Electromagnetic absorption efficiency of polypropylene/ montmorillonite/polypyrrole nanocomposites

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ABSTRACT

Electrical conductivity and dielectric properties have been studied for two types of polypropylene composites containing conducting phase. One type comprised conducting polymer-polypyrrole while the second employed montmorillonite particles coated with conducting polymer-polypyrrole. Composites' shielding properties were estimated based on their previously determined electromagnetic characteristics. Unlike a basic binary polypropylene/polypyrrole composite, the ternary sample with multicomponent montmorillonite particles exhibits higher dielectric losses and consequently a significant rise in shielding efficiency in the radio-frequency range of 0.1-1.5 GHz. This stems from the presence of highly polarizable multicomponent montmorillonite anisotropic lamellar particles with polypyrrole conducting layer, which considerably increases the complex permittivity of the composite.

1. Introduction

Polymer composites filled with electrically conducting particles become increasingly important for a variety of applications in science or technology. Owing to their unique electric and dielectric properties and mechanical and chemical stability, they can be applied as smart materials in the construction of various components of electronic appliances [1]. A wide range of their applications offers protection against radiation, e.g. microwave absorbers [2,3] for electromagnetic interference shielding of various devices [4]. For this purpose, composites of electrically non-conducting polymer matrix filled with anisotropic particles such as metal [5,6] or carbon fibres [7,8] have been proposed in the past. Conducting polymers, as polypyrrole (PPy) or polyaniline (PANI) have emerged as a new class of materials in the last years. Because of their high electrical conductivity and ease of preparation [9,10], potential applications of these materials such as microwave absorbers were proved [11]. The electromagnetic interference shielding properties were reported for chitosan/polypyrrole composite layers [12] where shielding by reflection prevails over absorption by the composite. De Paoli et al. [13] showed that in nanocomposites propyl- ene-ethylidene-norbornene rubber/polyaniline/organoclay the absorptions peak frequency can be easily manipulated by changing the thickness of the microwaves absorber. In polymer composites comprising short carbon fibres coated with polyaniline a significant influence of the conducting polymer layer on the shielding properties was described [14]. This finding indicated that conducting polymers could be utilized as an interesting filler for preparation of new electromagnetic absorption materials. With higher filler content, above the percolation limit, the radiation in the radio-frequency range (0.1-1.5 GHz) can penetrate the material where it is dampened and an absorption attenuation due to energy dissipation occurs. It is apparent that the shielding effectiveness is related to the high dielectric loss factor, which arises from the polarization effect produced by the anisotropic particles of the filler.

Montmorillonite (MMT) is a member of the smectite mineral group, naturally occurring layered materials having high aspect ratio and surface area. MMT is composed from aluminium silicate layers which were organized in a parallel fashion to form stacks with a regular van der Waal gap in between them called interlayer spacing or gallery [15,16]. MMT has high negatively charged surface that is compensated by cations Ca^{2+} or Na^{+} [17]. The MMT surface is easily amenable for modification. A series of electrically conductive polypyrrole/clay nanocomposites were synthesized by using one-pot emulsion oxidative polymerization of pyrrole in the presence of unmodified clay and using sodium dodecylbenzene sulfonate (DBSNa) as the anionic surfactant [18]. The authors showed that both pre-intercalation of pyrrole monomer between the clay gallery spaces before the beginning of the polymerization, as well as the concentration of DBSNa, influenced basal spacing of prepared polypyrrole/clay nanocomposites.

The existence successful intercalation of polypyrrole into the interlayer of sodium- and also organomodified MMT was investigated via an X-ray diffraction and X-ray photoelectron spectroscopy [19]. Conducting polymer composites of polyethylene and polypyrrole (PE/PPy), and polypropylene and polypyrrole (PP/PPy) were prepared by means of a chemical modification method, resulting in a network-like structure of polypyrrole embedded in the insulating polymer matrix [20].

