

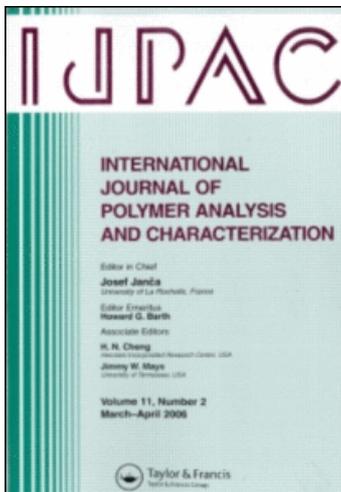
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Preparation and Characterization of Poly(2-halogenaniline) Composites with Al₂O₃, SiO₂, and Red Mud

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Preparation and Characterization of Poly(2-halogenaniline) Composites with Al₂O₃, SiO₂, and Red Mud

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Abstract: In-situ polymerizations were carried out in the presence of Al₂O₃, SiO₂, and red mud (RM) (host materials) to synthesize poly(2-halogenaniline)/Al₂O₃, poly(2-halogenaniline)/SiO₂, and poly (2-halogenaniline)/red mud composites. The 2-halogenanilines were polymerized without guest materials under the same conditions to compare the properties of the product with those of the composites. Homopolymers and composites were characterized by FT-IR and UV-vis spectroscopies, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction spectroscopy, magnetic susceptibility, and conductivity measurements. The inclusion of either of those monomer units in the resultant composites was confirmed by FT-IR analysis. The properties of the composites changed depending on the type of host materials. Thermal stability of materials follows the trend according to their residual amounts at 800°C of Al₂O₃ > RM > SiO₂. The enhancements in thermal behaviors of poly(2-halogenanilines) were studied in the presence of host materials (RM, SiO₂, Al₂O₃). SEM revealed interesting morphological features of the composites prepared using various inorganic materials and monomers. The analyses indicated typical structural differences between RM, SiO₂, Al₂O₃, and poly(2-halogenanilines). Magnetic susceptibility measurements revealed that the composites with SiO₂ and Al₂O₃ have diamagnetic properties, whereas composites in the presence of RM show paramagnetic conductivity mechanism. The conductivities

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of composites synthesized using three different materials were measured by a four-probe technique. The presence of Al_2O_3 , SiO_2 , and RM affected the conductivities of pure polymers.

Keywords: Al_2O_3 ; Composite; Poly(2-halogenaniline)s; Red mud (RM); SiO_2

INTRODUCTION

The organic electronic materials comprising conducting polymers (CPs) and their composites (micro and nano)/blends are receiving much research attention for their potential applications.^[1–4] One of the most innovative and successful developments is the discovery of nanocomposites.^[5–8] These materials have dramatically increased surface area compared with conventional-sized reinforcement materials. Speciality polymers such as polythiophene (PTP), polyaniline (PANI), polypyrrole (PPy), and polyfuran (PF) suffer from processibility limitations due to their intractable nature. To make all these polymers processible, a widely accepted procedure is to synthesize polymer-inorganic oxide nanocomposite systems. Nanodimensional inorganic oxides such as SiO_2 , SnO_2 , MnO_2 , ZrO_2 , and Al_2O_3 have been used as particulate dispersants in water in which water-soluble pyrrole (PY) or aniline (ANI) were injected in the presence of oxidants like FeCl_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$.^[9–15] The clays among other hosts are natural, abundant, and inexpensive minerals that have unique layered structure, high mechanical strength, and strong chemical resistance. Polymer/clay nanocomposites were first discovered and developed by the Toyota research group.^[16] Mehrotra and Giannelis^[17] and Qi and coworkers^[18] studied the intercalative polymerization of aniline into fluorohectarite (a mica type silicate) and sodium montmorillonite (MMT). Kim et al.^[19–20] synthesized polymer-clay nanocomposite particles with PANI-dodecylbenzenesulfonic acid (DBSZ) and Na^+ -MMT, using an emulsion intercalation method. Red mud (RM) emerges as a by-product from the caustic leaching of bauxites to produce alumina, and approximately 35–40% of the processed bauxite goes into waste as red mud. Red mud is the biggest problem in producing alumina. This waste presents serious problems of storing and environmental pollution. Serious disposal problems have led researchers to develop new methods for the use of red mud as filler for polymer reinforcement, an absorbent to remove H_2S from industrial emissions, and a constituent in building materials.^[21,22] Polyaniline is known for its good and stable conductivity properties. However, its halogen derivatives, especially their composites, would be expected to have some limitations, except 2-chloroaniline, because of their electronegativity, steric hindrance, and also poor conductivity.

