtained show higher tensile strength (~10%) and tensile modulus (20% higher for nanofiller amount equal to 0.2 wt.%/VCM) than PVC homopolymer. The impact strength of all samples made from PVC nanocomposites are higher than of PVC. Blends of nanocomposites containing 0.5 or 1.0 wt.%/VCM of nanofiller show the best impact strength: 31% and 37% better than PVC, respectively. Nanocomposites containing 0.5 wt.%/VCM of core-shell nanofiller show the highest stiffness. The nanofiller used practically does not influence thermal properties of the polymer. The use of PVC nanocomposites in typical PVC applications gives possibility to obtain the novel PVC products with the properties better than the present ones as well as the possibility to reduce processing costs *via* reduction of processing aids amounts, especially impact modifiers.

As it is well known in PVC industry that reduction of impact modifiers amount in rigid PVC blends involve the rising strength so PVC/core-shell nanocomposites make possible not only the blends cost cutting and impact strength improvement but the same time also strength of such products should be better.

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