This paper reports the results of investigation of the effect of montmorillonite (MMT) particles coated with conducting polymer polypyrrole (PPy) in polypropylene (PP) composite on the charge transport and dielectric properties. Montmorillonite clay, the lamellar structure of which is composed of silicate layers, about 1 nm thick and 100-500 nm thick in the lateral dimension, significantly increased the complex permittivity of the composite and provided the material with interesting shielding properties.

2. Experimental part

2.1. Materials

The polypropylene used for the preparation of composites and nanocomposites was a commercial unstabilized powder (Tatren FF 500, Slovnaft, Slovakia) with the particle size lower than 0.4 mm, melt flow rate (MFR= 10 g/10 min). Sodium montmorillonite MMT BJ-10 (Envigeo, s.r.o., Slovakia) was used as a nanofiller for the composite preparation. Pyrrole (Merck-Schuchardt, Germany) was purified by distillation under reduced pressure and stored in a refrigerator at 4 °C before use. Ferric chloride (FeCl$_3$, Lachema, Czech Republic), and dodecylbenzenesulfonic acid (DBSA, Fluka, Switzerland) were used as received.

2.2. Preparation of composites

Sets of composite samples have been prepared for this study. The basic binary sample contained a polypyrrole conducting phase in the polypropylene matrix. Montmorillonite particles coated with polypyrrole have been incorporated in the ternary composite. The details on the composite preparation were discussed in previous papers [10,20-22].

An aqueous suspension of 30 g PP powder with DBSA (molar ratio of pyrrole/DBSA = 5/1) [21] was prepared. Clay particles of montmorillonite (MMT) were added to the suspension of PP in a weight ratio of PP/MMT = 20/1, corresponding to 4.8wt.% MMT. The suspension was treated with ultrasound for 10 min to obtain better exfoliation of clay. Then the oxidant, FeCl$_3$ dissolved in 50 ml water, was added under vigorous continuous stirring. After 15 min pyrrole dispersed in 10 ml of water was inserted dropwise. The oxidation polymerization of pyrrole proceeded for 1 h under stirring. After 24 h the product was filtrated off, washed with distilled water, and dried at 60 °C. The prepared ternary composite contained 16.7 wt.% PPy. The binary PP/PPy composites with the same amount of conductive PPy (16.7 wt.%), but without MMT particles, were prepared using the same procedure as described above.

Both prepared composites were processed by compression moulding after addition of stabilizers (0.5 wt.% Irganox 1010 and 0.1 wt.% Irgafos 168 supplied by Ciba Speciality Chemicals, Switzerland) at 180°C for 2 min. The scanning electron microscopy study and X-ray scattering confirmed a partial exfoliation of the MMT in the composite as reported earlier.

2.3. Conductivity and dielectric measurement

The samples were compression moulded into discs of 13 mm in diameter and about 1 mm in thickness. The dc conductivity, $a_{¿Cf}$ has been calculated from the current-voltage dependencies measured in the two-point setup using electrodes of cylindrical shape (13 mm in diameter and covered by a layer of gold) with a programmable electrometer (Keithley 6517 A, USA) as follows:

$$\sigma_{dc} = \frac{I}{U} \cdot \frac{t}{S}$$

where / (A) is current, *U* (V) voltage, *t* (m) sample thickness and < (m^2) an area of the sample.

Dielectric characteristics involving the frequency dependence ol the real part (dielectric constant, *s')* and imaginary part of the complex permittivity (dielectric loss, e") in the frequency range ol 1 MHz-3 GHz were determined with an RF Impedance Analyze] (Agilent E4991A, USA) using capacitive method (on a dielectric material test fixture which comes furnished with the device). Having input the sample thickness the device automatically calculates and yields frequency dependence of complex permittivity *s**.

Ac conductivity, a_{ac}, was calculated from directly obtainec imaginary part complex permittivity, e", following an equation:

$$\sigma_{ac} = \varepsilon'' \omega \varepsilon_0$$

where £$_0$ is permittivity of vacuum and *CD (2nf)* angular frequency

2.4. Morphological study

Morphology of binary and ternary composite materials were analyzed by means of an SEM LEO 435 VP electron microscope (Leo Elektronenmikroskopie, Germany) operating with an acceleration voltage of lOkV on gold sputtered surfaces of composite films, which were etched in oxygen plasma for 240 s.