On the basis of the above review, we became interested in preparing RM-, SiO_2 -, and Al_2O_3 -based composites of poly(2-halogen aniline).

Nanosized SiO_2 was chosen in the present study because of its ultrasmall size (approximately 7 nm) compared with other host materials. The average size of Al_2O_3 layers is 5 μm . RM is both the cheapest material and has a particle size between SiO_2 and Al_2O_3 , nearly $< 1 \mu\text{m}$. Recently, the synthesis and characterization of P2ClAn/RM composite was elaborated,^[23] but its properties are not comparable with Al_2O_3 and SiO_2 . In this work, we selected all 2-halogenanilines and synthesized the composites of poly(2-halogen anilines) using different host materials (Al_2O_3 , SiO_2 , RM). Their properties were compared with each other based on both host materials and guest materials.

EXPERIMENTAL SECTION

Materials

2-Fluoraniline (2FAn), 2-bromoaniline (2BrAn), and 2-iodoaniline (2IAN) were obtained from Fluka and 2-chloroaniline (2ClAn) from Merck, and the monomers were under nitrogen prior to use. Red mud was provided by Etibank Seydişehir Aluminium Plant (Konya, Turkey); its analytical data are shown in Table I. Al_2O_3 (min 98%, cat no. 11028 (Riedel-De Haen), particle size of $\sim 5 \mu\text{m}$) and SiO_2 (silica 99.8%, cat no. 381268 (Aldrich), particle size of 0.007 μm) were received from Riedel-De Haen and Aldrich, respectively. N-methyl-pyrrolidone (NMP) was purchased from Aldrich.

Preparation of Homopolymers and Composites

Poly(halogenanilines) were synthesized using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant. A solution of 0.02 mol $(\text{NH}_4)_2\text{S}_2\text{O}_8$ dissolved in 100 mL of 1.5 M HCl was added dropwise to the 0.01 mol 2-halogen aniline solution with vigorous magnetic stirring at 5°C. The mol ratio of oxidant to monomer was two. After about

Table I. Chemical composition of the RM

Chemical composition	Composition ratio (%)
Al_2O_3	18.71 ± 0.59
Fe_2O_3	39.70 ± 0.67
TiO_2	4.90 ± 0.54
Na_2O	8.82 ± 0.96
CaO	4.47 ± 0.56
SiO_2	14.52 ± 0.37
Ig. Loss	8.35 ± 0.40

3 h, the precipitate of poly(2-halogenanilines) was collected by filtration, washed with the corresponding acid solution until the filtrate became colorless, then washed several times with distilled water to remove the acid, and finally dried at 50°C for 24 h. The yield of P2FAn and P2IAn (0.0645 and 0.0532 g) is lower than that of P2ClAn and P2BrAn (0.9479 and 0.4770 g) due to electronegative properties and steric effects, respectively.

A weighted amount of host matrix (SiO₂, RM, Al₂O₃) was taken in a conical flask containing 100 mL of 1 M HCl and stirred under nitrogen for 15 min. The amounts of all host matrixes in composites were 0.0212, 0.3159, 0.1602, and 0.018 g for P2FAn, P2ClAn, P2BrAn, and P2IAn, respectively. A known volume of 2-halogen aniline was injected into HCl solution including host matrix and stirred magnetically for 15 min. Thereafter, a particular amount of oxidant was added to this solution at a time (30 min) and at 5°C, and the reaction mixture was kept under stirring for 3 h at room temperature. The precipitate was filtered and washed with the corresponding 1 M HCl solution until the filtrate become colorless, then washed several times with distilled water to remove the acid, and finally dried at 50°C for 24 h. The calculated content of host matrix in all composites was 25% (wt).

Characterization

Infrared spectra were recorded using a Fourier transform-infrared (FT-IR) spectrophotometer (Perkin Elmer BX). The KBr technique was used to prepare the tested polymers. The morphology of the polymers was examined by a scanning electron microscope (SEM), JEOL 5600-LV. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer Thermogravimetry analyzer. UV-vis spectra were recorded on a Perkin Elmer λ 20 from 900 to 190 nm. The solutions of homopolymers and composites were prepared in NMP (N-methyl-pyrrolidone). X-ray diffraction patterns were measured by using a Philips X-ray diffractometer. The conductivity of compressed pellets of the polymers was determined using the standard four-point probe technique at room temperature. Magnetic susceptibility measurements were performed using a Sherwood Scientific model Gouy balance.

