Phthalocyanine/Laponite Nanocomposites as Multifunction Additives for Stabilization of Polymeric Materials

M. A. Abd El-Ghaffar, N. R. El-Halawany, H. A. Essawy

Polymers and Pigments Department, National Research Center, Cairo, 12311, Egypt

Received 24 April 2007; accepted 4 October 2007 DOI 10.1002/app.27558 Published online 4 March 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Novel phthalocyanine amide polymers (Pc) based on 1,8-naphthalenediamine (Ar) as an aromatic amine and 1,4-diaminobutane (Al) as an aliphatic amine, were synthesized to improve the limited stabilization modes of conventional phthalocyanines. The metal-free phthalocyanines polymers (MF-Pc) were moderately soluble in DMSO only while the metalized forms (Cu&Ni-Pc) were completely insoluble. The structure of the samples was confirmed using Fourier transform infrared (FTIR), ultraviolet-visible spectrometry (UV-vis) and nuclear magnetic resonance (NMR). Additionally, the thermal stability and glass transition temperatures (T_g) were investigated by thermal gravimetric analyzer (TGA) and differential scanning calorimeter (DSC), respectively. The intercalation of the metal-free phthalocyanines, based on the aliphatic amine (MF-PcAl) and aromatic amine (MF-PcAr), into laponite from DMSO solution, was proved by X-ray diffraction (XRD). The basal space of laponite increased from

INTRODUCTION

Polymer/clay nanocomposites are a new class of materials usually possess improved strength, enhanced modulus, decreased thermal expansion coefficient, increased thermal stability, and reduced gas permeability compared with pure polymers or conventional composites, due to the nanoscale dispersion of clay in polymer matrix, high aspect ratio of clay platelets, and interfacial interaction between clay and polymers.¹ For example, polyvinylchloride (PVC) is one of the most important thermoplastics owing to its wide applications and low cost. However, due to its inherent disadvantages, such as low thermal stability, poor resistance to UV degradation and brittleness, PVC is subject to some limitations in certain applications.² PVC/clay nanocomposites is thought to be one of the effective ways to improve the disadvantages of pure PVC, but few studies are

Journal of Applied Polymer Science, Vol. 108, 3225–3232 (2008) © 2008 Wiley Periodicals, Inc.



1.2 to 1.36 nm upon intercalation of MF-PcAl and extended more to 1.91 nm on using MF-PcAr as intercalant while the quaternized forms of MF-Pcs behaved likewise and could not widen the basal space of laponite to more than 1.43 nm which was attributed to the random distribution of the positive charges over the Pc chains which imposed confined arrangement inside the basal space and consequently narrower space than the attained one in the case of nonquaternized phthalocyanines. The plasticized PVC composites based on laponite treated with either MF-PcAl or MF-PcAr exhibited improved resistance to the UV radiation as revealed by the retention of the tensile strength and elongation at rupture after exposure to UV radiation for different time intervals. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3225–3232, 2008

Key words: phthalocyanines; laponite; PVC; nanocomposites; stabilization

reported so far in comparison with other polymer matrices. Phthalocyanines alone had been prepared and applied in polymers as stabilizers as being known for imparting thermal stability in addition to their resistance to chemical attack.^{3,4} Most of the polymers prepared from phthalocyanines failed to show the anticipated thermal stability which was mainly attributed to a low degree of polymerization and the presence of connecting units with poor thermal stability. As well, their stabilization mode is limited by the progressive decay observed due to the absorption of UV, especially the metalized forms of phthalocyanines.⁵ In the same time, phthalocyanine derivatives provide a unique opportunity to prepare a novel class of imide polymers with attractive properties⁶ and this may provide a good solution to overcome this decay upon exposure to UV. The presence of many amine centers with different chemical environments can also allow for the quaternization of these polymers and facilitate its application as a chemical modifier for the swellable clays such as laponite. Modification of laponite is generally required through an ion exchange reaction between organic cations (eg. quaternized phthalocyanine) and inorganic cations (lithium in the case of Li-laponite).

Correspondence to: H. A. Essawy (hishamessawy@yahoo. com).

