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A review on advances of high-resolution solid state NMR spectroscopy in structural studies of polymer/clay nanocomposites[*]

Summary — The new applications of one- and two-dimensional solid state (SS) NMR spectroscopy for investigations of polymer/clay nanocomposites were discussed. 1D SS NMR spectroscopy is applied to evaluate the structural and dynamic properties of composites. 2D SS NMR is used for detailed studies on polymer-nanofiller contacts what let understand the mechanism of these interactions on the molecular level.
Key words: solid state, nuclear magnetic resonance, polymer nanocomposites, aluminosilicates, structure, polymer–nanofiller interactions.

PRZEGLĄD POSTĘPÓW W STOSOWANIU SPEKTROSKOPII NMR WYSOKIEJ ROZDZIELCZOŚCI W FAZIE STAŁEJ W BADANIACH STRUKTURALNYCH NANOKOMPOZYTÓW POLIMER/GLINKA

Streszczenie — Omówiono nowe zastosowania jedno- (1D) i dwuwymiarowej (2D) spektroskopii magnetycznego rezonansu jądrowego w fazie stałej (SS NMR) w badaniach nanokompozytów polimer/glinka. Spektroskopię 1D SS NMR wykorzystuje się do oceny strukturalnych i dynamicznych właściwości kompozytów, a spektroskopię 2D — do szczegółowych badań oddziaływań polimer–nanonapełniacz, co pozwala na zrozumienie mechanizmu tych oddziaływań.
Słowa kluczowe: magnetyczny rezonans jądrowy w fazie stałej, nanokompozyty polimerowe, glinokrzemiany, struktura, oddziaływania polimer–nanonapełniacz.

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Nanocomposites are a newly emerged class of composite materials that contain relatively small percentages of nanometer-sized filler particles. Properties enhancements are achieved with addition of less that 10 wt. % of the nanoscale dispersion (exfoliated) of 1 nm thick silicate layers, of diameters between 20 and 500 nm. Polymer-layered mineral nanocomposites are considered as a new class of advanced organic-inorganic materials, not only on account of their potential technological applications, but also for providing suitable systems in view of the investigation of fundamental scientific issues concerning polymers. They find applications in automotive, food packaging and biomedical industries due to improvements in thermal, physical and gas permeability properties of the polymers attributed to the incorporation of relatively small percentages (<10 wt. %) of nanoscale-sized filler materials. This is in contrast to conventional fillers, such as talc, mica, silica, and carbon black, which require high concentrations (>30 wt. %) and may cause deterioration of fracture toughness and processibility of the polymer matrix. It has been predicted that the market for polymer/clay nanocomposites will grow at an a average growth rate of 18.4 % annually to reach USD 210 million by 2008 [1].

Nanocomposites are a part of the growing field of nanotechnology. Nanomaterials drastically change the electrical and thermal conductivity as well as the mechanical strength properties of the original material. Two major findings have stimulated the revival of interest in these materials: a report from the Toyota Research Group on Nylon-6 montmorilonite (MMT) nanocomposite (improvements in thermal and mechanical properties) [2] and some observations done by Vaia *et al.* (possibility of the polymers melt-mixing with layered silicates, without the use of organic solvents) [3]. This endows them with unique properties, which offer new technological and economic opportunities.

Today, nanocomposites are in scope of interests in both synthesis and characterization areas. Most research works are going to develope more efficient combinations of materials and methods allowing gaining insight into the structure of nanocomposites. Despite the vast research works in the field of polymer/clay nanocomposites several issues remain unresolved. One of the main issues in their design is to achieve a fine dispersion of clay platelets in the polymer matrix. Generally nanocomposites are prepared either by *in situ* polymerization or by melt compounding [4, 5]. Understanding the behavior of polymer chains (conformation, relaxation, crystallization) at the interface is paramount to understand the physical properties of a nanocomposite.

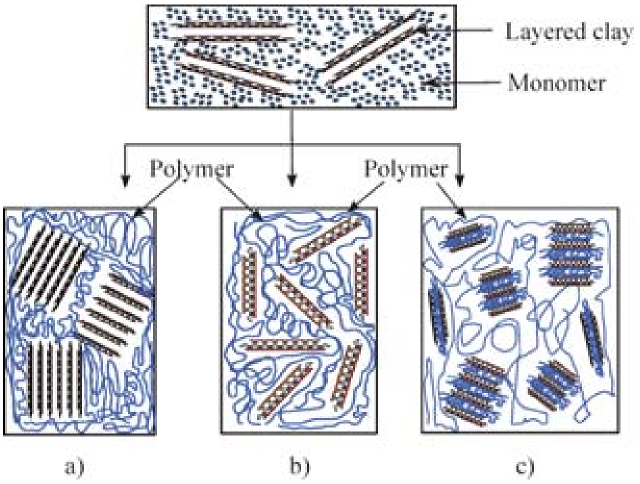

Fig. 1. Illustration of microcomposite (a) and exfoliated (b) or intercalated (c) polymer/clay nanocomposites morphologies. Reprinted from [6] with permission of Elsevier

Two categories of nanocomposites can be distinguished based on the extent of dispersion of filler particles: intercalated and exfoliated ones [6, 7] — Fig. 1. In this scheme, the nanocomposite is prepared by polymerization technique from the monomer and organo-modified layered clay (the fraction of clay is exaggerated for illustrative purpose). The properties of nanocomposites are greatly influenced by the degree of mixing, filler shape, nanoparticle size and interfacial adhesion between the filler and matrix [8]. A number of aspects related to the synthesis, properties and applications of nanocomposites were already reported in this journal [9—13]. Some useful information regarding this subject reader can find in the literature cited.