RESULTS AND DISCUSSION

FT-IR Spectra

Figure 1 shows FT-IR spectra of SiO₂, P2ClAn/SiO₂, pure P2ClAn, P2ClAn/RM, and RM, respectively. The peaks at 3435, 3469 cm⁻¹

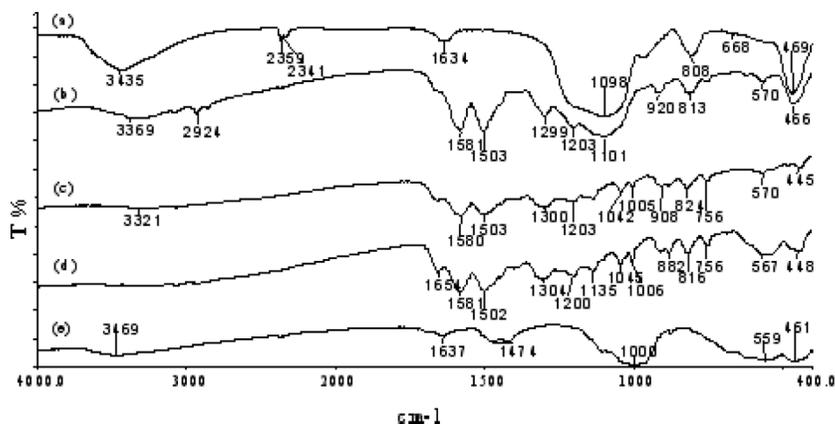


Figure 1. FT-IR spectrum of SiO₂ (a), P2ClAn/SiO₂ (b), P2ClAn (c), P2ClAn/RM (d), RM (e).

and 1634, 1637 cm⁻¹ in FT-IR spectra of SiO₂ and RM are due to the stretching vibration of the OH group and molecular H₂O respectively. In the spectrum of pure SiO₂, the peaks at 469, 808, and 1098 cm⁻¹ are due to the Si-O-Si bending modes, symmetric Si-O-Si stretching vibration, Si-OH torsion vibration, and asymmetric Si-O-Si stretching vibration, respectively.^[24,25] The spectrum of P2ClAn reveals the following characteristic absorption peaks: the FT-IR spectrum of pure P2ClAn shows four major vibration bands at 1042 cm⁻¹ (para-substituted) aromatic δ (C-H) in plane, 1300 (ν (C-N)), 1503 cm⁻¹ (benzenoid ring ν (C=C)), and 1580 cm⁻¹ (quinoid ring ν (C=C)), and these observed bands are in good agreement with previously published values.^[26] The bands at 460–810 and 460–560 cm⁻¹ are characteristic absorption bands for SiO₂ and RM, respectively. For P2ClAn/SiO₂ and P2ClAn/RM composite, the FT-IR spectra show characteristic bands of pure P2ClAn, as mentioned above, indicating the existence of P2ClAn. However, we note that there is a slight difference in their FT-IR spectra as shown in Figure 1, spectra b and d. Moreover, the additional peaks at 469, 448, 461, and 1101 cm⁻¹ (characteristic of SiO₂ and RM) appeared. The values of some bands belonging to P2ClAn show shifts in FT-IR spectra of composites. It is well known that in composite systems with PAn, strong guest-host interactions, such as hydrogen bonding, occur in the form of NH...O=V in V₂O₅ and NH...Cl in FeOCl.^[27,28] In the case of P2ClAn, these shifts can be due to similar interactions between P2ClAn and RM (or SiO₂). For all composites, FT-IR spectra were taken, and interactions and bands similar to those of P2ClAn were obtained. Their spectra are

almost identical to those of the pure poly(2-halogenanilines). However, all bands shift slightly, which indicates that some interaction exists between host and guest materials.^[29]

