



PERFORMANCE UNDER CORROSIVE ENVIRONMENT OF NYLON6/POLYPROPYLENE/ORGANOCLAY NANOCOMPOSITES

[Nabil Abacha], Masatoshi Kubouchi, Tetsuya Sakai, Ken Tsuda

abacha@chemeng.titech.ac.jp

Tokyo Institute of Technology

2-12-1-S1-17, O-okayama, Meguro-ku, Tokyo 152-8552, JAPAN

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Abstract

Properties of injection molded polyamide 6 and polyamide 6/ polypropylene (PA6/PP=70/30parts) blends containing 2wt% organoclay were prepared using Brabender like machine followed by injection molding. Maleic anhydride-grafted polypropylene (MAH-g-PP) was used as compatibilizer of the blend system. Moisture absorption, hygrothermal ageing and resistance to sulfuric acid were specifically investigated upon immersion into water and sulfuric acid at different concentrations and different temperature. Polyamide 6 alone exhibited high weight gain in water and poor resistance to sulfuric acid. A drastic decrease in water diffusion and better corrosion resistance were obtained in the case of the blend formulations. The incorporation of the organoclay in addition to the compatibilizer yielded a synergetic effect on the barrier properties for water and acid corrosion resistance.

1. Introduction

In recent years, the research on polymer nanocomposites has attracted great interest and is currently an expanding field of study due to the wide range of improved properties over their pristine polymers [1-2]. These nanocomposites exhibit superior properties such as enhanced strength, reduced gas permeability, and improved flame retardancy.

An original report from the Toyota research team [1] demonstrated such thermal and mechanical properties achieved from polyamide 6/ montmorillonite composite, while an other report from Vaia et al. [3] suggested that it is possible to melt mix polymers with silicates.

Other researches have focused on single polymer-clay nanocomposites including PP, Polyamide 6, PS, epoxy and so many others [4-6]. However,

thermoplastic nanocomposites based on blends of two or more polymers had been much less investigated according to literature [5].

PA 6 has good barrier properties against oxygen, but shows poor resistance to water, water vapor and acid that can be attributed to the presence of the amide group. On the opposite, PP exhibits excellent moisture barrier properties but poor oxygen barrier ones [7].

Hygrothermal aging is a degradation process that combines the effects of moisture and temperature resulting in substantial deterioration of the mechanical properties.

Many previous researches focused on the hygrothermal aging of polyamide 66, PP, epoxy and vinyl ester; however, there is still very limited literature on the hygrothermal aging of nanocomposite on one side and polymer blends on the other side, in addition few studies deals with corrosion of polymer blend.

In this paper, investigation of the resistance of polymeric materials blend containing organoclay to sulfuric acid as a corrosive environment is mainly focused.

The present study deals with the properties of a blend of PA6/ PP based nanocomposite. The blends containing organophilic-modified montmorillonite were prepared using Brabender-like machine. MAH-g-PP was used as a compatibilizer for the blend system. A minor portion of PP (30wt.%) was blended with the Nylon 6 matrix to improve water barrier properties and corrosion resistance to acid. Organoclay 2wt% was added; and the PA6/PP blend was studied both with and without the use of the MAH-g-PP as a compatibilizer.

2. Experimental procedures

2.1. Materials and formulations

A commercial Nylon 6 (UBE1013B) provided by UBE Industries, Ltd. was used as the matrix, isotactic polypropylene supplied from Mitsui Chemical, Inc., and MAH-g-PP (Polybond 3000) was kindly offered by BP Chemicals, Inc. The organoclay I.34TCN used was from Nanocor, Inc.; it is a Methyl dihydroxyethyl hydrogenated tallow ammonium treated montmorillonite. Table 1 summarizes the different formulations used in this study.

Table 1 Used formulation of the blends.

Code	Nylon 6 wt%	PP wt%	MAH- g-PP wt%	Organoclay I.34TCN wt. %
N	100	0	0	0
NP	70	30	0	0
NPM	100	25	5	0
NPC	70	30	0	2
NPMC	70	25	5	2

2.2. Preparation method

First, all components were overnight oven-dried prior mixing in a Brabender-like machine at 240°C and blade rotating speed was 140 rpm, the mixing time was fixed to 10 minutes. After mixing, the batch was grinded into pellets that were injection molded to produce samples having the following dimensions 5x2x2 mm. The injection molding temperature ranged from 210 to 240°C

2.3 Water absorption and sulfuric acid resistance

Samples were immersed in three different solutions: deionized water, 10 mass% and 5 mass% sulfuric acid solutions, in thermostated water bath set at 40, 60 and 80°C. Specimens were periodically removed from the water bath, fully wiped to remove excess penetrant; and the weight gain was recorded using a microbalance.