INVESTIGATION OF THE STRUCTURE AND DYNAMICS OF POLYMER CONTAINING NANOFILLERS BY MEANS OF 1D NMR SPECTROSCOPY

At a microscopic level, the structure of polymers containing nanofillers can be discovered by employing of different analytical techniques, *e.g.* Wide Angle X-ray Diffraction (WAXD), Small Angle X-ray Scattering (SAXS), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and others. Solid-state (SS) NMR spectroscopy is a technique that allows to investigate the polymer nanocomposites at a molecular level. Furthermore, it provides detail information about local and segmental molecular motions [14—17]. Various relaxation parameters are useful for elucidating molecular dynamics in the solid state, *e.g.* ^{13}C and ^{1}H spin-lattice relaxation times (^{13}C T_1 and ^{1}H T_1), carbon and proton rotating frame relaxation times (^{13}C $T_{1\rho}$ and ^{1}H $T_{1\rho}$), the C-H cross-relaxation time ($T_{C\text{-}H}$) and the proton relaxation time in the dipolar state (T_{1D}) [18]. Though not all of these parameters can provide direct information, using a complementary approach one can establish the amplitudes and motional frequencies for solids in a broad range. For instance, the ^{13}C T_1 and ^{13}C $T_{1\rho}$ measurements provide information on molecular motions in the megahertz and kilohertz frequency ranges, respectively.

Some interesting applications of ^{1}H and ^{13}C solid-state NMR for determining the structure and dynamics of polymer/clay nanocomposites were reported by VanderHart *et al.* [19]. Employing the SS NMR technique under discussion, several exfoliated nylon-6/layered-silicate nanocomposite materials were investigated and compared with pure nylon-6. It was found that clay promotes the growth of the γ-crystalline phase of nylon-6 while α-crystallites are characteristic for pure nylon-6. Moreover, during the sample preparation, the formation of noncrystalline phase was observed. Both phases can be easily recognized by ^{13}C CP MAS experiment (CP MAS = Cross Polarization Magic Angle Spinning) — Fig. 2.

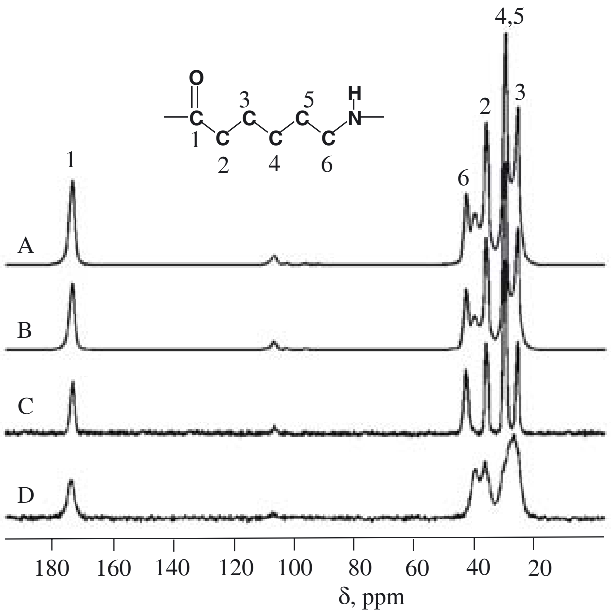

Fig. 2. Illustration of the $T_{1\rho}^{H}$- based method for separation 75-MHz ^{13}C CP MAS spectra into contributions arising from the crystalline and the noncrystalline regions (for explanation see text). Reprinted with permission from [20]. Copyright 2001 American Chemical Society

Experimental spectra (^{13}C CP/MAS), A and B have, respectively, 0 and 7-ms periods of proton spin locking prior to the 1-ms cross-polarization (CP) period. Spectrum A is relatively richer in the noncrystalline (NC) component compared to B because the intrinsic for protons in the NC region is much shorter than for those in the crystalline region (CR). Spectra C and D respectively represent the CP MAS spectra of the CR and NC regions; these spectra are different linear combinations of A and B, chosen to segregate the "CR" component (R-form here) with the narrower line widths from the "NC" component with the broader line widths. Apparent NMR crystallinity is determined from the relative integrals of the CR and NC contributions which sum is spectrum A. Corrected values of the crystallinity can be taken from the measurement of the differential amounts of $T_{1\rho}^{H}$ decay during the 1-ms period of CP pertaining to spectrum A [19—22].