Quaternized phthalocyanines can exhibit a high ion exchange ratio, higher interlayer spacing, and a higher decomposition temperature if compared with the conventional and commonly used modifiers such as long carbon-chain alkylamines or ammonium salts which consequently allow for a nanoscale dispersion of clay in polymer matrix and permits to modulate the properties of many polymeric materials. Moreover, the anchored phthalocyanine amide polymers to the clay is anticipated to provide both thermal and UV stabilization. As well, the huge number of nitrogen centers can absorb the liberated hydrogen chloride from PVC as an example during degradation which acts as a second stabilization line and delays the degradation to a minimum level. It is also worthy to mention that the clay platelets can act as a flexibilizer⁷ which may replace the addition of external plasticizer such as dioctylphthalate, therefore it is of economical advantage. In addition, clays and phthalocyanines are known for their effectiveness as radical scavengers.⁶ The aim of the present work is to gather this package of stabilization effects in one component multi-stabilizing system that can be consequently used for many polymeric materials upon compounding with laponite treated with different amide polymers based on phthalocyanines, PVC is being among these polymers.

EXPERIMENTAL

Materials

The 1,8-naphthalenediamine and urea were purchased from Riedel-de Haeen while 1,4-Daminobutane, *N*-dimethylformamide (DMF) and nickel chloride (NiCl₂) were obtained from Merck-Schuchardt, Germany. Cupric chloride, $CuCl_2 \cdot 2H_2O$ was provided from Polskie Odczynniki Chemiczne S.A., Poland. Laponite RDS was provided by Southern Clay Products Texas, USA. Commercial PVC in the form of a white powder with k value of 67 was used. Linear dioctylphthalate as plasticizer and dibutyltin maleate as thermal stabilizer were of technical grade.

PROCEDURES

Preparation of metal free tetracarboxy phthalocyanine (MF-TcPc)

MF-TcPc was prepared by urea fusion technique in the dry method as follows. A mixture of trimellitic acid (0.4 mol) and urea (excess) in the presence of ammonium molybdate as a catalyst were fused together with continuous stirring at 200°C for about 4 h until a stable green color was formed. The solid mass was cooled, ground and washed several times with boiled water, dilute hydrochloric acid and finally methanol, collected by filtration and dried at 110°C for 4 h. The dried mass of tetracarboxyamide Pc was hydrolyzed by treatment with a solution of 0.5–1% sodium hydroxide at 80°C until all the ammonia was evaporated in order to convert all the $-CONH_2$ groups to free carboxyl groups. The samples were subjected to further purification via soxhlet extraction in acetone.

Preparation of Cu&Ni-tetracarboxy phthalocyanines (Cu&Ni-TcPc)

Cu-TcPc and Ni-TcPc were prepared also by urea fusion technique in the dry method as follows. A mixture of trimellitic acid (0.4 mol), copper acetate or nickel chloride (0.1 mol) and urea (excess) in the presence of ammonium molybdate as a catalyst were fused together with continuous stirring at 200°C for about 4 h until a stable green color was formed. The resulting solids were cooled, ground and washed several times with boiled water, dilute hydrochloric acid and finally methanol, collected by filtration and dried at 110°C for 4 h. The dried mass of Cu&Ni-tetracarboxyamide Pc were hydrolyzed by treatment with a solution of 0.5–1% sodium hydroxide at 80°C until all the ammonia was evaporated in order to convert all the $-CONH_2$ groups to free carboxyl groups. The samples were subjected to further purification via soxhlet extraction in acetone.

Preparation of MF-TcPc, Cu&Ni-TcPc amide polymers

Amide polymers of MF-TcPc, Cu&Ni-TcPc were prepared by charging 0.01 mol of each in 20 mL DMF and 0.01 mol of 1,4-diaminobutane and 1,8-diaminonaphthalene in 20 mL DMF, independently. The reactants were subjected to reflux in presence of polyphosphoric acid for 24 h at 150°C. The reaction medium was left to cool to room temperature and poured into large excess of water-methanol mixture (3 : 1). Finally, the reaction medium was filtered off and the product was washed several times with boiled distilled water, hot methanol, and finally soxhlet extracted with acetonitrile-methanol mixture (20 : 80), and left to dry under vacuum at 60°C for 24 h.

