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## Polymerization of vinyl chloride in the presence of nanofillers — effects on the shape and morphology of PVC grains

**Summary** — Suspension polymerization of vinyl chloride has been carried out in the presence of various types of nanofillers chosen from clays, silica (pure or functionalized), silicone polymer or hybrid core/shell ones. Nanofillers used in VC polymerization significantly influence the structure and shape of PVC grain: from typical one in case of control sample and in the presence of silica to “cake-like” in case of functionalized silica, “sea-shells” with silicone polymer use or “balls” and “dented balls” — not typical for suspension PVC — in the presence of hybrid core/shell particles. The last ones look just as emulsion PVC although were prepared in suspension polymerization process. It has been found, using SEM and TEM methods, that distribution of nanofiller in polymer was rather uniform. MMT is semiintercalated/semiexfoliated in PVC grain. Some regions showing mesoporosity were also found (especially in the presence of silica) suggesting the formation of more ordered structures in the grain. We can foresee that not only the presence and distribution of nanofillers in PVC grain but also the change of PVC grain shape caused by them can both influence the final properties of PVC and its processability.

**Key words:** suspension VC polymerization, nanofillers, silica, montmorillonite, core/shell hybrid nanofillers, PVC grain morphology, mesoporosity.

### POLIMERYZACJA CHLORKU WINYLU W OBECNOŚCI NANONAPEŁNIACZY — WPŁYW NA KSZTAŁT I MORFOLOGIĘ ZIARNA PVC

**Streszczenie** — Suspensyjną polimeryzację chlorku winylu (VC) prowadzono w obecności różnych typów nanonapełniaczy; były to glinki [montmorylonit (MMT) czysty lub funkcjonalizowany], krzemionka (czysta bądź funkcjonalizowana), polimer silikonowy albo hybrydowy układ typu rdzeń/otoczka. Stwierdzono, że nanonapełniacze zastosowane jako składniki mieszaniny polimeryzacyjnej w istotny sposób wpływają na strukturę i kształt ziarna PVC: od typowego w próbce kontrolnej otrzymanej w nieobecności nanonapełniaczy (rys. 1) oraz w próbkach powstających w obecności krzemionki niefunkcjonalizowanej (rys. 2) lub montmorylonitu interkalowanego oktadecyloaminą (rys. 3) poprzez “ciastka” czasem przypominające “wgniecioną piłeczkę” w przypadku krzemionki funkcjonalizowanej (rys. 4), “muszelki” (w obecności polimeru silikonowego, rys. 6) aż do regularnych okrągłych kulek (nietypowych dla PVC suspensyjnego) i ziaren typu “wgniezionej piłeczki” — w obecności nanocząstek o budowie rdzeń/otoczka (rys. 5). Ten ostatni produkt bardziej przypomina PVC emulsyjny, choć otrzymano go w procesie suspensyjnym. Metodami elektronowej mikroskopii skaningowej (SEM) i transmisyjnej (TEM) stwierdzono, że rozkład nanonapełniacza w ziarnie PVC jest dość jednorodny (TEM — rys. 7 i 8). Funkcjonalizowany montmorylonit ulega co najmniej częściowej interkalacji i eksfoliacji w ziarnie PVC (rys. 11). Znalezione regiony w ziarnie PVC (w szczególności otrzymanym wobec krzemionki) wykazujące mezoporowatość (rys. 10), co potwierdzałoby tworzenie bardziej uporządkowanych struktur. Silne oddziaływania występujące pomiędzy nanonapełniaczami funkcjonalizowanymi lub hybrydowymi a stabilizatorami suspensji sprzyjają aglomeracji nanocząstek (rys. 8 i 9).

**Słowa kluczowe:** suspensyjna polimeryzacja VC, nanonapełniacze, krzemionka, montmorylonit, hybrydowe napełniacze typu rdzeń/otoczka, morfologia ziarna PVC, mezoporowatość.

One of the first papers on PVC nanocomposites *via* polymerization by Aguilar-Solis [1] described emulsion

or suspension polymerization of vinyl chloride (VC) in the presence of various ways treated montmorillonite (MMT) as a component of polymerization mixture. Gong *et al.* also polymerized VC in the presence of MMT [2] and investigated the thermal properties of nanocom-

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posites obtained [3] as well as some mechanical properties [4]. Significant improvement (30–50 %) in mechanical properties (tensile strength, Young modulus, toughness, and impact strength) has been found [4]. Improvement in some mechanical properties of PVC were always found when MMT was introduced into PVC matrix *e.g.* by melt blending [5, 6] or solution blending [7]. Emulsion polymerization of VC on MMT has been also reported by authors of [8].