The importance of polypropylene in industrial usage prompted several research groups to monitor the different modified polypropylene nanocomposites employing large palette of analytical techniques [23, 24]. Tavares and coworkers, using ^{13}C NMR spectroscopy, have revealed the changes in the nanomaterial morphology related to sample preparation [25]. Polypropylene/Brazilian clay nanocomposites were prepared using two methods; in the first, molten polymer was pressed for 15 min and then cooled at room temperature, in the second method a plastograph mixer was used with a twin screw operating at the melting temperature of polypropylene for 10 min. Important information was obtained from the measurement of ^{13}C decays and proton-spin lattice relaxation times in the rotating frame ($T_{1\rho}^{H}$). It was concluded that better clay dispersion and better homogeneity was reached in the latter method of nanocomposite preparation.

In most cases nanocomposite are obtained by intercalation of a filler with polymer prepared outside the galleries of the clay or prepared by the use of an external initiator. Cholli and colleagues reported an application of solid state NMR spectroscopy to study the *in situ* polymer obtained on the lamellar surface of MMT without the pretreatment of the surface by an organic modifier and/or initiator [26]. The applicability of ^{13}C CP/MAS experiment for investigation of *in situ* polymerized 2-ethynylpyridine is shown in Fig. 3. Inspection of the spectra of monomer (a) and polymer (b) clearly shows the absence of acetylenic carbons (82.9 and 77.7 ppm) in the solid-state ^{13}C spectrum of the polymer nanocomposite. It indicates an almost complete and spontaneous polymerization of the monomer. More advanced analysis of ^{13}C CP MAS spectra and cross-polarization kinetics suggest the presence of highly anisotropic motions of the polymer chains inside the interlamellar space of the insertion complex. They have presented a comparative analysis of ^{13}C and ^{1}H spectra for protonated and deprotonated bulk polymers [26].

Usually ^{13}C and ^{1}H nuclei are used as probes for determining the structure and dynamics of polymer nanocomposites. Application of other nuclei is not common because of the problem of sensitivity or difficulties related to data interpretation. The situation is not so complex when selectively or uniformly labelled nanomaterial is available. Recently Goddard *et al.* have reported the application of deuterium NMR spectroscopy for the observation of ^{2}H enriched polyaniline and polyaniline/clay nanocomposite [27].

From the point of view of NMR spectroscopy, there are significant differences among ^{1}H, ^{13}C and ^{2}H nuclei. The deuteron nucleus has a spin of 1, what means that in the presence of magnetic field there are three energy levels and the NMR experiment consists in transitions be-

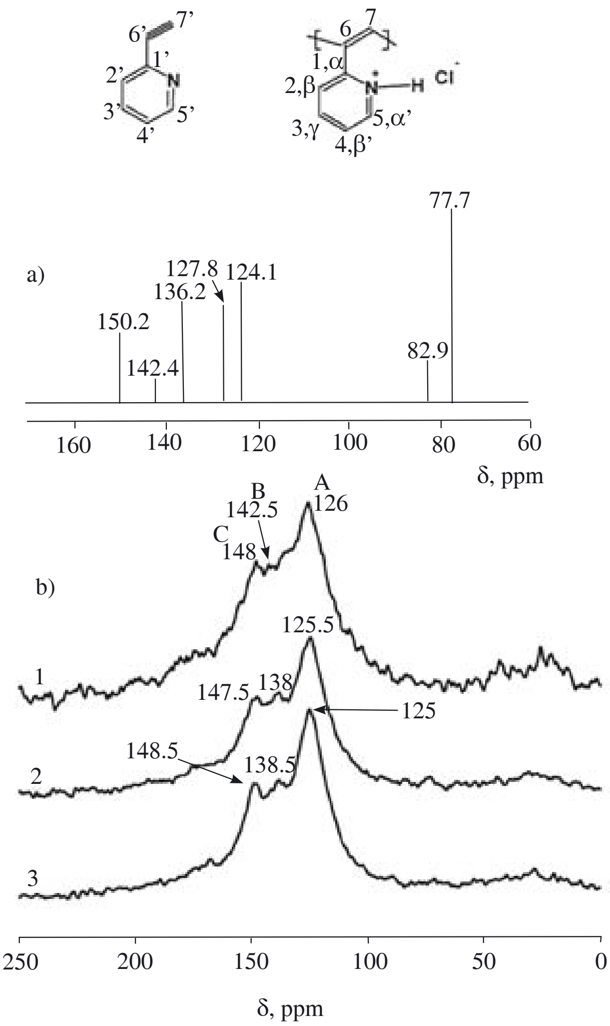

Fig. 3. Solid state ^{13}C CP MAS spectra for monomeric 2-ethynylpyridine (a) and for in situ polymerized 2-ethynylpyridine within the galleries of MMT with different adsorption yield of polymer (b): 1) 8 %, 2) 15.3 %, 3) 21.3 %. Reprinted with permission from [26]. Copyright 2003 American Chemical Society