Intercalation of phthalocyanine polymers into laponite

The prepared phthalocyanines (0.2 g) were dissolved in DMSO and 0.5 g of laponite was subsequently added and the mixture was stirred at 60° C for 6 h. Finally, the clay was separated by centrifuge, washed several times with DMSO before drying under vacuum at 80° C for 24 h. Moreover, the

	Aliphatic			Aromatic		
Solvent type	MF-PcAl	Cu-PcAl	Ni-PcAl	MF-PcAr	Cu-PcAr	Ni-PcAr
DMSO	S	Ι	Ι	S	Ι	Ι
NMF	Ι	Ι	Ι	Ι	Ι	Ι
CHCl ₃	Ι	Ι	Ι	Ι	Ι	Ι
Acetone	Ι	Ι	Ι	Ι	Ι	Ι
Methanol	Ι	Ι	Ι	Ι	Ι	Ι
Acetonitrile	Ι	Ι	Ι	Ι	Ι	Ι
CH_2Cl_2	Ι	Ι	Ι	Ι	Ι	Ι
MEK	Ι	Ι	Ι	Ι	Ι	Ι
THF	Ι	Ι	Ι	Ι	Ι	Ι

 TABLE I

 Solubility of the Prepared Phthalocyanine Amide Polymers in Different Solvents

S:, soluble; I, insoluble.

phthalocyanine polymers were converted to the quaternized forms by dropwise addition of HCl to suspension of the phthalocyanines in ethylacetate and the pH was brought to 1, the suspension was kept under continuous stirring for 3 h at 60°C. The ethylacetate was removed by filtration while the solid was washed several times with ethylacetate to remove any excess of the acid before introduced to drying under vacuum for 24 h at 80°C. Finally, the aforementioned intercalation steps into laponite were repeated using the quaternized phthalocyanines.

Preparation of PVC-laponite/MF-PcAl and/or laponite/MF-PcAr composites

The PVC (125 parts) was charged to a melt-blender running at low speed, then the heat stabilizer (5 parts) was added simultaneously with 37.5 parts of plasticizer, and the rotor speed of the blender was increased. Lastly, 5 parts of either laponite or treated filler (laponite/MF-PcAl or laponite/MF-PcAr) were incorporated and the temperature was elevated to 180°C. The mixing process was continued for 5 min. The samples (each) were withdrawn from the blender and sheets of 0.7 mm thickness were prepared by compression molding using a hot press at 180°C and 20 MPa for 5 min, followed by cooling to room temperature.

Techniques

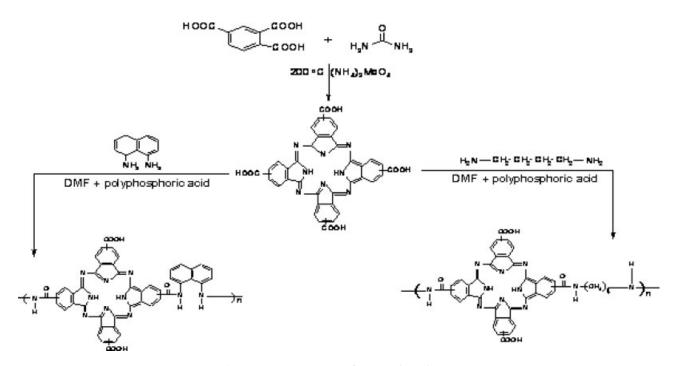
Fourier transform infrared spectra of the samples were collected from KBr pressed disks of the grinded samples using FTIR spectrophotometer, Nicolet, Nexus 821, Medison, USA, in the range 400–4000 cm⁻¹. UV–vis spectrophotometer type LKB Ultra Spec Plus was used for recording the absorption spectra. The thermal stability and glass transition temperatures were evaluated on Perkin–Elmer, thermal gravimetric analyzer (TGA) and differential scanning calorimeter (DSC), using about 20 mg of the