UV-Vis Spectroscopy

The solutions of poly (2-halogenanilines) and composites were prepared in NMP (N-methyl-pyrrolidone). Maximum absorbance wavelengths are listed in Table II. The peak at around 310 nm corresponds to the π - π^* transition of the polymer backbone benzenoid rings (B), while the peak at around 600 nm is ascribed to an excitation located in the quinoid ring (Q).^[30] The peak at around 360 nm shows the transition to the polaron structures. As can be seen in Table II, the shifts are observed at the wavelength of maximum absorbance of polymers when the groups bonded to the ring change. This can be explained as a result of steric and electronic effects of the substituents.^[26] The maximum absorption wavelengths of the composites shifted to shorter wavelengths according to their homopolymers. Among poly(2-halogenanilines), the composites of P2ClAn exhibited the biggest shifts of their wavelengths. These shifts in wavelengths indicate interactions between poly(2-halogenanilines) and the host matrix.^[31]

Table II. UV-vis results of samples

Sample	λ_1 (nm)	λ_2 (nm)	λ_2 (nm)
P2FAn	311	360	—
P2FAn/SiO ₂	290	357	558
P2FAn/RM	311	365	550
P2FAn/Al ₂ O ₃	311	363	—
P2ClAn	311	—	600
P2ClAn/SiO ₂	311	—	544
P2ClAn/RM	315	—	559
P2ClAn/Al ₂ O ₃	315	—	555
P2BrAn	312	—	604
P2BrAn/SiO ₂	311	—	575
P2BrAn/RM	311	—	586
P2BrAn/Al ₂ O ₃	313	—	569
P2IAn	311	353	—
P2IAn/SiO ₂	312	—	—
P2IAn/RM	312	—	—
P2IAn/Al ₂ O ₃	313	—	575

Thermal Stability

The thermal stability of the poly(2-halogenanilines)/Al₂O₃, SiO₂, and RM composites was investigated using thermogravimetric analysis. Figure 2, curves a, b, and c, shows TGA curves of P2IAN, P2IAN/RM, and P2IAN/SiO₂, respectively. TGA curves that belong to P2IAN are given as examples. The decomposition temperatures obtained from TGA thermograms of polymers are shown in Table III. As can be seen from Table III, P2FAn/Al₂O₃, P2ClAn/Al₂O₃, and P2IAN/Al₂O₃ show decomposition with three-step weight loss, while others indicate decomposition with two-step weight loss. In decomposition occurring in three steps, the first weight loss is a result of the release of free water.^[32] Additionally, RM, SiO₂, and Al₂O₃ are hydrophilic materials. Thus they show little weight loss indicating removal of water and volatile impurities. The second and third weight losses of homopolymers and composites occur between 275° and 354°C for P2FAn/Al₂O₃, and this weight loss indicates removal of dopant anions from P2FAn/Al₂O₃.^[33] The last decomposition steps indicate decomposition of skeletal structure of polymer chains.^[34] In decomposition with two steps, the first weight loss indications are due to the loss of acid dopant bound to the polymer chain. The second decomposition occurs between 341° and 690°C, showing the

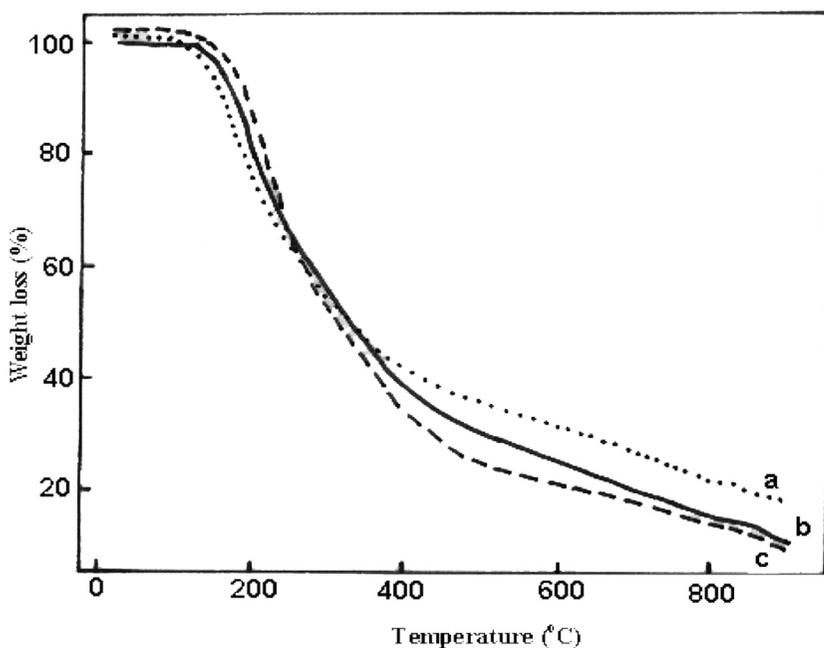


Figure 2. TGA thermograms of P2IAN (a), P2IAN/RM (b), P2IAN/SiO₂ (c).