The aim of this work was to find the changes in PVC grain morphology when vinyl chloride was polymerized in the presence of various nanofillers, especially nanospheres, including hybrid ones. The results were compared with those for the samples obtained in the presence of MMT or without addition of any nanofillers to polymerization mixture. Eventual changes in PVC morphology are very important as PVC gelation, processability and final properties of the product depend on it significantly [9–11].

### EXPERIMENTAL

The polymerization of VC (by Anwil SA) has been carried out in laboratory 1.5 l autoclave (Büchi AG) at temperature 53 °C using typical suspension stabilizers [methyl cellulose derivative “Methocel” (by Dow) + poly(vinyl alcohol) “Alcotex C74” (by Synthomer), 1:1, in concentration 0.07 wt. %/VC] and initiators system: 1,1,3,3-tetramethylbutyl peroxyneodecanoate “Peroxan OPN” + di(2-ethylhexyl) peroxydicarbonate “Peroxan EPC-75” (both by Pergan GmbH), 1:1, in concentration 0.1 wt. %/VC. The nanofillers have been selected from hybrid core/shell nanospheres, silica nanospheres, functionalized silica nanospheres as well as the clays (montmorillonite and functionalized montmorillonite) for comparison. Except neat MMT and MMT pre-treated with octadecylamine, the nanofillers were specially prepared for this work. They have been added to the polymerization mixture at the beginning of the process either in the form of sol or as a dried powder, what is marked in results discussion. The amounts used were 2 or 3 wt. %/VC. The images obtained by the methods of scanning electron microscopy (SEM 515 Philips) and transmission electron microscopy (TEM, JEM-1200 Ex II Jeol) were analyzed to study the morphology of PVC formed.

### RESULTS AND DISCUSSION

Polymerization processes have been carried out in nearly identical conditions given above, except the types and amounts of nanofillers. It has been found using SEM method that distribution of nanofiller in polymer was rather uniform. SEM images show also the shape of PVC grain changed. The significant changes in morphology of PVC grains were found: from typical PVC-S shape (PVC polymerized without nanofiller, Fig. 1) also in the



Fig. 1. SEM image of typical suspension PVC grain (control sample)

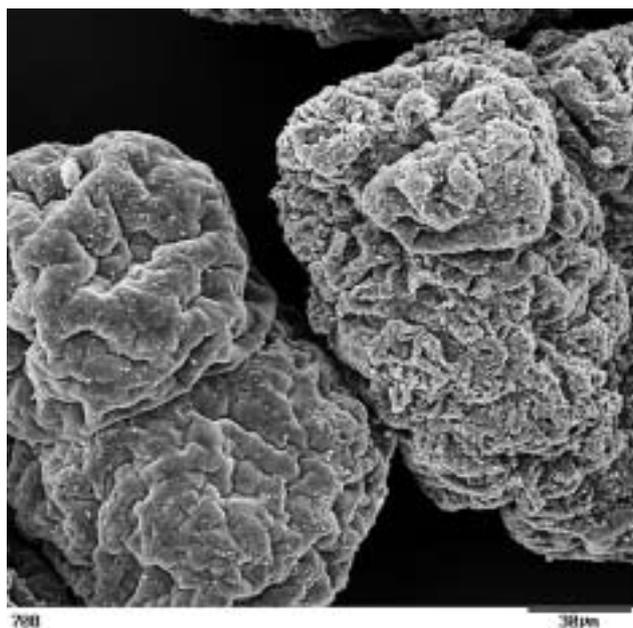


Fig. 2. SEM image of the product of VC suspension polymerization in the presence of silica nanospheres, given as a powder

presence of silica, given in powder form (Fig. 2) or MMT (pre-treated with octadecylamine) (Fig. 3) to “cakes”, a bit similar to “dented balls” in case of functionalized silica nanospheres in sol (Fig. 4). In the presence of hybrid core/shell nanospheres (given in sol) PVC grains look like “dented balls” or even uniform regular spheres (Fig. 5) — as if they were obtained in emulsion not suspension polymerization. Using of the silicone polymer, applied by us as a “core”, (given in sol) as nanofiller we obtained “sea-shell”-like PVC-S grains, also not typical for PVC-S (Fig. 6). It must be stressed that the change in