2.5. WAXS (wide angle X-ray spectroscopy)

Structure of MMT, PP/PPy and PP/MMT/PPy were studied WAXS using a Philips PW 1830/PW 1050 equipment with Cu Ko radiation at the wavelength of 0.154 nm. Measurements were conducted at 40 kV and 35 mA. The WAXS pattern of MMT was recorded in the form of natural powder while composites were analyzed in the form of 1 mm plates.

3. Results and discussion

3.1. Composite preparation

Polymeric composites are usually prepared by the simple mell mixing of the polymer matrix with the filler. From our previous studies [20,22] it is known that by the melt mixing of PP with conducting PPy powder synthesized by chemical oxidative polymerization, prepared composites have low electrical conductivity Composite of PP containing 34 wt.% PPy reached a conductivity of only about 10~^{5} S nrf^1 due to the separation of the conducting PPy into aggregates within the isolating PP matrix. When polymerization of pyrrole was done in water/methanol suspension of PF powder particles, PP/PPy composites with higher conductivity ol about 1 Sm^{-1}, where prepared. Anionic surfactants can be usee for the preparation of a stable suspension of PP particles in water which is the first step for successful modification of hydrophobic PP powder particles. Anionic surfactant also increases the conductivity of PPy [10]. This kind of surfactant is incorporated into the PPy structure as a co-dopant and influenced morphology of Pfy particles. For this study we choose dodecylbenzenesulfonic acic (DBSA) as anionic surfactant since this compound positively influences conductivity and also the thermo-oxidative stability of PPy For obtaining conducting composite with MMT particles, first PF powder particles were dispersed in water/DBSA solution. Ther MMT was added into suspension. The silicate layers exfoliated ir solution and after applying ultrasound. MMT and PP powders under stirring created homogeneous dispersion. After the insertior of pyrrole, PPy forms at the surface of the exfoliated MMT layers as well as on the dispersed PP particles. PPy formation is demonstrated by changing of the suspension colour from light brown (colour of MMT) to the black. A powder mixture consisting of PP particles coated with PPy and PPy-modified MMT agglomerates was obtained after drying. Ternary composite contains 4.8wt.% MMT and 16.7 wt.% PPy. The compression moulding of PP/MMT/ PPy powder after adding stabilizers was used for preparation of 1 mm thick sheets. Scanning electron microscopy study and X-ray scattering, confirm partial exfoliation of the MMT in composite as was reported earlier [19]. For comparison of shielding properties, binary PP/PPy composites with the same amount of conductive PPy (16.7 wt.%), but without MMT particles, was prepared by the same procedure as described above.

3.2. Conductivity and permittivity properties

The dc conductivity determined for PP/PPy, *a_{dc}* = 8.6 x 10^{-3} S m$_{-}^{1}$, was lower by one order of magnitude than the conductivity of PP/MMT/PPy which is cr$_{dc}$ = 1.6 x 10$_{-}^{1}$ Sm“^{1}, This indicates a larger amount of conducting paths in the latter composite. It is well known [23] that the shape of the frequency spectra of conductivity cr$_{ac}$ and permittivity *s'* suggests the character of the transport of charges in the material. Based on the analysis of the properties of the effective complex permittivity of a disordered system the following power law behaviour has been proposed [24]

$$\sigma_{ac} \propto f^{x} \qquad (3)$$

$$\varepsilon' \propto f^{-y} \qquad (4)$$

where the critical indices *x* and *y* are the slopes of the linear part of the double logarithmic plots of frequency spectra. Figs. 1 and 2 demonstrate a lower *x* = 0.52 and higher *y = 0.27* for the PP/MMT/ PPy composite than in a PP/PPy sample (x = 0.72 and *y* = 0.11) indicating a better ac conductivity. Also dielectric losses in the composite containing MMT particles are rather high (Fig. 3) which initiated an examination of the shielding properties of PP/MMT/PPy composite material.