The percentage weight gain at any time t (Mt) as a result of solution absorption was determined by Eq.1

$$Mt(\%) = (Wt - Wo) / Wo \times 100 \dots\dots\dots \text{Eq.1}$$

Where Mt , Wt and Wo are the solution content at a given time, weight of the sample at the time of the measurement and the initial sample weight,

respectively. The percentage equilibrium or maximum absorption (Mm) was calculated as an average value of several consecutive measurements that showed no appreciable additional absorption. The diffusion coefficients were estimated using eq.2

$$Mt/Mm = 4/h (Dt/\pi)^{0.5} \dots\dots\dots \text{Eq.2}$$

where D is the diffusion coefficient and h is the thickness of the sample

2.4. Scanning Electron Microscopy (SEM) and Energy dispersive X-ray spectrometer (EDS)

The fractured surface of selected PA6/PP blends were inspected using a JEOL SEM JSM-5310LV, the micrographs of gold-coated samples were taken with 15 kV acceleration voltage at different magnification. A penetration depth of the sulfur (S) element was monitored using the coupled SEM/EDS analysis on the cross section of the immersed samples in sulfuric acid.

2.5. X-ray diffraction

X-ray diffraction (XRD) analysis was performed using a Philips Xpert MPD PW3050 X-ray diffractometer with a $\text{CuK}\alpha$ as a radiation source ($\lambda = 1.54$), operated at 40 kV and 30 mA. Samples were scanned at diffraction angles (2θ 's) from 2° to 10° at a scanning speed of 0.016°/s.

3. Results and discussion

3.1. Nanocomposite morphology

XRD has been used to analyze the dispersion of the organoclay within the matrix polymer, and it is considered among the most useful analysis for the measurement of the d -spacing of ordered immiscible and ordered intercalated materials, although it may be insufficient for the measurement of disordered and exfoliated materials that give no peak.

Fig.1 illustrates the XRD spectrum of the pristine organoclay, PA6/organoclay and the PA6/PP blend nanocomposites. The basal spacing of the pristine organoclay is about 17.65 Å presented as a single peak around $2\theta = 5^\circ$. This peak disappeared when mixed with either PA6 or PA6/PP blend to form the nanocomposite materials. This is an indication that the polymer was intercalated between the layers of clay during mixing, which eventually expands or exfoliates the clay layers; the d -spacing was shifted from the original value to higher than 40Å. However, to achieve a complete investigation of the

morphology transmission electron microscopy (TEM) should be performed to confirm the complete or the partial exfoliation of the organoclay.

3.2. Diffusion test

3.2.1 Moisture absorption

The results of the performed immersion tests of the cited formulations into water at different temperatures are discussed below.

Fig.2 (a-c) illustrates one of the examples of the weight gain as function of the square root of immersion time in water at a temperature of 80°C and that of Mt/Mm at 60°C by the different formulations. An initial linear relationship between Mt and $t^{1/2}$ was observed in each case, prior to saturation condition. This indicates that Fick's law could be applied. The equilibrium weight gain Mm and the diffusivity D values calculated using Eq.2 are summarized in Table 2.

Table 2 Diffusivity (D) and Moisture content (Mm) of the different formulation

Code	Immersion temperature					
	80°C		60°C		40°C	
	Mm %	D $m^2/sec \cdot 10^{-12}$	Mm %	D $m^2/sec \cdot 10^{-12}$	Mm %	D $m^2/sec \cdot 10^{-12}$
N*	9.28	21.00	9.15	7.47	9.65	2.21
NP	6.15	7.03	6.41	2.67	6.77	1.01
NPM	5.49	18.6	5.95	5.92	5.80	1.36
NPC	6.81	7.28	7.08	2.22	6.91	0.99
NPMC	5.63	12.9	5.64	4.19	6.12	1.59

*For moisture uptake of PA6 at 80°C a decrease is observed after saturation this was attributed to some salvation due to the high immersion temperature above PA6's glass temperature.