tween these levels. In addition, the deuteron is quadrupolar and there is a nonspherical charge distribution at the nucleus. The interaction of the quadrupolar moment with the electric field gradient (EFG) tensor at the nucleus causes a substantial perturbation of the Zeeman spliting. Deuteron solid state NMR spectra are completely dominated by the quadrupole coupling and the lines are very broad. The typical static ^{2}H NMR spectrum of powder sample, recorded employing quadrupole echo pulse sequence, is recorded as a characteristic doublet. Another approach bases on recording of spectra under magic angle with fast sample spinning [28]. Both methods have been applied to observe the different forms of polyaniline (PAni) and polyaniline with MMT clay layers intercalated with PAni can exist in several oxidation states ranging from a completely reduced base state to a completely oxidized one. The most extensively studied form is called "emeraldine" in which the numbers of reduced and oxidized units are equal. Figure 4 shows a typical static ^{2}H NMR spectrum of PAni/MMT recorded with quadrupole echo pulse sequence. ^{2}H MAS spectrum of the same composite recorded with sample spinning speed 7.5 kHz is shown in Fig. 5.

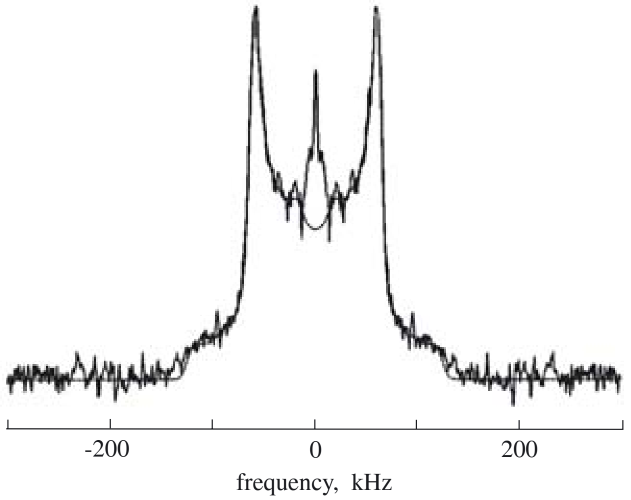

Fig. 4. Experimental (solid line) and simulated (dashed line) quadrupole echo spectra of PAni/clay nanocomposite at ambient temperature. Reprinted with permission from [27]. Copyright 2003 American Chemical Society

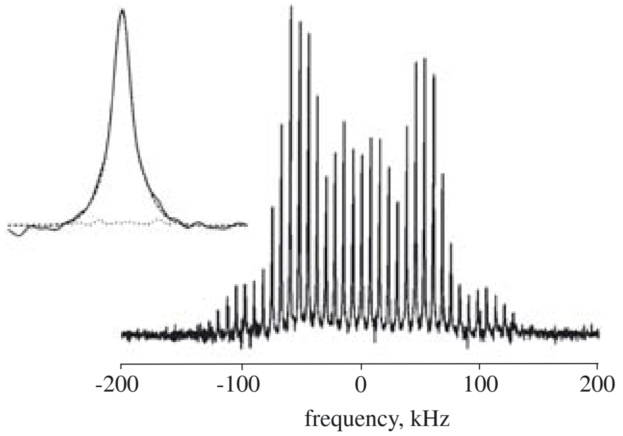

Fig. 5. Experimental deuteron MAS (7.5 kHz) spectrum of PAni/MMT clay nanocomposite at 263 K. The inset illustrates a spinning sideband. The dashed line is the best fit, achieved by nonlinear Levenburg-Marquardt iterations on a normalized, weighted sum of two Gaussian functions. The dotted line is the difference between the experimental and calculated data. Reprinted with permission from [27]. Copyright 2003 American Chemical Society

Employing the line-shape analysis of the static ^{2}H spectra authors revealed different fractions of fast flipping phenyl rings for conductive emeraldine and nonconductive emeraldine base samples. Such dynamic processes were not observed for the PAni/MMT nanocomposite.

Of course, the literature describing 1D SS NMR applications for the determination of structure and dynamics of polymer nanocomposites is quite extensive. There is no way to mention all the papers related to this subject, however some important contributions are worthy of note. Wang *et al.* used variable temperature solid-state ^{13}C NMR to report the conformational mobility and heterogeneity of surfactant molecules within the montmorillonite intercalated complex with an emphasis on interfacial binding and chain conformation and dynamics [29, 30]. In a pioneering study by Mathias and colleagues solid-state NMR was used to probe into the interaction of nylon-6 chains with the lamellae of aluminosilicate [31—33]. Intercalated PEOX nanocomposites were investigated by Zax's group [34—36]. ^{13}C CP MAS NMR was used to study the chain dynamics of intercalated PEOX and to determine the relative mobility of polymer bulk and interface.