The effectiveness of microwave absorption depends on the skin depth, <5, defined as the depth to which the radiation penetrates, while its intensity decreases to e^{-1} of its original strength [25]. The skin depth <5 is a function of the frequency, as well as the ac conductivity and the magnetic permeability, *ji*,

$$5 = (nnfa_{3C})^{\sim\upsilon 2} \qquad (5)$$

The absorption part of the attenuation of the electromagnetic radiation is expressed by the equation

$$A = 20\log\left[\exp\left(\frac{t}{\delta}\right)\right] \qquad (6)$$

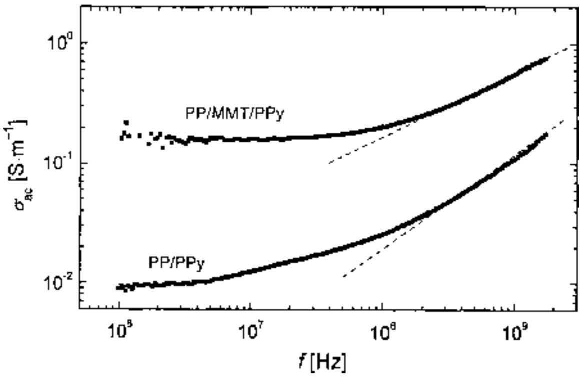

Fig. 1. The frequency dependence of ac conductivity.

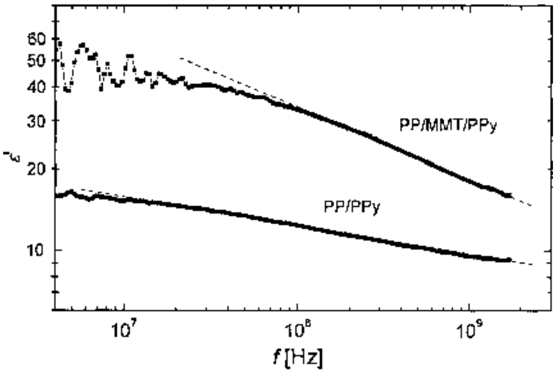

Fig. 2. The frequency dependence of permittivity, *s'*.

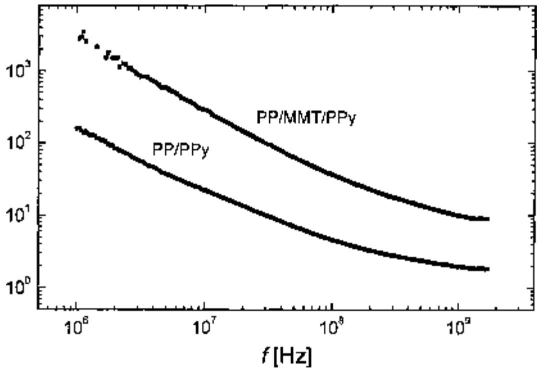

Fig. 3. The frequency dependence of dielectric loss, *s"*.

where t is the thickness of the shielding material. The magnetic permeability for non-magnetic MMT/PPy particles can be considered as the magnetic permeability of free space, /i = = *An* x 10^{-7} H m“^{1}.

Although both systems exhibit the decrease of skin depth with frequency, in the case of ternary system the figures reach typically one third those of binary composite (Fig. 4). This in accordance with Eq. (6) results in PP/MMT/PPy composite’s higher absorption of electromagnetic radiation compared to PP/PPy as depicted in (Fig. 5). As the absorption part of shielding efficiency enhances with frequency one usually needs to adequately adjust the thickness of an absorber in order to obtain sufficient effect *(A* > 10 dB at least) even for lower frequencies.