samples at a heating rate of 10° C/min in nitrogen atmosphere. ¹H NMR spectra were obtained with JEOL 270 MHz spectrometer using deuterated dimethylsulfoxide (DMSO) as a solvent. XRD patterns of the phthalocyanines/laponite nanocomposites were recorded on a Diano X-ray diffractometer using Co K α radiation source energized at 45 kV while the elemental analysis was carried out at the Micro Analytical Center of Cairo University. The composites sheets were cut into dumbbell-shaped species for tensile strength measurements using Zwick 1425 tensile testing machine, after being exposed to UV radiation using UV lamp of 340 nm and 20 MW/cm² intensity for different time intervals.

RESULTS AND DISCUSSION

The solubility of the different phthalocyanine amide polymers were checked in many solvents and reported in Table I. None of the metalized-phthalocyanine polymers dissolved by any of these solvents, while the metal-free phthalocyanine polymers could be dissolved by a strong aprotic solvent only (DMSO). This means that the solubility of the samples is metal dependent, as the involvement of the nitrogen centers in coordination bonds with the metal prevents the participation of these centers in the solubility process as expected (not available for interaction with the solvent) which confirms the decisive role of the nitrogen sites in the solubility process.

Scheme 1 shows the steps performed for the synthesis of the phthalocyanine amide polymers. Trimellitic acid was reacted with urea as an aminating source using the catalyst ammonium molybdate in the absence and presence of metal salts to give metal-free tetracarboxy phthalocyanine (MF-TcPc) and its metalized forms (Cu&Ni-TcPc), respectively. The phthalocyanine amide polymers were obtained by further reaction of either MF-TcPc, Cu or Ni-TcPc forms with 1,4-diaminobutane and 1,8-diaminonaph-



Scheme 1 Preparation of Pc amide polymers.

thalene in DMF medium in the presence of polyphosphoric acid as a dehydrating agent. The samples are denoted as follows, MF refer to metal-free and Cu/Ni refer to the type of the metal while Al signify the polymers based on the aliphatic amine while Ar signify those based on the aromatic amine. So Ni-

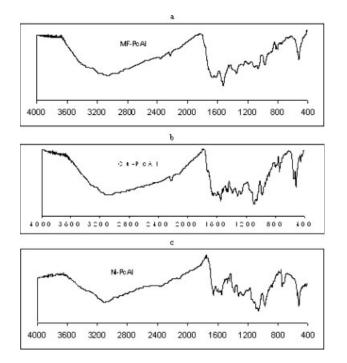


Figure 1 IR spectra of Pc amide polymers (a) MF-PcAl, (b) Cu-PcAl, (c) Ni-PcAl.

PcAr as an example means Ni-phthalocyanine amide polymer of 1,8-diaminonaphthalene.

The IR spectra of the prepared metal-free phthalocyanines as well as the metalized equivalents based on both aliphatic and aromatic amines are displayed in Figures 1 and 2. The spectra are generally rich with bands of weak to medium intensity that are in most cases overlapping with each other. All phthalocyanine samples showed the typical absorptions peaks characterizing any phthalocyanine unit irrespective to the type of the amine incorporated, 642– 730 cm⁻¹ (out of plane, C—H deformation in benzene ring); 822 cm⁻¹ (C—H of benzene ring), 1080–

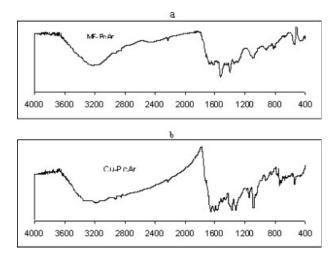


Figure 2 IR spectra of Pc amide polymers (a) MF-PcAr, (b) Cu-PcAr.

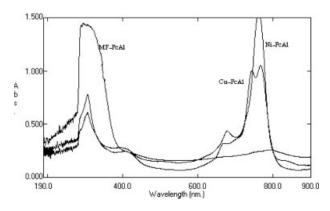


Figure 3 UV–visible spectra of phthalocyanine amide polymers based on 1,4-diaminobutane.