It is noticed from the above graphs and from the data in Table 2 that blending PA6 with PP enhances its barrier properties against water due to the fact that PP is a non-polar polymer that resists water diffusion. It is also observed that the maximum water uptake decreases drastically when PP is blended with PA6. A pair of two sets was formed which are PA6/PP and PA6/PP/organoclay compatibilized with MAH-g-PP on one side and those uncompatibilized on the other side.

When the compatibilizer was used, the maximum moisture uptake was lowered; this is due to the compatibilization effect between PA6 and PP, since these two polymers are immiscible over the wide range. The addition of the MAH-g-PP decreased the

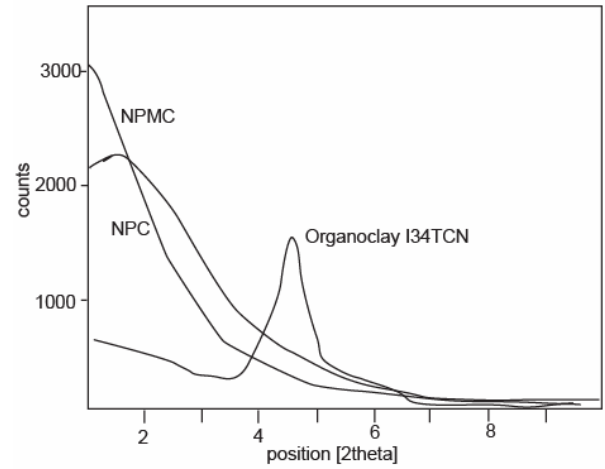


Fig.1 XRD of the organoclay and PA6/PP blend

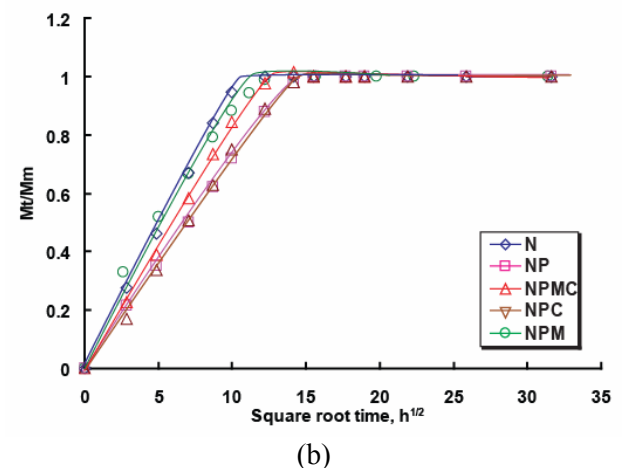
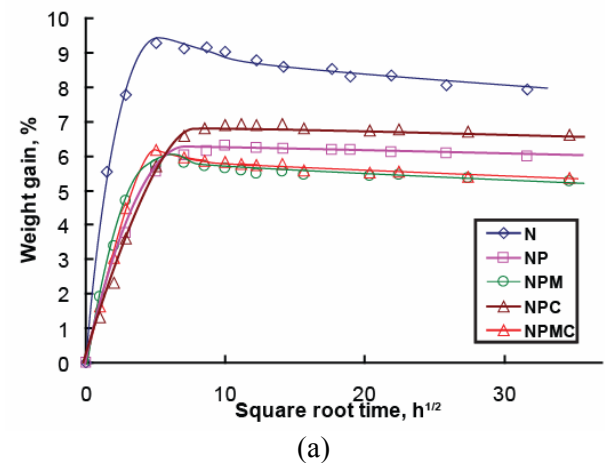


Fig.2: Weight gain in water at: -a 80°C, -b 60°C

average size of the PP particle and thus decreased the free volume and voids as illustrated in Fig.3, by increasing the affinity between PA6 and PP.