It is generally known that high shielding effectiveness in a radio frequency band is related to increased dielectric loss of composite

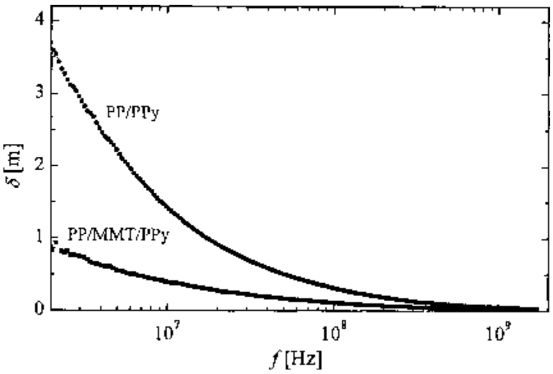

Fig. 4. The frequency dependence of the skin depth.

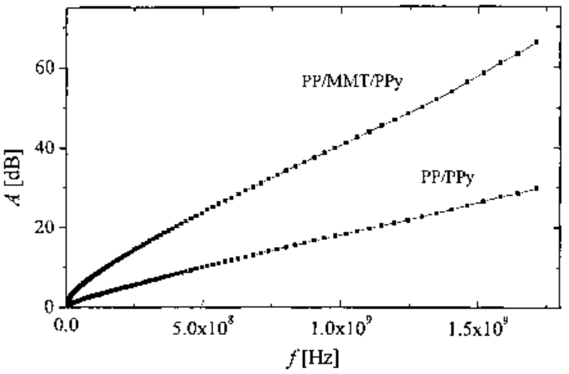

Fig. 5. Absorption part of shielding efficiency *(A)* as a function of frequency for the composite of 0.1 m thickness.

due to the presence of a high quantity of individual polarizable dipoles dispersed in a non-conducting polymer matrix. In case of PP/ PPy composite the structure of compact isotropic PP particles coated with PPy does not change after compression moulding (Fig. 6a) and the content of polarizable particles in the material is negligible [10]. Consequently, the ac conductivity and dielectric properties are rather low. On the other hand, in the presence of MMT particles the structure of composite is quite different (Figs. 6b and 7b).

As shown schematically on (Fig. 6b), before PPy polymerization in water, dispersion of PP particles and MMT in exfoliated state are present in water solution containing anionic surfactant. During the pyrrole polymerization, preferential coating of exfoliated MMT particles occurs, which, due to a strong mutual PPy interaction, afterwards agglomerate into anisotropic bundles spread between isotropic PP particles coated with a relatively thin PPy layer. Thus, after compression moulding, a great number of polarizable MMT/ PPy bundles in the composite is a cause of a much higher dielectric loss and shielding effect of PP/MMT/PPy in contrast to the simplei PP/PPy composite material.

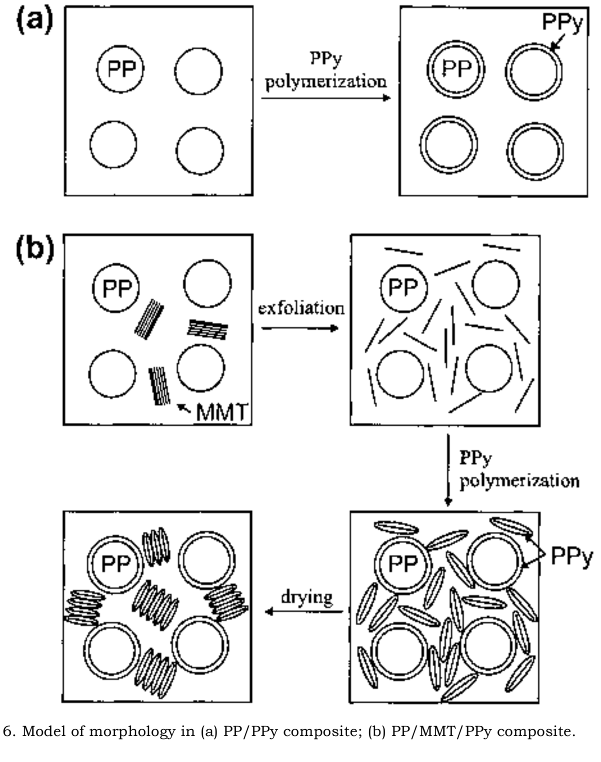

Fig. 6. Model of morphology in (a) PP/PPy composite; (b) PP/MMT/PPy composite.

