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Thermal Stability of Hybrid Nano Composites PA6/MMT/MH with Dual Response Method

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This work has investigated the thermal properties of PA6/MMT/MH Nano composite. For this, a series of Nano powders (montmorillonite, magnesium hydrate) were used in Nano composites systems by using polyamide 6 that were prepared using twin screw extrusion techniques at different levels of Nano powders and different processing parameters (Barrel temperature profile and screw rate). The results showed that the thermal stability improves in both delay in combustion process and increased remain material by increasing Nano powders up to 4 %, using thermal gravimetric analysis method concern changes in the thermal decomposition behaviour. Using dual response system optimal factor setting with minimum repetition and FTIR, DSC and XRD were used to further understand the mechanism.

Key Words: Thermal stability, Nano montmorillonite, Nano magnesium hydrate, Dual response system, Polyamide 6.

INTRODUCTION

Polyamide 6 (PA6) is one of the most widely used plastics in modern industrial field. To overcome the disadvantages of PA6, such as low toughness and thermal stability, researchers have tried to improve it's properties. Along with the well known effect of silicate Nano composite systems with polymer matrix since 1990s report of Toyota Research Central laboratory, generated significant interest in industry and academic researchers and up to now it is observed in new age of study[1,2].

On the other hand old fire retardants materials like halogen based compounds have many negative characteristics, such as corrosiveness and toxicity thus halogen free additives like magnesium hydrate (MH) extensively used. Nevertheless they

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have some disadvantages (high loading which deteriorate the mechanical properties and low flame retardant efficiency), to solve the problems two methods used: (i) surface treatment (ii) decrease particle size.

In recent years, Nano metal hydroxides (NMH) have aroused great attention[3-8].

This work contributes the understanding of Nano particles of montmorillonite (MMT) and magnesium hydrate (MH) on thermal stability characterization of the Nano composites. It is determined by X-Ray (XRD), thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC) and fourier transform infrared (FTIR).

EXPERIMENTAL

The polyamide 6 used in this study was SB from Aliaf Co.(Tehran, Iran) which is unreinforced Nylon 6 prior to use, the Nano clay used was organically modified montmorillonite (MMT) from South Clay Products Inc. (Gonzales, TX,USA) for modification used methyl to allow *bis*-2-chloride hydroxy ethyl, quaternary ammonium (Closite 30 B), the Nano magnesium hydroxide used was "3320 HT" from Nano structured and amorphous materials Inc. (Houston, USA).

A lab scale co-rotating twin screw extruder (ZSK 25,L/D:40) manufactured by Coperion Co. was used for the compounding operations. All the materials were dried before processing. PA6, MMT and MH were dried at 110 °C for 24, 12 h, respectively.

Experimental design: DRS method used for three response surface as shown in Table-1.

Spend time (ST): Spend time for weight changing on the other word slant in TGA curve, It's ideal when increased.

Weight change (WC): This item adherence of follow function:

Weight change = initially weight - remain weight

The goal is to achieve minimum of this item.

WC/ST: rate of weight change on time change. It's obvious the variable is ideal when it's minimum.

Response surface methodology was used to design experiments and analyze the effects of considered parameters. Nano powder (MMT, MH) amount were considered parameters in three surface ST,WC,WC/ST once a model was selected, an analysis of variance was calculated to assess how closely the model represents the data.

The analysis of variance was carried out to compare the relative significance of each parameter and develop a polynomial model for each objective response.

General procedure: Table-1 is shown formulation design according to the dual response surface method and mixing of all component parts done in one stage as shown in it, rotation speed of the screws and die temperature have changed. water bath and granulator were carried out granules, Thermal press obtained granules to get specimens for tests[9-11].

TABLE-1
FORMULATION DESIGN OF PREPARING SAMPLES

Run No.	MMT (%)	MH (%)	Temp. (ºC)	Speed (rpm)	Spent time (min)	Weight change (%)	WC/ST
1	3.00	3.00	260	125	29.2610	90.409	3.089744028
2	3.00	3.00	260	125	28.8810	91.160	3.156400402
3	4.00	4.00	265	110	30.0000	88.438	2.947933333
4	4.00	2.00	255	140	29.6410	90.613	3.057015620
5	3.00	3.00	260	125	29.0520	92.122	3.170934875
6	3.00	1.30	260	125	30.6070	91.834	3.000424739
7	4.00	4.00	255	110	31.3460	86.946	2.773751037
8	3.00	3.00	260	150	29.0790	90.578	3.114893910
9	3.00	3.00	260	125	29.1930	91.202	3.124105094
10	3.00	3.00	260	100	29.1270	90.857	3.119339445
11	4.70	3.00	260	125	30.1630	90.319	2.994363956
12	3.00	3.00	252	125	28.9610	90.776	3.134422154
13	2.00	2.00	265	110	29.1480	91.771	3.148449293
14	2.00	2.00	255	110	29.2550	91.678	3.133754914
15	3.00	4.70	260	125	29.0270	90.108	3.104282220
16	2.00	4.00	265	140	29.9660	91.782	3.062871254
17	1.30	3.00	260	125	28.5860	94.734	3.313999860
18	3.00	3.00	270	125	28.6710	91.341	3.185832374
19	4.00	2.00	265	140	30.0230	91.38	3.043666522
20	3.00	3.00	260	125	29.1182	91.198	3.131993049
21	2.00	4.00	255	140	29.9690	92.572	3.088925223