1092 cm⁻¹ (conjugated system of phthalocyanine), 1344–1349 cm⁻¹ (C–N stretching), 1523 cm⁻¹ (C=C stretching in aromatic system), 1618–1675 cm⁻¹ (C=N), 1743 cm⁻¹ (C=O), very broad band ranged from 3058 to 3223 cm⁻¹ corresponding to (C-H stretching in aromatic ring, O-H stretching of free COOH, amide N—H stretching). These bands are in complete accordance with the data obtained by our group⁸⁻¹⁰ and by Bannehr and co-workers¹¹ for the metal-free as well as the metalized phthalocyanines. It is worthy to notice that these bands are metal dependent and perturb slightly to higher wavenumbers in case of metalized phthalocyanines (compare spectrum a with b and c in Fig. 1 and spectrum a with b in Fig. 2). Furthermore, the peak at $1450-1470 \text{ cm}^{-1}$ is ascribed to the CH₂ bending of the aliphatic amine [Fig. 1(a-c)]. On the other hand, the naphthalene unit of the aromatic amine is characterized by two peaks at 415 and 570–649 cm⁻¹ [Fig. 2(a,b)].

The UV-vis spectra of two series of phthalocyanine polymers based on aliphatic amine (1,4-diaminobutane) and aromatic amine (1,8-diaminonaphthalene) are displayed in Figures 3 and 4. It is clear that beside the strong absorption of all the polymers in the UV region at 290 nm, with its intensity decreasing upon coordination with Cu or Ni in both types, there is a strong absorption in the visible range at 700-770 nm with comparable intensity and even higher for the polymers based on 1,4-diaminobutane and this was not experienced in our previous work during the synthesis of different classes of phthalo-cyanine amide polymers.^{8–10} This strong absorption in the visible region disappears completely in the case of the metal-free samples irrespective of the type of amine incorporated in the structure which confirms that it is metal dependent. The weak acid resistance of the metal-free samples is thought to be responsible for the disappearance of this absorption band, as the samples are nearly unstable in the presence of strong acids on the contrary to the Ni&Cu phthalocyanine amide polymers. The metal variation

is slightly affecting the intensity of the band appeared in the visible region, with Cu causes splitting of this peak into two peaks with maximum absorption at 715–765 nm.

The thermal gravimetric analyses (TGA) of some representing phthalocyanine amide polymers are displayed in Fig. 5(a–c). Obviously, the samples show weight loss of about 4% at 200°C, may be due to evaporation of bounded water. After that degree, the decomposition of the samples occurs gradually with the temperature up to 600°C before finally retaining about 10% from the initial mass for the metal-free amide polymer and about 15% for the metalized one. However, it might be observed that the decomposition profile was to some extent slower for the metalized polymer with respect to its metal-free equivalent.

Figure 6 shows the DSC thermograms of MF-PcAl, MF-PcAr in addition to their metalized counterparts with nickel. It is obvious that the endotherms appeared at the beginning and up to 150°C are ascribed to the liberation of strongly adsorbed water at the hydrophilic surface of phthalocyanines. The MF-PcAl attained a glass transition temperature (T_g) around 191°C, which increased slightly to 193°C in the case of Ni-PcAl. On the other hand, the MF-PcAr acquired a higher T_g than its aliphatic equivalent (198°C) while its metalized form with nickel showed T_g at 208°C. This infers that the metalized phthalocyanine forms have higher T_{gs} than their unmetalized counterparts which can be correlated with the complete insolubility of these forms in DMSO in comparison to the weak solubility of MF-Pcs in DMSO.

The compositions of the metal free phthalocyanines were further elucidated by ¹H NMR. From the figures (not shown here), the MF-PcAl showed a signal belongs to methylenic protons appeared as multiplet at 2.7–3.4 ppm, in addition to a signal extends from 4.1–5.2 ppm contribute to the N—H protons. Also, the phenylic protons were detected as a small

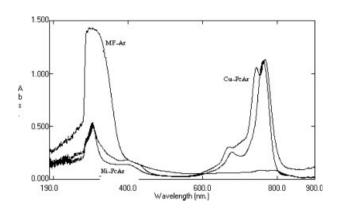


Figure 4 UV–visible spectra of phthalocyanine amide polymers based on 1,8-diaminonaphthalene.