Table III. TGA results of polymers

Sample	T _i 100	T _m 178	T _f 261	Residue % at 800°C
RM	261	272	287	88
	627	655	687	
SiO ₂	154	490	822	72
Al ₂ O ₃	185	200	218	96
P2FAn	150	265	387	
	387	550	718	0
P2FAn/SiO ₂	155	255	359	
	359	522	690	12
P2FAn/RM	151	239	341	
	341	482	631	78
P2FAn/Al ₂ O ₃	164	248	338	
	275	315	354	
	354	528	700	
P2ClAn	111	476	835	0
P2ClAn/SiO ₂	155	468	778	10
P2ClAn/RM	272	582	870	25
P2ClAn/Al ₂ O ₃	164	248	338	
	538	584	631	
P2BrAn	137	429	724	0
P2BrAn/SiO ₂	155	318	487	35
P2BrAn/RM	150	458	782	35
P2BrAn/Al ₂ O ₃	207	341	466	
P2IAn	136	265	387	35
P2IAn/SiO ₂	161	300	440	20
P2IAn/RM	155	287	418	20
P2IAn/Al ₂ O ₃	176	345	512	
	512	586	679	

T_i: initial degradation temperature; T_m: maximum degradation temperature; T_f: final degradation temperature.

degradation of polymer chain. In decompositions occurring in one step, the decomposition corresponds to both removal of dopant anions and degradation of polymer structure.

The thermal stability of the composites was investigated by measuring the initial decomposition temperatures, which were determined from the first derivative of the TGA curves (Table III). Decomposition temperatures increased remarkably in all composites. This result indicates that the thermal stability of the composite materials was significantly improved compared to the pure polymers. Among host materials, Al₂O₃ increased thermal stability of pure polymers much more than

SiO₂ and RM. All composite systems are more thermally stable than the pure poly(2-halogenanilines), which can be explained by the fact that an interaction between host and guest materials restricts thermal motion of the poly(2-halogenaniline) in the composites and enhances thermal stability of the composites.

Morphology

RM, SiO₂, and Al₂O₃ have different morphologies and particle sizes (Figure 3(a)–(c)). SiO₂ has the smallest particle dimensions, and Al₂O₃ has a structure with layers having different dimensions. P2BrAn shows not only globular structure but also have different particle sizes and stacks (Figure 3(d)). When the SEM micrographs of P2FAn/Al₂O₃, P2ClAn/SiO₂, and P2BrAn/RM composites are analyzed in detail, many kinds of surface morphologies can be seen (Figure 3(e)–(g)). The results show that the RM particles, which are about 50–100 nm in size, can be observed to be well dispersed in all composites that are synthesized by RM.^[21] In these morphologies, Al₂O₃ and SiO₂ would be present not only on the particle surface, but also distributed throughout the interior of the particles.^[35,36] Al₂O₃, SiO₂, and RM particles appear to be moderately dispersed in poly(2-halogenanilines) matrix. From SEM results, it is understood that particular sizes increased and surface morphologies changed in all composites.

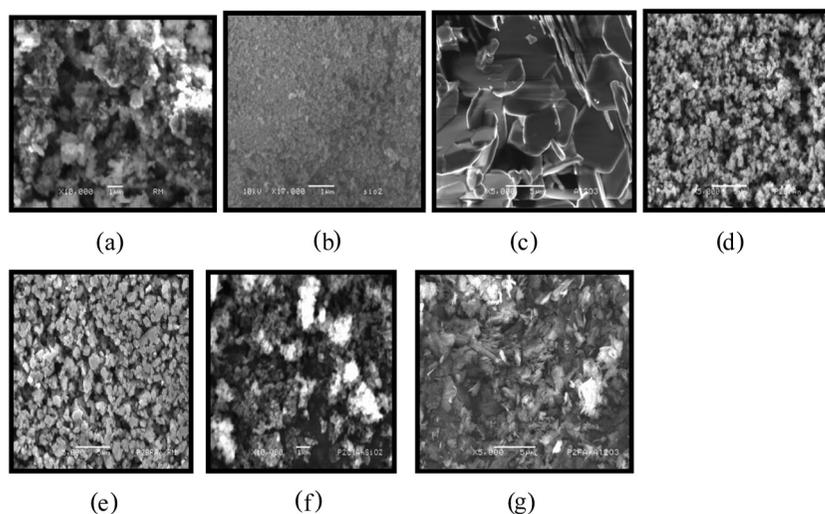


Figure 3. SEM micrographs of all samples: RM (a), SiO₂ (b), Al₂O₃ (c), P2BrAn (d), P2BrAn/RM (e), P2BrAn/SiO₂ (f), P2ClAn/Al₂O₃ (g).