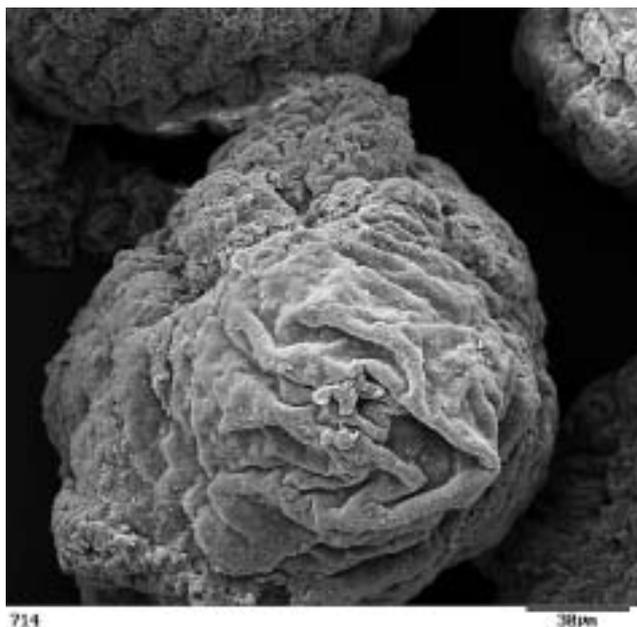


Fig. 3. SEM image of the product of VC suspension polymerization in the presence of MMT pre-treated with octadecylamine, given as a powder

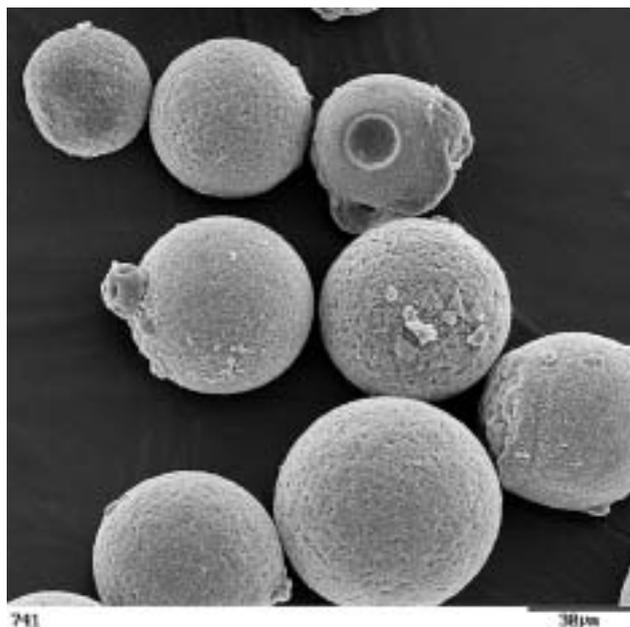


Fig. 5. SEM image of the product of VC suspension polymerization in the presence of hybrid core/shell nanospheres, given in sol

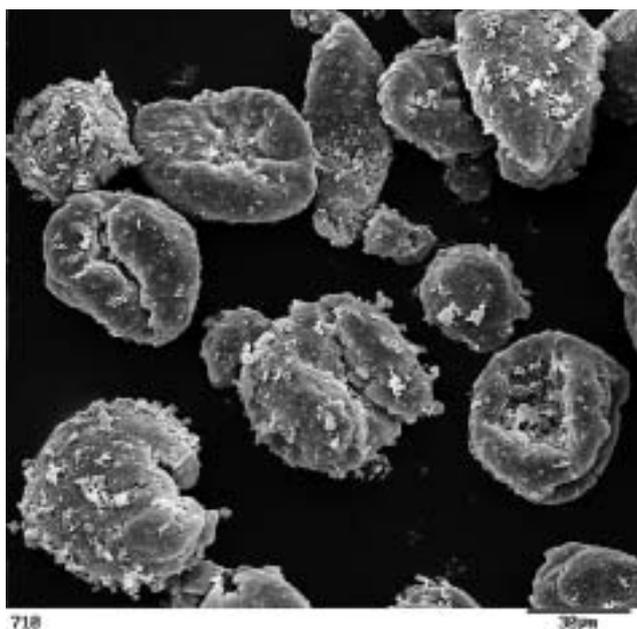


Fig. 4. SEM image of the product of VC suspension polymerization in the presence of functionalized silica nanospheres, given in sol