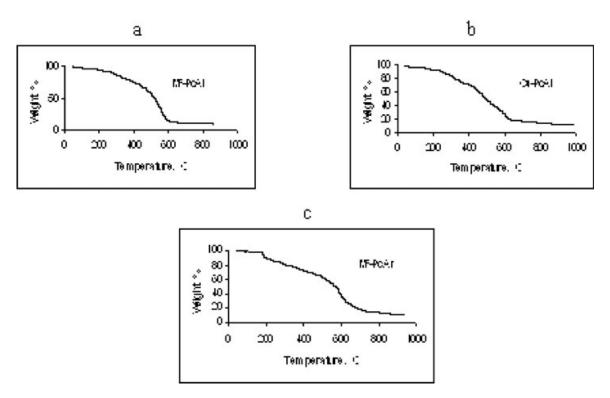


Figure 5 TGA thermograms of (a) MF-PcAl, (b) Cu-PcAl, (c) MF-PcAr.

singlet at 7.2 ppm and finally the COOH protons at 8.3 ppm. The ¹H NMR spectra of the MF-PcAr was approximately the same as that of MF-PcAl with the

only exception that the peak of the methylenic protons characterizing the butyl group of the aliphatic amine disappeared completely.

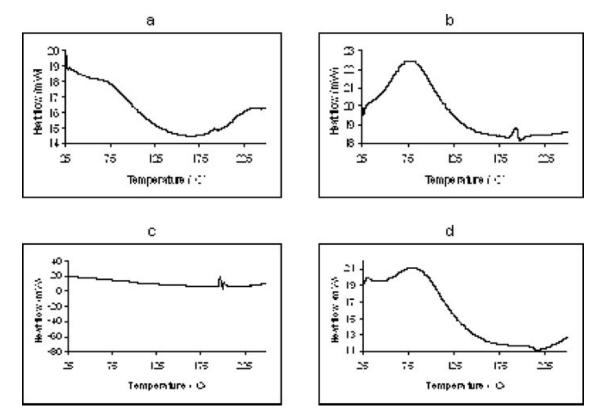


Figure 6 DSC thermograms of (a) MF-PcAl, (b) Ni-PcAl, (c) MF-PcAr, (d) Ni-PcAr.

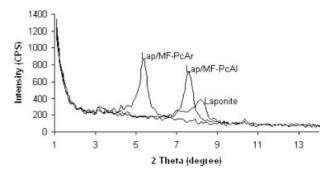


Figure 7 XRD patterns of laponite and its intercalated counterparts with phthalocyanine polymers.

Laponite is a two-dimensional inorganic polymer with six octahedral magnesium ions sandwiched between two layers of four tetrahedral silicon atoms. The silicon and magnesium atoms are balanced by 20 oxygen atoms and four hydroxyl groups. Sometimes, magnesium is replaced by lithium ions, and a negative charge is developed within the interlayer gallery space, which is compensated by exchangeable sodium or lithium ions. Thus, laponite has a hydrophilic nature due to the high content of exchangeable cations in its basal space, the hydration power of the clay increases greatly as the ionic radius of these cations decrease. Also, hydroxyl groups and small positive charges mostly located at the broken edges of the crystal are responsible for imparting polar nature on the clay surface.^{12,13} The first step in order to prepare organic/inorganic hybrids is to verify homogeneous dispersion of the inorganic phase in the organic polymer one. The high polar nature of the phthalocyanine polymer is suggested to be a strong driving force that facilitate the impregenation of the clay by these polymers, in particular, in the basal space of the clay because of its polar nature. The prepared phthalocyanines in this study were intercalated into the basal space of laponite from DMSO solution under continuous stirring at 60°C for 6 h. They could successfully penetrate into the basal space of laponite, the Pc-Al caused expansion from 1.2 to 1.36 nm while the Pc-Ar resulted more widening of the basal space, 1.91 nm. So the prepared phthalocyanine/laponite nanocomposites exhibited intercalated nature as demonstrated by the XRD, Figure 7. Furthermore, we think that these intercalated nanocomposites can be of dual function additives for plastics and rubbers as enhancer of mechanical properties in addition to the expected stabilization against UV irradiation.