INVESTIGATION OF NANOFILLERS AND POLYMER-NANOFILLER INTERACTIONS

The properties of nanocomposites are greatly influenced by the degree of mixing, filler shape, particle size and interfacial adhesion between the filler and matrix. Another factor influencing the nanocomposite properties is the type of filler. From the literature it is apparent that clay is the best filler for forming of nanocomposites. Clay is the name of a huge family of layered aluminosilicates the so-called phyllosilicates [19, 37]. The most commonly used ones are: montmorillonite (MMT), hectorite and saponite. More detailed information concerning the properties of these fillers are presented in Fig. 6 and Table 1. The surface of the clay layer is made of silica tetrahedra with octahedrally coordinated aluminum cation Al^{+3} placed in the central plane of the layer. This cation is non-stoichiometric frequently substituted and can be replaced by Mg^{+2}, Li^{+} or occasionally, by Fe^{+3} cations.

The concentrations of the other ions, especially magnesium or iron, are of high importance for two reasons. First, the substitution of the Al^{+3} ion with the Mg^{+2} magnesium cation in the silicate network generates a negative charge in the clay and must be neutralized by the cation on the surface. The neutralizing cation may be either inorganic, like usually Na^{+}, or organic cation — like a tetra-substituted ammonium ion. In the latter case, the so-called organically modified (OM) filler is obtained.

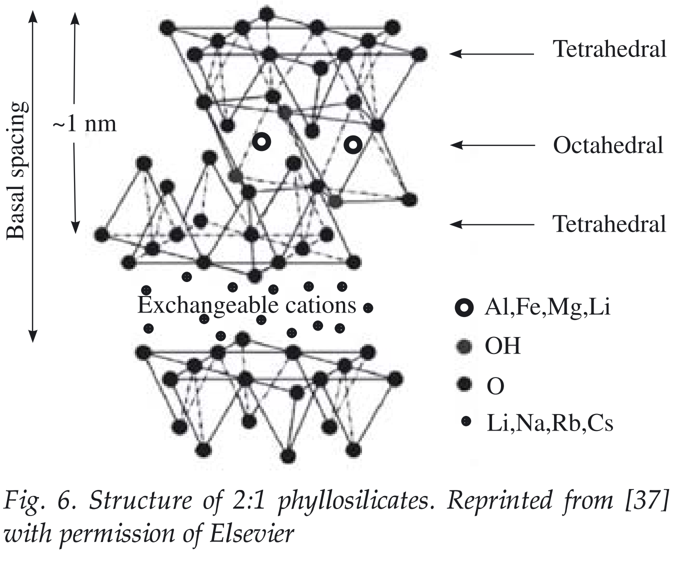

Fig. 6. Structure of 2:1 phyllosilicates. Reprinted from [37] with permission of Elsevier

Table 1. Chemical formule and characteristics parameters of commonly used 2:1 phyllosilicates*). Reprinted from [37] with permission of Elsevier

Phyllo-silicates	Chemical formula	CEC mequiv/100 g	Particle length, nm
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110	100—150
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200—300
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	88.6	50—60

*) M — monovalent cation; x — degree of isomorphous substitution (between 0.5 and 1.3); CEC — Complex Equilibrium Concentration.

Iron cation shows high paramagnetic properties and disturbs the relaxation processes of protons and carbon atoms nuclei placed in the vicinity of Fe^{+3} in nanocomposite network. This influence depends both on the concentration of iron ions in the clay and on the average distance between clay layers; hence, the presence of paramagnetic additives of Fe^{+3} in the common montmorillonite clay can hamper the NMR studies.

Naturally occured phyllosilicates, containing hydrated sodium and potassium cations, can only be mixed with hydrophilic polymers, *e.g.* poly(ethylene oxide) (PEOX) or poly(vinyl alcohol) (PVAL). To prepare layered silicates miscible with other polymer matrices, it is necessary to convert their hydrophilic surface into an organophilic one. Commonly, it can be done by an ion-exchange process in reaction with cationic surfactants, *e.g.* alkylammonium [38] or alkylphosphonium cations. These cations lower the surface tension and additionally provide functional groups, which can react with the polymer base or even reinforce the interaction between the inorganic filler and polymer matrix [39, 40]. Both, the chemical treatment of the clay surface with alkyl-cations and the presence of many cations in the clay network (see Fig. 6), provide great possibilities for using the solid state NMR spectroscopy to investigate the morphology of the nanocomposites, properties of both native and organically modified (OM) fillers and polymer matrices-nanofillers interactions [41].