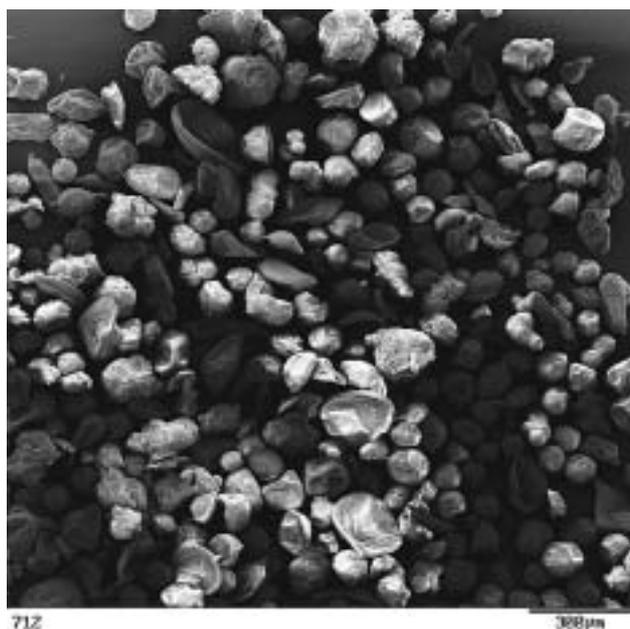


Fig. 6. SEM image of the product of VC suspension polymerization in the presence of silicone polymer, given in sol

polymer grain shape is an additional very important factor influencing the further processability of the polymer, independently on the change in the properties caused by the presence of nanofiller in the grain.

TEM images confirmed the uniform distribution of nanofillers in PVC grain. For neat silica (given as a powder) and core/shell nanospheres (in sol) we have found their good distribution in PVC grain (Fig. 7 and 8, respectively).

The strong interactions between functionalized or hybrid nanofillers and suspension stabilizers occurred, causing an agglomeration of nanofillers (shown by the arrows in Fig. 8 and 9). Partial agglomeration of core/shell nanofiller is clearly visible in Fig. 8. In case of use of functionalized silica nanospheres (in sol) it looks as if silica functionalization caused interactions with suspension stabilizers and the tendency of its agglomeration was also observed (Fig. 9).

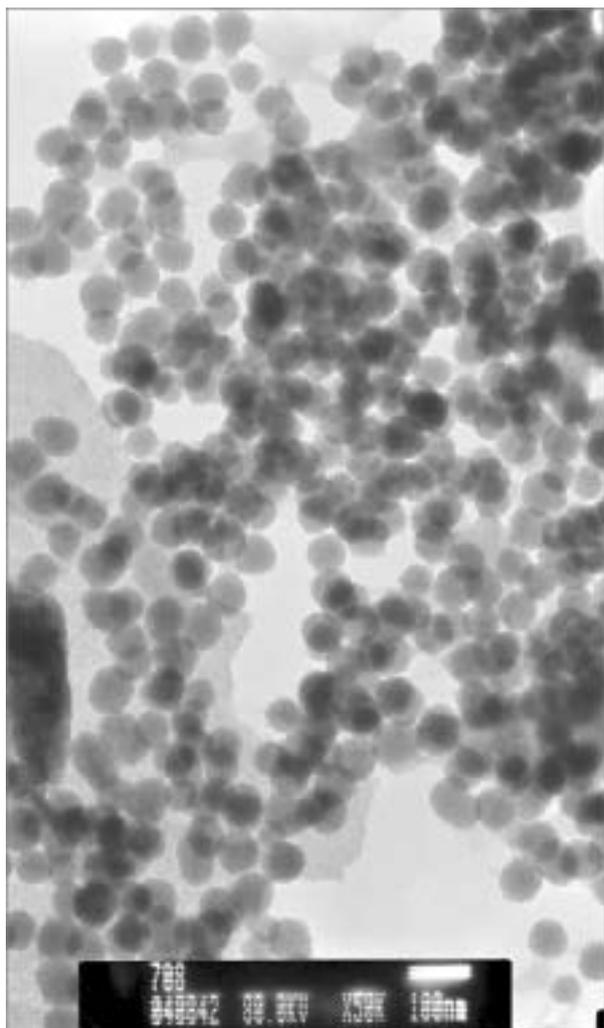


Fig. 7. TEM image of silica nanospheres (given as a powder) distribution in PVC grain