The conversion of the phthalocyanines to the quaternized forms was identified by the detection of 4.34, 4.83% of chloride for MF-PcAl and MF-PcAr, respectively via elemental analysis. These ratios give rise to the fact that not all the nitrogens were involved in the quaternization process, as it occurs preferentially at the secondary amide centers only. Otherwise, these ratios should have reached higher values (six times the found ratios based on the molecular weight of one repeating unit of each of the target polymers). The quaternized phthalocyanine amide polymers were also intercalated into laponite from DMSO and their XRD patterns are displayed in Figure 8. It was not surprising that the phthalocyanine polymers behaved similarly (coincided) and could not expand the basal space of laponite beyond 1.43 nm. An explanation is that the random distribution of the positive charges over the phthalocyanine chains obliged them to acquire confined arrangement inside the basal space and as a result narrower expansion than that attained in the case of nonquaternized phthalocyanines.

For investigating the effect of UV radiation on plasticized PVC, different PVC compositions were formulated, the first one contained no laponite (C1) and the second one contained the unintercalated laponite (C2). Likewise, two other formulations based on the intercalated laponite with MF-PcAl (C3) and MF-PcAr (C4) were prepared. The various additives (plasticizer and heat stabilizer) were included in all formulations. The heat stabilizer was added to the samples even the blank (C1) to keep the samples away from any thermal degradation resulting from the elevated temperature that stems from the continuous exposure to UV lamp so our investigation is concerned with the degradation caused by the UV radiation only. The mechanical properties (tensile strength and elongation at rupture) of the samples were measured before and after different exposure intervals to UV radiation as shown in Table II. Before the exposure to UV radiation, an obvious increase in the tensile strength (TS) is noticed upon incorporating treated laponite, 17% increase for C3 and C4, respectively which can be attributed to the increased polarity of the laponite after the intercalation therefore better compatibility with PVC is expected, while the improvement is very little for the untreated laponite (C2). After 24-h exposure to UV radiation, a distinct deterioration was observed, the TS decreased significantly for the

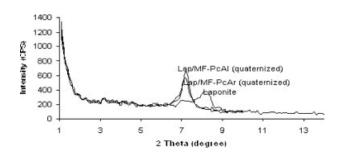


Figure 8 XRD patterns of laponite and its intercalated counterparts with quaternized phthalocyanine polymers.

TABLE II Influence of the Exposure to UV Radiation on the Tensile Strength and Elongation at Rupture of the Prepared Composites After Different Time Intervals

Property	C1	C2	C3	C4
TS (MPa)	13.8 (0)	14.5 (0)	16.18 (0)	16.64 (0)
	8 (24)	11.1 (24)	16 (24)	14 (24)
	6.8 (48)	10.7 (48)	13 (48)	14 (48)
	3.6 (72)	9.5 (72)	13 (72)	13.7 (72)
	2.6 (144)	7 (144)	9.5 (144)	13 (144)
E (%)	115 (0)	160 (0)	150 (0)	160 (0)
	90 (24)	130 (24)	150 (24)	140(24)
	80 (48)	110 (48)	120 (48)	130 (48)
	80 (72)	110 (72)	120 (72)	120 (72)
	60 (144)	60 (144)	95 (144)	120 (144)

sample containing no laponite (C1) as compared with the other samples and the loss in TS reached 42%, it declined to 23% for C2 and decreased more to 16% in case of C4 whereas C3 was not affected which reveals the laponite capability to block any active radical sites that arise from the liberation of hydrogen chloride during degradation in particular when incorporated in its intercalated form with phthalocyanines. It is thought that phthalocyanines dissipate the UV light energy in the form of heat in addition to their potential as radical scavenger.⁶