X-Ray Diffraction Analysis

Figure 4 shows the X-ray diffraction (XRD) patterns of the pure P2ClAn, P2ClAn/SiO₂, P2ClAn/RM, and P2ClAn/Al₂O₃ composites. The pure P2ClAn powders exhibit a “broad peak” at 2θ angles around 26° . This peak is a characteristic of the polyaniline family, and it is sharper in polyaniline.^[37] It indicates polymer crystallization to a certain extent. P2ClAn has amorphous structure due to its broad peaks at $2\theta = 26^\circ$. It is seen that XRD peaks for P2ClAn/SiO₂ composite are mostly similar to those of pure P2ClAn, indicating that the crystal structure of SiO₂ was not modified by P2ClAn. These results also indicate that P2ClAn is amorphous in the nanocomposite, which suggests that the addition of SiO₂ nanoparticles impedes the crystallization of the P2ClAn and P2BrAn molecular chains. XRD patterns of P2ClAn composites with RM and Al₂O₃ show characteristic and sharp diffractions at $2\theta = 25; 35,5; 38; 44; 53; 58; 67; \text{ and } 68^\circ$, $2\theta = 24; 33; 35,5; 39; 41; 49,5; 54; 56; 62,5; 64; 69,5; \text{ and } 72^\circ$ belonging to Al₂O₃ and RM, respectively. But, the crystallization degree of SiO₂, RM, and Al₂O₃ decreased after polymerization of P2ClAn. It implies that poly(2-halogenanilines) are deposited on the surface of Al₂O₃, SiO₂, and RM. It suggests also that an interaction exists at the interface of poly(2-halogenanilines) and inorganic materials, which

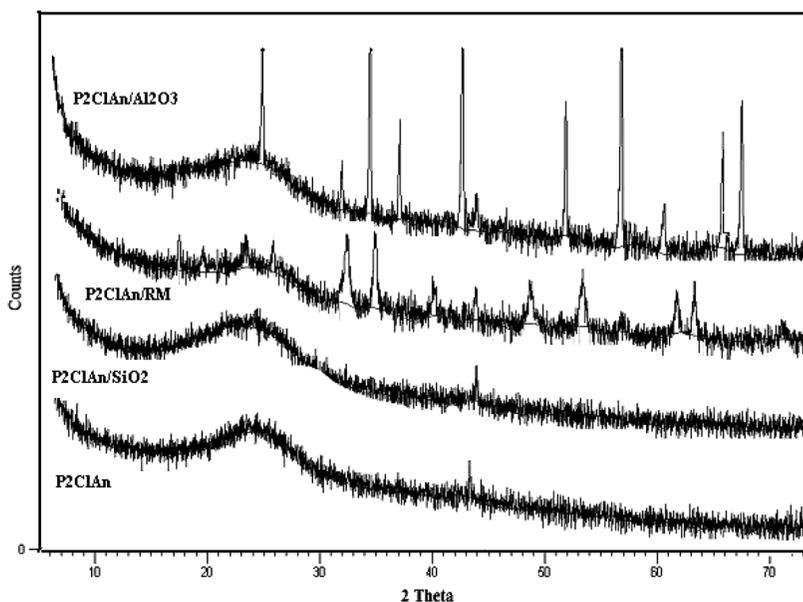


Figure 4. X-ray diffraction patterns of P2ClAn, P2ClAn/SiO₂, P2ClAn/RM, P2ClAn/Al₂O₃.

restricts the poly(2-halogenaniline) from forming bulk polymer by aggregation.