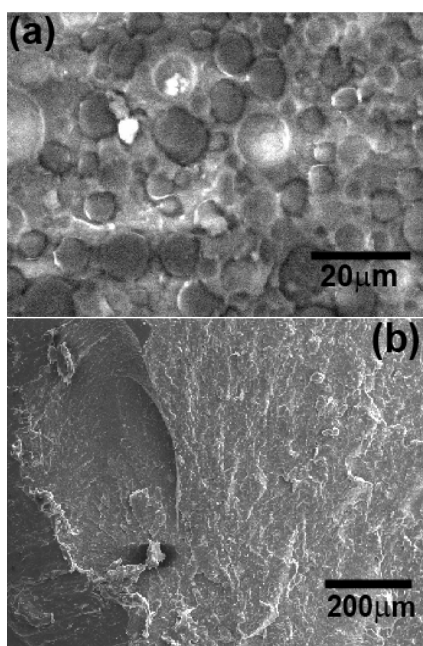


Fig.3: SEM micrograph of: -a- N6/PP and -b- N6/PP/MAH-g-PP /Organoclay

Addition of 2wt% organoclay within these blends seems to have little effect on the maximum water uptake when no compatibilizer is added. This may be attributed to the hydrophilic nature of the organoclay intercalants i.e. octadecylamine which once the organoclay is intercalated or exfoliated, some of these intercalants will be available for interaction with water molecules [4]. However, the diffusivity decreases when the organoclay is added to the compatibilized blend, illustrating the synergetic effect of the compatibilizer and the organoclay as a barrier property improvement for PA 6. Diffusivity is much more reduced for the case of non compatibilized blend than when MAH-g-PP is used, due to the fact that when mold injection is achieved, a phase separation between the two incompatible polymers may occurred forming the so called skin and core morphology [9], SEM analysis enabled to focus on the blend morphology, it is observed from SEM micrographs (Fig. 3a) that PP particles are randomly dispersed, with large particle size without any apparent adhesion with PA6. However, when the compatibilizer was added, the PP particle size became smaller, with better dispersion, (Fig.3b), this decreased the large domain size of PP thus allowing the penetrant to diffuse more rapidly into the matrix.

3.2.2 Sulfuric acid absorption

Samples of the different formulations listed in Table1 were immersed into 10 mass% and 5 mass%

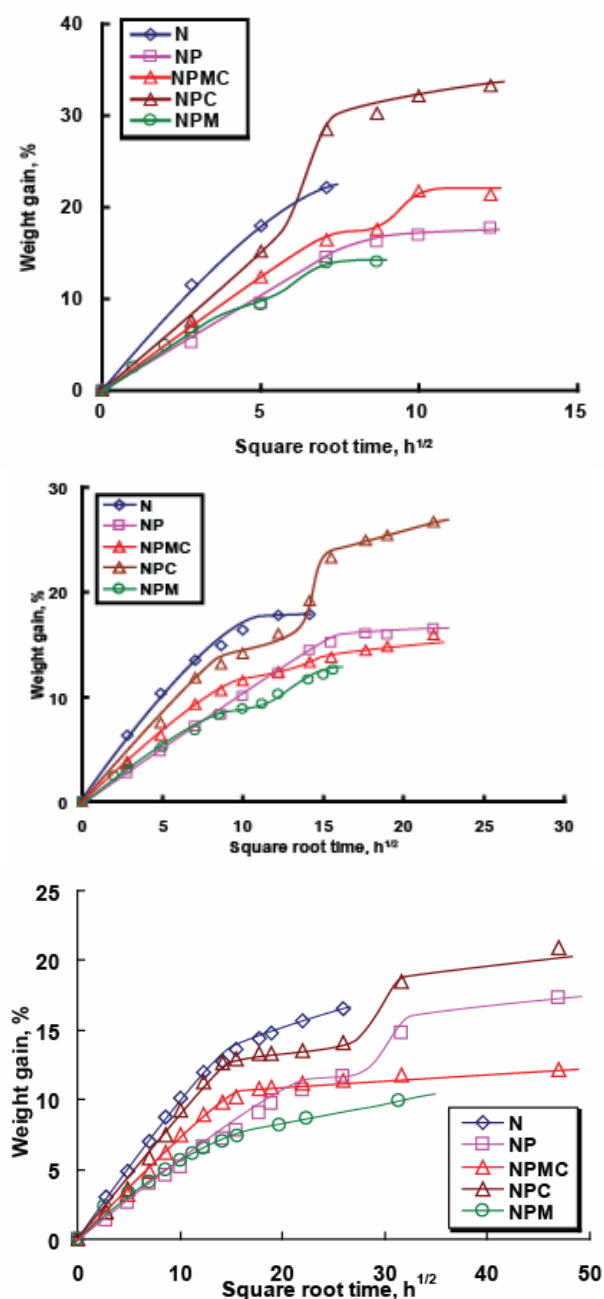


Fig.4 Weight gain in acid 10 mass% at: -a- 80°C, -b- 60°C, and -c- 40°C.

sulfuric acid solution at three different temperatures 40, 60 and 80°C.