3.3. Morphology and structure of nanocomposites

Study of the morphology of prepared composites may help tc understand the higher shielding efficiency and conductivity ol the material containing montmorillonite. During preparatior MMT is dispersed in water/DBSA solution, the silicate layers exfoliated, later the PP powder under stirring was added. After the introduction of oxidant and pyrrole monomer, PPy had coatec the surface of the exfoliated MMT layers as well as the dispersec PP particles. For the morphology study of prepared binary and ternary composites compression moulded sheets were etched in oxygen plasma. The etching rate of PP is much higher than these of the MMT, PPy, or MMT/PPy phases, which appear as elevated structures on the surface. Fig. 7a shows the morphology of plasma etched PP/PPy films prepared by modification of PP particles with PPy. Fine and homogeneous distribution of the PPy phase in PP matrix is visible, but also few domains of the PPy phase larger thar 1 |nm are visible on the etched surface.

The morphology of the ternary composite etched surface is depicted in (Fig. 7b). Large agglomerates with layered structures which are built up from individual lamellas of MMT each having thickness of approximately 1 nm (Fig. 7c), in compression mouldec PP/MMT/PPy samples containing 16.7 wt.% PPy were detected. The thickness of the MMT layers covered with PPy, which are separatee by PP, is in the 100 nm range, while the other two dimensions car be in the range of a few |im.

Partial exfoliation of MMT in ternary composite was also confirmed by a WAXS measurement. The diffraction curves of MMT PP/MMT and PP/MMT/PPy composites are shown in (Fig. 8). WAX5 diffraction pattern of MMT shows two peeks (Fig. 8, curve a) corresponding to interlayer distances of 1.32 nm and 0.99 nm. Both the position and the shape of the peak suggest that the second diffraction belongs to illite. Illites and micas commonly occur in natura bentonites. MMT and PP powder mixture were treated with DBSA/water solution and compression moulded after drying MMT corresponding peak is shifted to lower 2(9 angles and value of 1.52 nm for peak maximum was determined (Fig. 8, curve b) Due to unfavourable interactions between inorganic clay and high unpolar PP it is rather impossible to get intercalated or exfoliatec structure of MMT in PP matrix. The sharp peak indicates a well defined, regular gallery structure, probably due to the homogeneous incorporation of the DBSA surfactant and water molecules into the MMT layers. Diffraction patterns of PP/MMT/PPy composites are shown in (Fig. 8, curve c). Two reflections instead of one appeal in the PP/MMT/PPy sample and the distances of the galleries are 1.98 nm and 2.99 nm. The appearance of two peaks indicates twe populations of gallery distances. The weak peaks intensity indicates a partial exfoliation of MMT in the composite sample as depicted in (Fig. 7b). The gallery distances of MMT are increasing by covering with conductive PPy layers. Polypyrrole formed by oxidative polymerization using $FeCl_3$ as oxidant contains about one positive charge on each 3 or 4 pyrrole units. This charge is compensated by chlorine ions. MMT layers are negatively charged, during pyrrole polymerization the charges of the MMT and that of the Pfy can compensate each other. However, when the positive charges ol the PPy chain are partially compensated by the surfactant [10], e larger amount of PPy is necessary for the compensation of the negative charges of the MMT layers and wider interlayer distances car be expected in the final composite. The nature of the second regular distance of about 3 nm is still unclear, it can be connected with illite exfoliation which is part of clay we used for nanocomposite preparation.