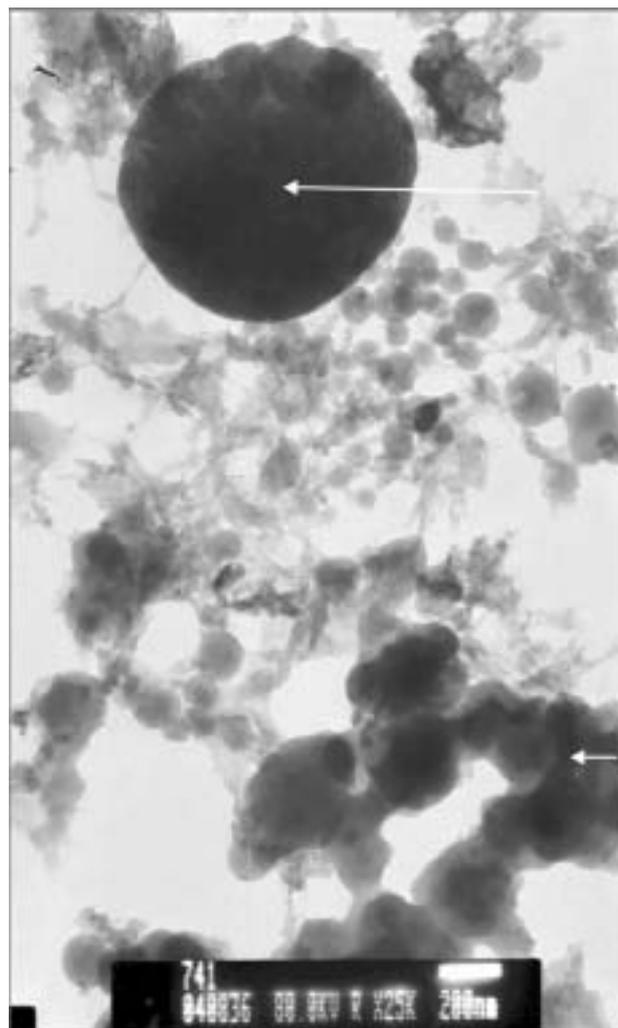


Fig. 8. TEM image core/shell nanospheres (given in sol) distribution in PVC grain; agglomeration of nanofiller is clearly visible

Interesting structures showing ordered regions suggesting a mesoporosity have been found by TEM in PVC/silica system (the same sample as presented in Fig. 2 and 7). These regions demonstrate sets of parallel pores of very small diameter ( $\sim 2$  nm) (Fig. 10) pointing the formation of more ordered structures. Functionalized MMT looks to be semiintercalated/semiexfoliated in PVC matrix (Fig. 11). Its separated layers are either parallel (intercalation; the distance between the plates about 50 nm) or randomly distributed as single plates (exfoliation).

The distance of about 50 nm between MMT platelets, found in our PVC samples, is the same as reported lately by Dubois in PCL obtained by polymerization of  $\epsilon$ -caprolactone in the presence on MMT [12], what is very interesting. The surface of dissociated platelets of nanofiller is homogeneously coated by the *in-situ* grown polymer chains, as in so called "Polymerization-filling" technique (PFT) [12], and thermo-mechanical properties of the products should be better than those of nanocomposites obtained in processing step, even if the concentration of nanofiller is in polymerization step smaller

than that one in processing one. The properties of the polymers obtained are the subject of another paper, in preparation.

## CONCLUSIONS

Use of nanofillers in vinyl chloride suspension polymerization influence both shape of the grain and its structure — a new morphology of PVC-S has been obtained. TEM images of PVC obtained *via* polymerization in the presence of various types of nanofillers show that they are rather uniformly dispersed in PVC matrix. Partial agglomeration of nanofillers, caused by interaction with suspension stabilizers, was observed especially in case of using functionalized ones. Some ordered regions showing mesoporosity were found — regular sets of parallel nanopores, not observed in control PVC samples (polymerized in the absence of nanofillers), are visible in the samples polymerized in the presence of nanospheres, especially silica. MMT is semiintercalated/semiexfoliated in PVC grain and the distance between