Conductivity and Magnetic Susceptibility

Table IV shows the conductivity and magnetic susceptibility values of P2ClAn and P2BrAn composites with SiO₂, RM, and Al₂O₃. The conductivity value of P2ClAn and P2BrAn was determined as 4.6×10^{-7} and 6.1×10^{-7} S cm⁻¹, respectively. P2ClAn/SiO₂ has higher conductivity than P2ClAn/Al₂O₃. A similar change was observed for polyaniline composites with SiO₂ and Al₂O₃.^[38,9] The conductivity values of PPy/SiO₂^[10] and PPy/Al₂O₃^[39] were analyzed and it was found that composite with Al₂O₃ has higher conductivity than SiO₂ and these values were lower than for pure PPy. As shown in another study, the conductivity of PPy was enhanced by preparing the composite with Al₂O₃.^[40]

In our study, Al₂O₃ increased the conductivity of P2ClAn, whereas it did not change that of P2BrAn. The main reason accounting for the enhancement in conductivity is probably that P2ClAn is formed on the surface of the Al₂O₃. The lowest conductivity values were obtained in RM composites. As seen both from our results and literature data, there is no clear point in conductivity change. When we compared the conductivities of different particle sizes, the highest conductivity was obtained in P2ClAn/SiO₂. SiO₂ has the smallest particle size but much higher conductivity than others. However, P2BrAn did not exhibit the same behavior due to steric hindrance.

The mechanism of conduction in polymers, e.g., polyfuran, polyindole, and polyaniline, is very complex, since such materials exhibit conductivity in a range of about 10 orders of magnitude by changing their doping. To explain the electronic phenomena in these systems, the concepts of solitons, polarons, and bipolarons have been used.^[41]

Table IV. Conductivity and Gouy balance measurement of polymers

Sample	Conductivity (S/cm)	Magnetic susceptibility
P2ClAn	4.6×10^{-7}	(-)
P2ClAn/SiO ₂	1.3×10^{-5}	(-)
P2ClAn/Al ₂ O ₃	3.7×10^{-6}	(-)
P2ClAn/RM	1.7×10^{-7}	(+)
P2BrAn	6.1×10^{-7}	(-)
P2BrAn/SiO ₂	1.4×10^{-8}	(-)
P2BrAn/Al ₂ O ₃	6.0×10^{-7}	(-)
P2BrAn/RM	8.5×10^{-8}	(+)

The conduction in conducting polymers (enhancing or dipping) is influenced by a variety of factors: polaron length, conjugation length, overall chain length, and charge transfer to adjacent molecules.^[42] In the particular case of polyaniline, its conductivity can be changed using different substituents bonded to the aromatic ring. Both conjugation length and redox potential are affected by their nature and substituent positions on the ring.^[43] Hosts as Al_2O_3 , SiO_2 , and RM affect the movement of the charges in the polymer. These results show that the conductivity of the composites is different than the conductivity of pure polymers.

The magnetic properties of the composites have been considered by measuring the magnetic susceptibility. The composites with RM were paramagnetic because they contained unpaired electrons. The composites with Al_2O_3 and SiO_2 became diamagnetic. The analyses indicate that the conduction mechanism of paramagnetic polymers is of polaron nature, whereas diamagnetic polymers are of bipolaron nature.^[44] RM is a paramagnetic material and also includes Fe_2O_3 component together with SiO_2 and Al_2O_3 in its structure. Fe_2O_3 can be responsible for paramagnetism.

CONCLUSIONS

Poly(2-halogenaniline) composites containing SiO_2 nanoparticles (about $0.007\ \mu\text{m}$ in diameter), RM (under $1\ \mu\text{m}$), and Al_2O_3 (average $5\ \mu\text{m}$) were synthesized by “in situ” polymerization in the presence of hydrochloric acid (HCl) as the dopant. The properties of poly(2-halogenaniline) composites with RM, which is cheaper and is a waste product, are useful in application areas of conducting polymers. In this study, RM was evaluated as host material and its properties were found to be near to other composites with SiO_2 and Al_2O_3 . All the composites were found to be more thermally stable than that of the pure poly(2-halogenaniline). These enhancements in thermal stability of the composites are ascribed to the interaction between host and guest materials. Among guest materials, Al_2O_3 with the biggest particle size gave the highest thermal enhancements, except P2ClAn/RM. When we compared conductivity changes with changing host molecules, we observed two different behaviors. SiO_2 with the smallest particle size increased the conductivity value of P2ClAn, whereas RM showed a negative effect on the conductivity properties. FT-IR and UV-vis results indicated that poly(2-halogenanilines) host materials (Al_2O_3 , SiO_2 and RM) are simply not blended or mixed up. A strong interactive force may be attributed to the tendency to form a coordination compound between host and guest molecules in poly(2-halogenaniline).

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