Fig. 4 illustrates some examples of the weight gain in the acid solution at different temperatures. It was noticed that at 80°C a rapid degradation of PA6 occurred either at 10 or 5 mass% sulfuric acid with no saturation, this is due to the high environmental temperature, which is higher than PA6's glass transition one (around 50°C).

Table 3 maximum weight gain in sulfuric acid

Code	80°C						60°C					
	5 mass%			10 mass%			5 mass%			10 mass%		
	<i>Mm</i> %	<i>Meq</i> %	<i>D</i> m ² /sec 10 ⁻¹²	<i>Mm</i> %	<i>Meq</i> %	<i>D</i> m ² /sec 10 ⁻¹²	<i>Mm</i> %	<i>Meq</i> %	<i>D</i> m ² /sec 10 ⁻¹²	<i>Mm</i> %	<i>Meq</i> %	<i>D</i> m ² /sec 10 ⁻¹²
N	17.33	11.38	5.86	22.14	-	-	13.26	13.26	2.91	17.83	17.83	3.03
NP	15.04	10.56	4.50	17.35	17.35	2.31	18.22	9.66	1.45	16.16	16.16	0.74
NPMC	10.93	10.93	5.28	21.33	17.06	4.14	13.55	9.00	2.58	15.04	15.04	1.49
NPC	21.55	21.55	11.90	33.33	15.16	7.44	20.82	9.83	2.34	26.77	14.43	2.51
NPM	11.87	8.48	9.13	14.24	14.00	5.35	10.67	10.67	1.74	12.12	12.12	1.55

Table 3 maximum weight gain in sulfuric acid

Code	40°C					
	5 mass%			10 mass%		
	<i>Mm</i> %	<i>Meq</i> %	<i>D</i> m ² /sec 10 ⁻¹²	<i>Mm</i> %	<i>Meq</i> %	<i>D</i> m ² /sec 10 ⁻¹²
N	13.05	13.05	1.21	16.09	16.09	0.94
NP	9.88	9.88	0.50	17.30	10.73	0.45
NPMC	9.34	9.34	0.81	11.62	11.62	0.63
NPC	13.24	10.51	0.85	20.89	13.08	0.71
NPM	7.75	7.75	1.16	9.29	9.29	1.17

In the case of PA 6 resin, the chemical reactions of degradation and diffusion penetration are known to occur simultaneously [10,11]. However, blend samples (due to the presence of PP phase) withstand the corrosive environment longer and showed an increase in weight gain as function of time before saturation occurred.

Based on the study of the blend, and the knowledge that PP is good water and acid resistance compared to PA6 it can be concluded that the blend corrosion resistance is better than that of PA6.

The weight gain was to the penetration of sulfuric acid solution; presented in general two stages of saturation, the first one reached at around 200h for temperature 40°C and 100h at 60°C, and the second stage at longer time. The first saturation correspond to the case where sulfuric acid solution had fully penetrate the cross-section of the specimen as detected by SEM/EDS analysis shown in Fig.5 and 6 that illustrate micrographs of the cracks that occurred during immersion. It can be noticed that polyamide 6 is in advance high degree of degradation and presented many cracks just within 24h of immersion in 10 mass% acid at 80°C, while

the same level of degradation was observed for blend formulation NPC at 50 h.

At lower immersion temperature crack appeared first on PA6, then on PA6/PP/MAH-g-PP, and no cracks were observed for PA6/PP before saturation was reached as exemplified by the blend PA6/PP (NP) immersed in 5 mass% H₂SO₄ at 60°C for 100 h (Fig.5d), however, after saturation the appearance of cracks were noticed, and hence the weight increased more sharply.

This could be attributed to the swelling that occurred due to the voids and holes at the interphase between PA6 and PP. The penetrant can easily find a path between the two components interphase and had to first fill the voids or holes in polymer, and since PP is not so much affected by the acid, thus the swelling is more greater when the compatibilizer is not used, in contrast when the compatibilizer is used, the interphase decreases, lowering thus the weight gain of the penetrant.