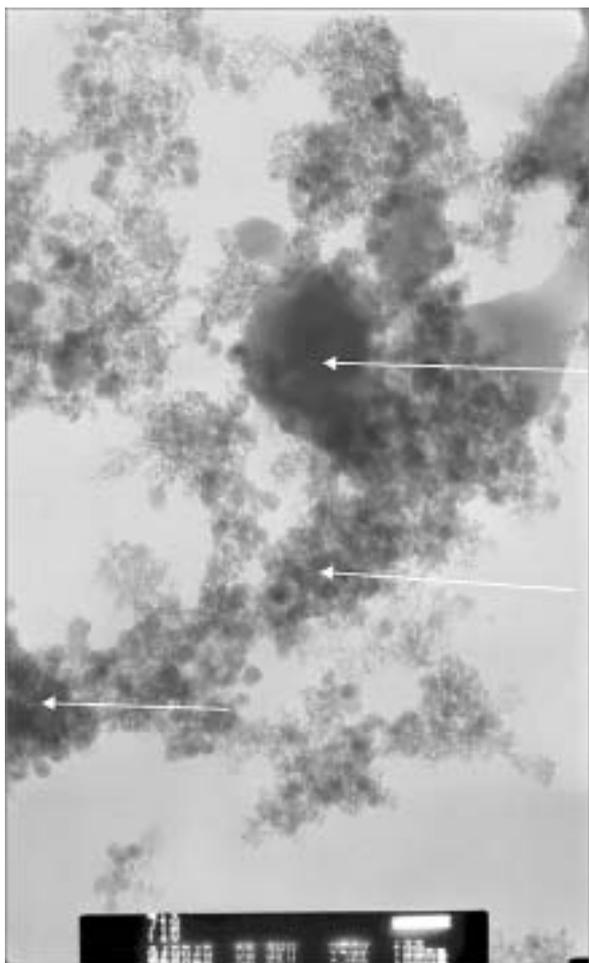


Fig. 9. TEM image of functionalized silica nanospheres (given in sol) distribution in PVC grain; agglomeration of nanofiller is clearly visible

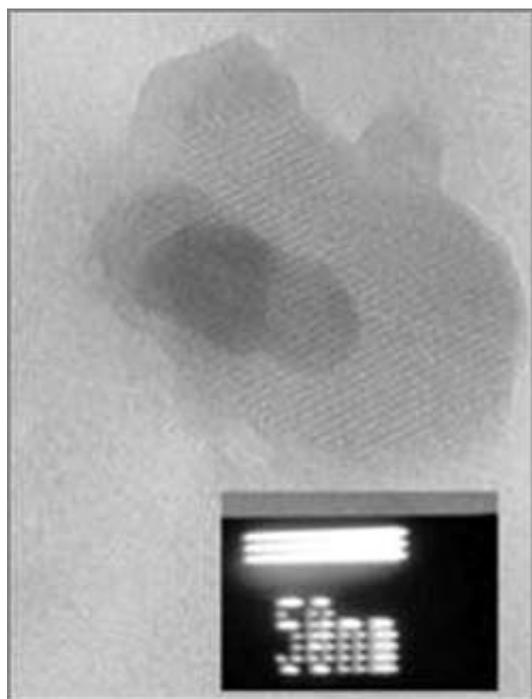


Fig. 10. TEM image of mesoporosity region in PVC/silica system

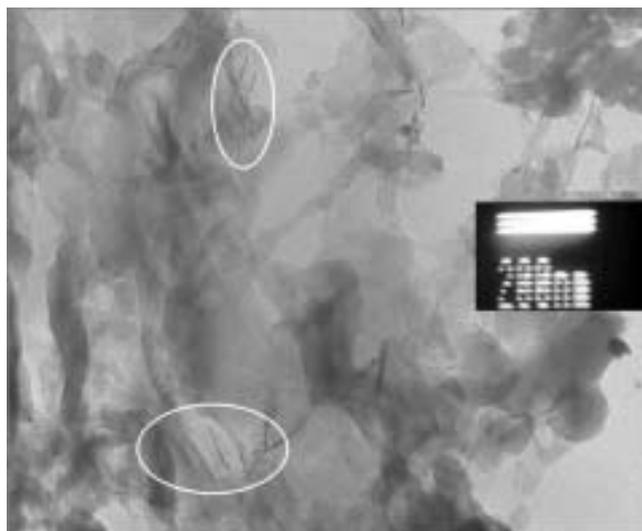


Fig. 11. TEM image of PVC/functionalized MMT system

its layers (often about 50 nm) is similar as in PCL/MMT *in-situ* nanocomposites.

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