Kubies *et al.* [42] used ^{13}C and ^{29}Si SS NMR as a probe for testing of the properties of laponite clay (LAP) intercalated with octadecylamine (ODA) and hexadecyltrimethylammonium salt (HDTA) (LAPODA and LAPHDTA appropriately). On the basis of ^{13}C and ^{29}Si detected proton relaxation times [T_1(H), $T_{1\rho}$(H) and

$T_{1\rho}$(C)] measurements, it was concluded that in the modified laponites both the all-*trans* and *gauche* conformations of the surfactant hydrocarbon chain coexist. T_1 values, measured for these modifications, indicated a higher mobility of the all-*trans* conformer. In contrast to the earlier studies of ODA-modified montmorillonite (MMTODA) [30], for laponite modifications a higher fraction of *gauche* conformation was found. Moreover, the T_{CH} values obtained for LAPODA and LAPHDTA are an order of magnitude greater than those of MMTODA. This fact evidently shows the higher mobility of the hydrocarbon chain in LAPODA and LAPHDTA. Furthermore, in LAPODA modification, the ^{29}Si detected $T_{1\rho}$(H) was found to be described by two components that have been associated with the structural Si^{+4} ions of laponite near the organic molecules and the nonexchanged sites. The differences in the mobility of hydrocarbon chain alter the properties of the filler surface and could play a role in the formation of the resulting polymer nanocomposites.

An understanding of the mechanism of nanocomposite formation is crucial in polymer nanocomposites' syntheses. For this reason the possibility of controlling its formation step by step is of high importance. Osman and co-workers used the ^{13}C SS NMR spectroscopy for an investigation of the structure and dynamics of alkylammonium cations monolayers assembled on the montmorillonite [43] and mica [44] platelets during the organic modification process. The structure and properties of ultra thin films are important for the final properties of the nanocomposite because they influence the particle-particle and particle-matrix interactions. In both cases, hydrocarbon chains adopt the all-*trans* conformation. The results obtained were consistent with FTIR data and gave a better insight into the conformational heterogeneity and packing differences of the hydrocarbon chains at the interfaces.

Obviously, ^{13}C and ^{29}Si are not the only SS NMR methods for investigation of nanocomposites. Hrobarikova *et al.* used ^{31}P and ^{13}C CP MAS NMR techniques for the investigations of surfactant and polymer chains motions in montmorillonite-poly(ε-caprolactone) nanocomposites. These nanocomposites were obtained *via* synthesis with Na-saponite pretreated with alkylammonium or alkylphosphonium salts. On the basis of ^{31}P relaxation times measurements of the intercalated phosphonium surfactant, the higher mobility after nanocomposite formation was confirmed [45].

The presence of exchangeable ions in the clay lattice (see Fig. 6) opens the possibility of using alkali metals NMR spectroscopy as a tool for studying the interactions in the bulk nanocomposite.

Reinhold and *co*-workers [46] employed ^{7}Li and ^{23}Na solid state NMR measurements for the study of polymer—nanofiller interactions in PEOX-montmorillonite nanocomposites. Two types of PEOX nanocomposites were investigated: one with pristine montmorillonite and the other with a synthetic one (Fig. 7). ^{7}Li and ^{23}Na NMR experiments provided important insights into the effect of PEOX on the environment and dynamics of the interlayer cations. Although the lithium line shape should be sensitive to local changes in the environment, the only effects observed upon the increasing degree of PEOX caused by intercalation, were small line broadening and the slightly more negative chemical shift. This observation suggested that Li^+ remains in the same structural environment regardless of the amount of PEOX in the interlayer and that the ions weakly interact with PEOX.

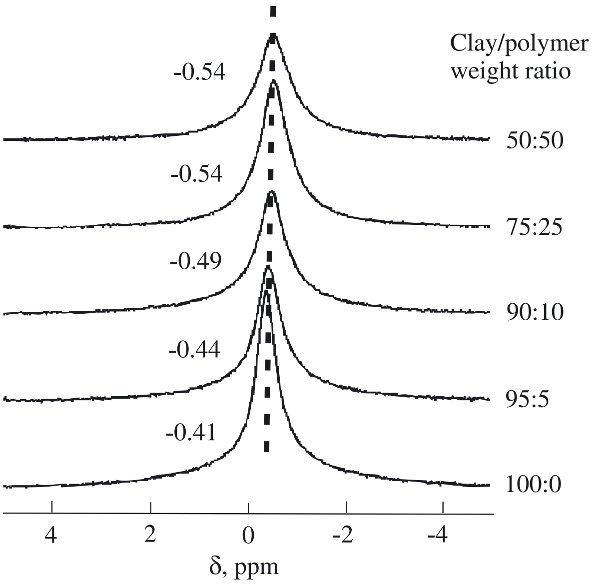

Fig. 7. ^{7}Li MAS NMR spectra of Li-MMT pristine clay and PEOX nanocomposites at selected clay:PEOX ratios. Reprinted with permission from [45]. Copyright 2005 American Chemical Society

A different picture was observed for Na-MMT clay. In this case ^{23}Na spectra showed the presence of sodium cations in multiple hydration states; intercalation by PEOX causes the Na^+ ions taking on the inner sphere coordination. The differences observed between Na^+ and Li^+ containing PEOX-MMT nanocomposites are in good agreement with differences in electrical conductivity observed for the two modifications of nanocomposites. Ikeda and colleagues [46] proposed the use of ^{23}Na triple quantum (3Q) MAS NMR technique to study the behavior of interlayer cations in montmorillonite.