These two stages were not observed at low acid concentration that is 5 mass% or at low temperature 40°C where no crack occurred for the case of compatibilized blend as a consequence of the decrease of the PP particle size and thus the free volume; the same behavior was observed for the case of the compatibilized PA6/PP/organoclay.

For this reason - presence of the two-saturation stages-, the measurement of the diffusivity was done just by only considering the first one.

Table 3 summarizes the maximum weight gain *Mm*, the equilibrium weight gain of the first stage *Meq*. The diffusivity was calculated according to Eq.3 substituting the value of *Meq*. Note that for some samples the *Meq* is the same as *Mm*, this means only one saturation was observed. It must be noted that for the case of PA6, the weight gain reached the

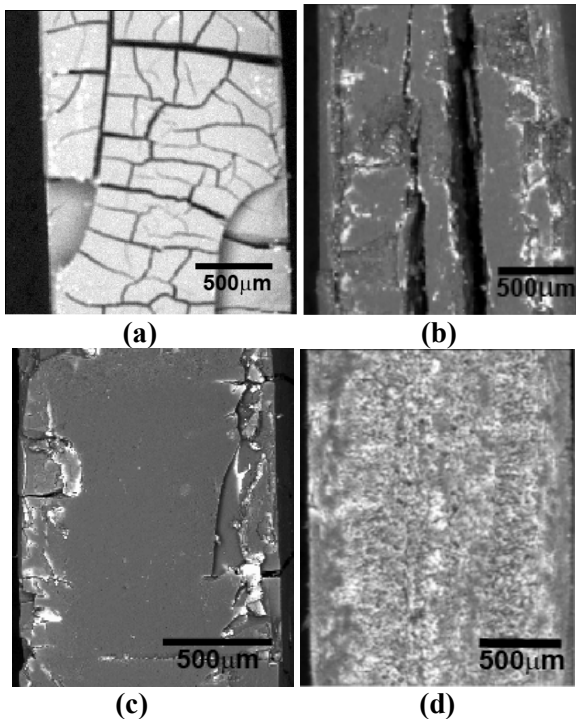


Fig. 5 SEM micrograph of immersed samples: -a- N 24h in 10mass% H₂SO₄ at 80°C -b- NPC 50h in 05 mass% H₂SO₄ at 80°C -c-N:75h in 10 mass% H₂SO₄ at 60° C and -d- NP 100h in 10 H₂SO₄ at 60°C

maximum earlier compared to the blend formulations and it presents the highest diffusivity as compared to its blends. Also, it is clearly observed that the diffusivity is function of the immersion temperature and the concentration of the acid. The lower the temperature and the concentration of the sulfuric acid the lower is the diffusivity. It globally decreases when organoclay is added with the compatibilizer.

As for the case of immersion in water, similar behavior of the addition of the organoclay in the blend without compatibilizer was observed that is higher maximum weight gain was obtained when organoclay was added; a synergetic effect was also obtained when used with the compatibilizer.

EDS analysis enabled to measure the penetration depth of the sulfuric acid by detection of the element S. Typical curves of the EDS micrographs are illustrated in Fig.6 where the dark-red line expresses the profile of the element S along to depth from surface, the penetration depth was calculated to be the distance from surface to level off the profile. Fig. 7(a,b) illustrates the penetration depth of element S for two cases immersion in sulfuric acid 10 mass% and 5 mass% at 60°C. It is found that second polymeric material fraction i.e. PP when blended

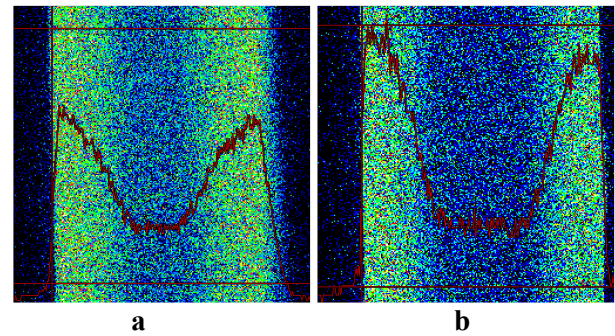


Fig. 6 EDS micrograph of immersed samples: -a- NPC 100h in 10 mass% H₂SO₄ at 40°C -b- N 75h in 05 mass% H₂SO₄ at 40°C