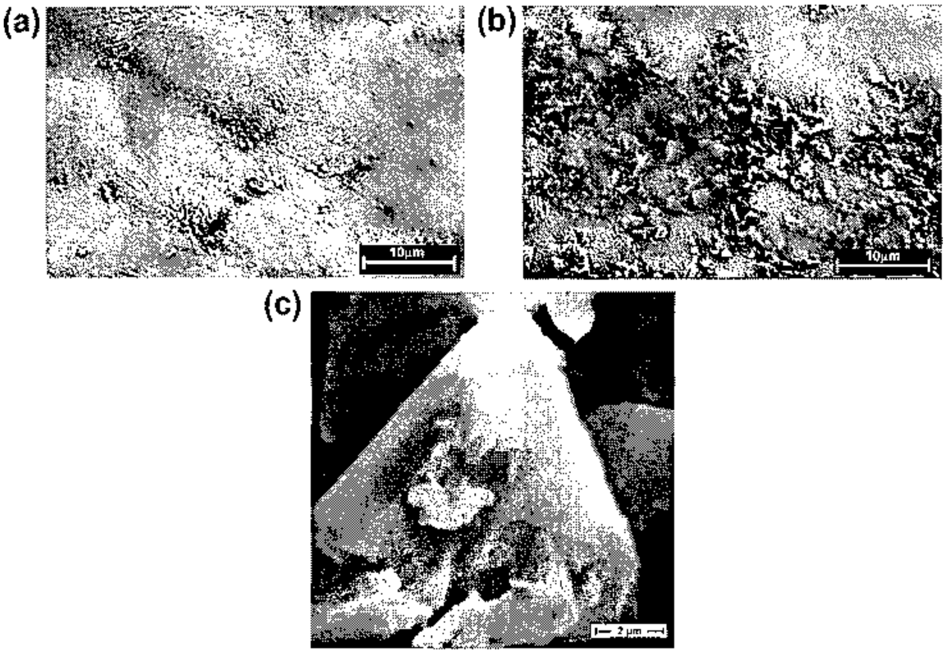

Fig. 7. SEM of plasma etched surfaces of PP/PPy composite containing 16.7 wt.% PPy prepared in water/DBSA and processed by direct compression moulding (a), and PP/ MMT/PPy composite containing 16.7 wt.% PPy (b and c).

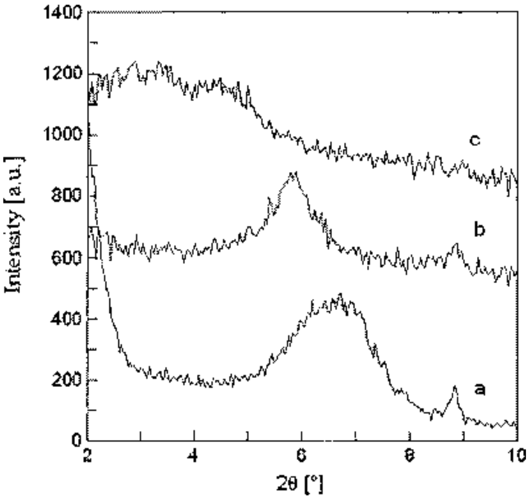

Fig. 8. WAXS diffraction patterns of MMT (a), PP/MMT treated in water/DBSA solution (b), and PP/MMT/16.7 wt.% PPy composite (c).

4. Conclusions

Electrical conductivity and dielectric properties of electrically conductive ternary polypropylene/montmorillonite/polypyrrole nanocomposites have been studied with the aim of examining their shielding efficiency in the telecommunication frequency band. The obtained results show that shielding effectiveness of ternary polypropylene/montmorillonite/polypyrrole nanocomposites is two times higher than that of binary polypropylene/polypyrrole composite due to higher dielectric losses in ternary components system. The changes in the structure of the montmorillonite after pyrrole polymerization, namely their partial exfoliation in the composites were documented by morphology studies and by wide angle X-ray scattering investigation. These highly polarizable montmorillonite anisotropic lamellar particles covered with polypyrrole conducting layer considerably increases the complex permittivity of the ternary composite. The main advantage of the developed material is the simplicity of the technology and good shielding ability that can be used in the design of microwave absorbers.

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