APPLICATION OF 2D SS NMR SPECTROSCOPY FOR THE UNDERSTANDING OF POLYMER NANOCOMPOSITES

The knowledge about specific interactions between polymers and clay mineral solid surfaces is essential for understanding the nanocomposites' structures. As we described in previous section, 1D NMR experiments can provide detailed information in regard to the structure and/or dynamics but identification of the specific fragments of the polymer interacting with the nanofiller is usually not possible. For this purpose, 2D SS NMR is the method of choice.

An important contribution showing the power of 2D method in structural studies of nanocomposites was reported by Hou and Schmidt-Rohr [48]. The authors applied 2D ^{1}H-^{29}Si NMR correlation experiment to monitor the polystyrene (PS) and poly(methyl methacrylate) (PMMA) nanocomposites with hectorite (HCT). Signals observed at ^{1}H-^{29}Si HETCOR spectra represent the protons near the silicate surface.

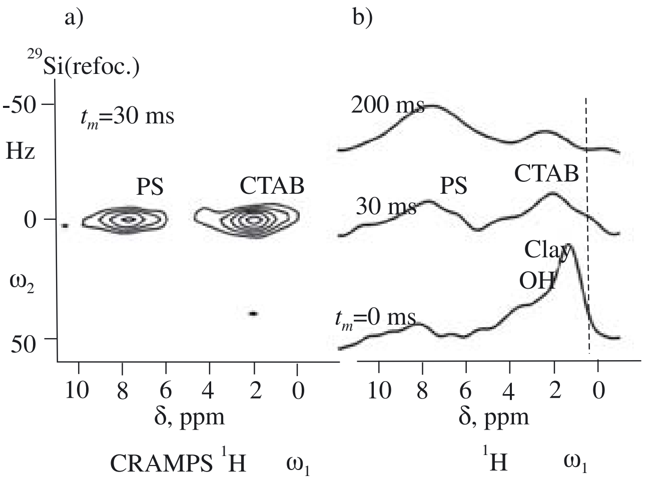

Fig. 8. a) 2D ^1H-^{29}Si HECTOR NMR spectrum with 30 ms of ^1H spin diffusion before CP for PS(50k)-HCT at rotation 5 kHz. Frequency-switched Lee-Goldburg (FSLG) homonuclear decoupling was applied during t_1 evolution, so the proton spectrum obtained in the ω_1 dimension reflect the chemical shifts of organic matter whose magnetization diffuses to the clay OH protons that cross polarize the ^{29}Si nuclei. This spectrum is rotated by 90^o from the conventional representation, to display the proton dimension more conveniently. b) Cross sections along ω_1 taken at the center of the ^{29}Si peak in ω_2, obtained from 2D spectra for three spin-diffusion times. Reprinted with permission from [47]. Copyright 2003 American Chemical Society

Spectrum obtained with a mixing time of 30 ms for ^{1}H spin diffusion from the organic segments to OH protons of the clay is presented in Fig. 8a. Figure 8b shows cross sections through the centers of ^{29}Si signals obtained from a series of 2D spectra. The ^{1}H peak at 0.4 ppm in the spectrum of t_m = 0 ms has been assigned to the Si-OH protons within the silicate layers. After 30 ms of spin diffusion, the intensity of the clay OH peak has been reduced, and a peak at 1.2 ppm has grown, indicating magnetization transfer between the Si-OH protons and the surfactant (CTAB). At the same time the presence of an aromatic PS peak indicates that polymer segments are also near the silicate surface. 2D experiments confirmed that the clay is intercalated in the surfactant-covered silicate and prove that the intercalated clay stacks are dispersed in the polymer matrix.

Analogous strategy was applied for investigation of the poly(styrene-ethylene oxide) block copolymers with HCT clay intercalated [49]. Two kinds of nanocomposites were investigated: one — PS30EOX-HCT — with 30 kDa PS block and the other — PS4EOX — composed of 4 kDa PS block; in both cases PEOX block were of *ca.* 7—8 kDa. From two dimensional ^{1}H-^{29}Si, ^{1}H-^{1}H and ^{1}H-^{13}C correlation experiments with ^{1}H spin diffusion the extent of intercalation of hectorite clay in PS-*b*-PEOX copolymers was determined. Moreover, it was found that in PS4EOX-HCT at least 80 % of 7 kDa PEOX blocks is introduced into the silicate galleries.