This can be also observed upon prolonging the exposure time where C1 deteriorated intensively after 72 h with 74% loss in TS, on the contrary, the other samples showed greater resistance to the effect of the UV radiation in the order C4 > C3 > C2. At the same time laponite could facilitate the molecular motion of the polymeric chains⁷ consequently it improved the elongation at rupture (E). The treatment of laponite seems to increase the polarity and hence its compatibility with PVC so better performance not only as UV stabilizer but also as enhancer of the mechanical properties is expected which was actually the case. As can be seen in Table II, the elongation retention after 144-h exposure to UV radiation was 37.5% for C2, 63% for C3 and 75% for C4 although it limited to 52% only for C1 which suggests that MF-PcAr is superior over MF-PcAl as UV stabilizer. In the mean time, C2 can be evaluated as better than C1 since the elongation was initially improved by the incorporation of untreated laponite thus the retained E (37.5%) should not be judged worse than that of C1 (52%).

CONCLUSIONS

The limited stabilization modes of the conventional phthalocyanines may be overcome by the synthesis of novel phthalocyanine polymers based on aliphatic and aromatic amines. The metal-free phthalocyanine samples are moderately soluble in DMSO while the metalization with Cu or Ni vanished the solubility due to the involvement of the nitrogen centers in the coordination process, which proves their responsibility for the interaction with solvents. The absorption intensity in both UV and visible regions can be tuned by changing the amine type incorporated in the structure and by the metalization as well. The thermal stability of the samples can be enhanced by metalization while the aromatic amine based phthalocyanines can acquire higher glass transition temperatures especially after metalization with respect to their metal-free equivalents based on the aliphatic amine and even after metalization. Nanocomposites based on laponite can be obtained by the intercalation of metal-free phthalocyanine polymers in their nonquaternized forms into the basal space of laponite. The quaternization of the samples leads to random distribution of positive charges over the phthalocyanine chains leading also to intercalation in the basal space of laponite but with narrower expansion than that can be obtained using the nonquaternized MF-PcAr as an intercalant. The produced nanocomposites may be used as multi-function additives for polymeric materials especially PVC. The resistance of PVC to UV radiation can be enhanced by constructing composites based on treated laponite with different types of phthalocyanines.

References

- Zhu-Mei, L.; Chao-Ying, W.; Yong, Z.; Ping, W.; Jie, Y. J Appl Polym Sci 2004, 92, 567.
- 2. Dietrich, B. Vinyl Addit Tech 2001, 4, 168.
- Abd El-Ghaffar, M. A.; Botros, S. H.; Younan, A. F.; Yehia, A. A. J Pigment Resin Technol 1990, 19, 4.
- 4. Botros, S. H.; Abd El-Ghaffar, M. A. J Elastomers Plast 1997, 29, 219.
- 5. Slota, R.; Dyrda, G. Inorg Chem 2003, 42, 5743.
- 6. Vogel, H.; Marvel, C. S. J Polym Sci 1961, 50, 511.
- 7. Abd El-Hakim, A. A.; Badran, A. S.; Essawy, H. A. Polym Plast Tech Eng 2004, 43, 555.
- Abd El-Ghaffar, M. A.; Moore, J. A. Proceedings of 3rd Arab International Conference on Polymer Science and Technology, Mansoura, Egypt 4–7 September, 1995.
- Abd El-Ghaffar, M. A.; El-Halawany, N. R.; Yassin, A. A. Proceedings of 4th Arab International Conference on Polymer Science and Technology, Cairo, Egypt 8–11 September, 1997.
- 10. Abd El-Ghaffar, M. A.; Youssef, E. A. M.; El-Halawany, N. R.; Ahmed, M. A. Die Angew Makromol Chem 1998, 254, 1.
- 11. Bannehr, R.; Meyer, G.; Woehrle, D. Polym Bull 1980, 2, 841.
- 12. Grim, R. E. Clay Mineralogy; McGraw-Hill: New York, 1968.
- Herrera, N. N.; Letoffe, J. M.; Putaux, J. L.; David, L.; Lami, E. B. Langmuir 2004, 20, 1564.