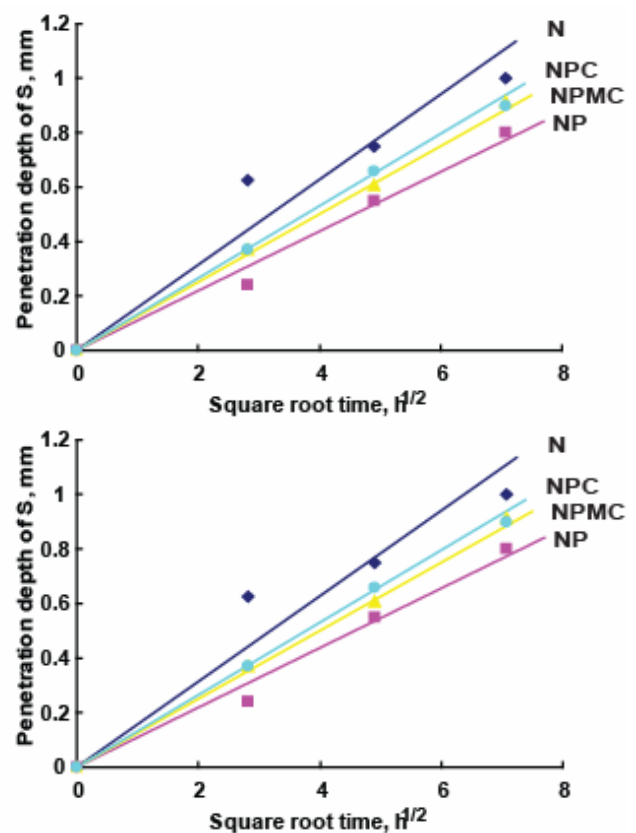


Fig.7 penetration depth of Sulfur element S as function of square root time at 60°C for: -a- 10 mass% and -b- 5 mass%.

with nylon decreases the ability of the sulfuric acid to penetrate. On the other hand, the addition of the organoclay decreased the penetration depth when used with the compatibilizer as compared to the case where MAH-g-PP is not used.

4. Conclusion

The environmental solution diffusion was investigated and analyzed in terms of weight change and diffusion parameters. It was found that both

addition of organoclay and blending with PP improve the barrier properties of Nylon 6 and also enhance its diffusion parameters. These performances depend on the dispersion of the organoclay within Nylon 6 and also on the improvement of the compatibility of the blend system by using MAH grafted PP as a compatibilizer. A drastic decrease in water diffusion is obtained when blending with PP, higher decrease is obtained for non-compatibilized one compared to the compatibilized blend.

Addition of organoclay enhanced the barrier properties mainly in the presence of MAH-g-PP

5. Reference

- [1] A.Usiki, Y.Kojima, A.Okada, *et al.*, J.Mater. Res., 8, 1179 (1993).
- [2] M.S.Wang, T.J.Pinnavaia, Chem. Mater., 6, 468, (1994).
- [3] R.A. Vaia, H. Ishii, E.P. Giannelis, chemistry materials, 5,1694, 1993
- [4] M.L.Lopez-Quintanilla, S.Sanchez-Valdes, et al., J.Appl. Poly. Sci., 100, 4748 (2006).
- [5] O.Becker, R.J. Varley, G.P.Simon, Euro. Poly. J. 40, 187 (2004).
- [6] Z.A. Mohd Ishak, B.N.Yow, B.L. Ng, H.P.S.A. Khalil, H.D.Rozman, J. Appl. Polym. Sci. 81, 742, 2001
- [7] W.S.Chow, A. Abu Baker, Z.A.M. Ishak, J. Appl. Poly. Sci., 98, 780 (2005).
- [8] N.Abacha, S.Fellahi, Polym. Int., 54, 909 (2005).
- [9] S. Fallahi, B.D. Favis, B.Fisa, Polymer, 37,13,2615-2626 (1996).
- [10] M. Kubouchi, Corrosion Eng. 51, 741-752 (2002).
- [11] Abastari, T.Sakai, H Sembokuya, M. Kubouchi, K. Tsuda, Polym. Degradation and stability, 92, 3, (2006).