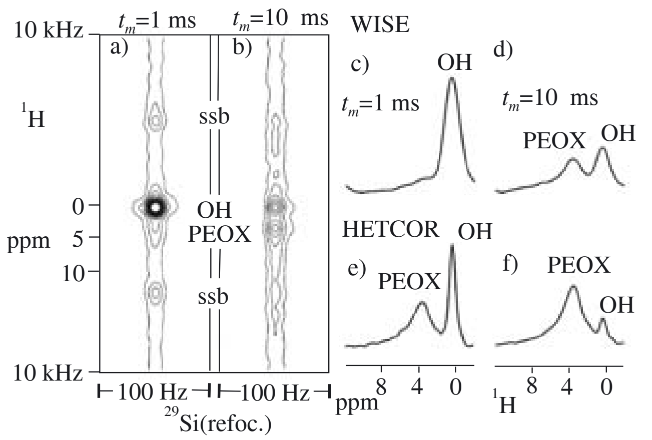

Fig. 9. Two-dimensional ^1H-^{29}Si WISE NMR spectra with spin diffusion for PS4EOX-HCT for spin diffusion times of (a) 1 and (b) 10 of LGCP (the labels "ssb" mark spinning sidebands); (c, d): cross sections through the spectra in (a) and (b), respectively, exhibiting only a small signal fraction of mobile PEOX; (e, f): for reference, cross sections through 2D ^1H-^{29}Si HETCOR NMR spectra at spin diffusion time of 1 and 10 ms, respectively. Reprinted with permission from [48]. Copyright 2003 American Chemical Society

The mobility along the polymer chain was investigated by means of 2D ^{1}H-^{29}Si WISE NMR experiment (wide-line-separation). From the analysis of the spectrum obtained for PS4EOX-HCT nanocomposite (see Fig. 9) it was concluded that the mobility of the PEOX segments is strongly reduced. The PEOX block does not pull the 4 kDa PS block into the silicate galleries. In the PS30EOX-HCT sample, which has a much longer 30 kDa PS blocks and therefore a lower PEOX fraction, the amount of PEOX introduced into clay galleries is small, and a significant fraction of PEOX is outside galleries.

Similar procedures can be applied to probe the conformational heterogeneity and mobility of surfactant molecules in the intercalated clay. Surfactants are used in the processes of preparation of novel mesoporous ceramic materials and polymer-ceramic nanocomposites.

On the basis of XRD data, various models have been proposed for the molecular conformation of the surfactant in the clay. However, XRD does not provide direct information on how the surfactant molecules are oriented in the clay and what are the local conformations of the surfactant molecules. This information is crucial for the understanding of effectiveness of the surface treatment.

Bordia and *co*-workers [30] used 2D ^{1}H-^{13}C WISE NMR together with variable temperature ^{13}C SS NMR for studying the conformational heterogeneity and mobility of ODA surfactant in intercalated montmorillonite. 2D experiments showed coexistence of two kinds of 1-octadecylamine molecules on the MMT surface: ordered — containing only all-*trans* conformers, and disordered — the mixture of all-*trans* and *gauche* conformers. This clearly shows the conformational heterogeneity of the surfactant in the clay. 2D WISE experiments together with the cross-polarization time constants measurements suggest that molecules in the ordered conformations are as rigid as those in most solid crystalline materials. Disordered conformation is similar to that found in liquid crystalline state. It is worth noting that upon heating, the ODA molecules in the disordered conformation remain unchanged, while the molecules in the ordered conformation become disordered. The data obtained were in excellent agreement with FTIR data published by Vaia *et al.* [50].

Another application of 2D heteronuclear solid-state NMR technique was presented by Agarwal *et al.* [51]. Authors applied 2D ^{1}H-^{29}Si NMR correlation with frequency-switched Lee-Goldburg homonuclear (FSLG) decoupling to characterize the vinyl polymer/colloidal silica nanocomposites. Two silica nanocomposites were investigated: poly(4-vinylpyridine) (P4V)/silica and polystyrene (PS)/silica. From those studies it was deduced that molecular interactions between the polymer and silica phases in the P4V nanocomposite involve hydrogen bond formation between the nitrogen nuclei of pyridine and the silica surface hydroxyl protons. In contrast, π-interactions between the aromatic ring and the silica surface is the most likely model of PS containing nanocomposite. Additionally, it was concluded for both investigated composites that nonspecific binding interactions do not play an important role in the formation of nanocomposite particles. Some other aspects and detailed discussion concerning the SS NMR studies of clays and polymer-clay nanocomposites can be found in review published by Grandjean [52].

Very recently, Gougeon and co-workers showed the application of 2D ^{1}H-^{27}Al heteronuclear SS NMR to monitor the interactions between the inorganic host and the organic guest. They observed the interactions of poly(D-glutamic acid) and poly(D-lysine) on the surface of intercalated montmorillonite [53, 54]. However, review of these types of bio-nanocomposites is out of the scope of this article.

CONCLUSIONS

The field of polymer nanocomposites is very challenging and a number of research groups are working on the synthesis and improvement of new nano-materials. During last 10 years over 7000 scientific papers were published showing different aspects related to polymer nanocomposites [55]. To date the solid-state NMR spectroscopy is not the leading analytical technique used in structural studies of these kinds of materials. In the same period (10 years) only 150 articles presented applications of SS NMR. In this review we have shown different applications of NMR and a rich palette of methodological approaches, which can be employed to study the structure and dynamics of polymer matrix, nanofiller and/or the interaction of these two components, what is a unique feature of SS NMR. We believe that with better access to instruments dedicated to solid state NMR studies the role of this technique will rapidly grow.

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