Detection method

X-ray diffraction (XRD): X-ray diffraction were used to characterize the formation of Nano composites. XRD patterns were obtained using a Rigaku G-Cu-Ni. The X-ray beam was operated at 40 mA, 40 kV, data collection between 1-40° (2θ). As shown in Fig. 1 peak of MMT 4.80° (2θ) and peak of MH occurred in 28° (2θ).

Differential scanning calorimetry (DSC): The analysis of the crystallinity was carried out by means of DSC instrument model Maia 200 F3 (Netzsch-Germany), under N_2 gas, flow rate 50 mL/min, pressure 5 bar, range 20-250 °C (rate 10 °C/min). Follow up to Fig. 2 Tg and endothermic effect are increased. It is near 26.07 % form min to max. It is show maintenance in crystallinity.

Thermogravimetric analysis (TGA): The thermal stability of layered Nano composites was investigated by using TGA instrument, model: TGA-PL (Polymer laboratories -England), with heating rate of 10 °C/Min from room temperature to 680 °C.

Fourier transmitter infrared (FT-IR): Infrared spectra were recorded in the spectral zone 0-4000 cm^{-1} using NEXUS 870 FT-IR-(THERMO NICOLET- USA), mirror velocity: 0.6329.

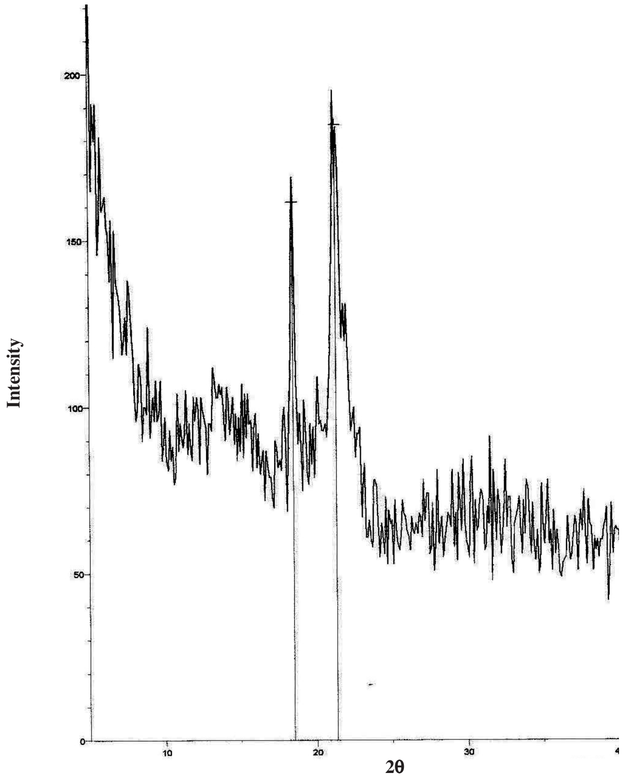

Fig. 1. X-Ray of run 7

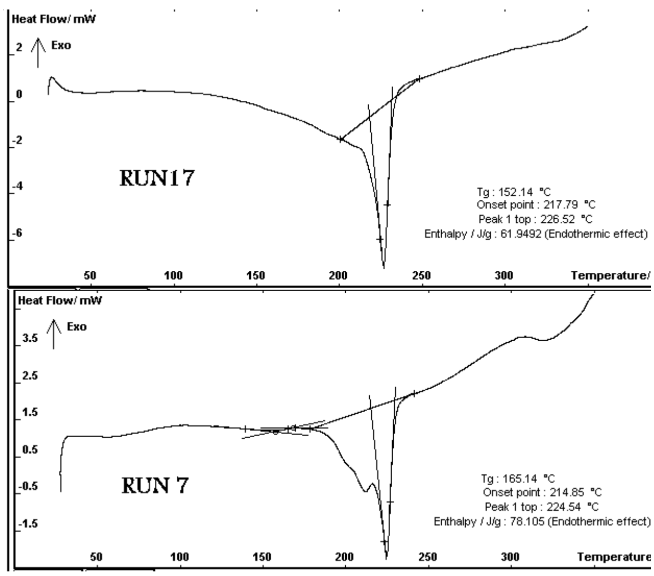

Fig. 2. DSC of run 7 and 17 (max and min)

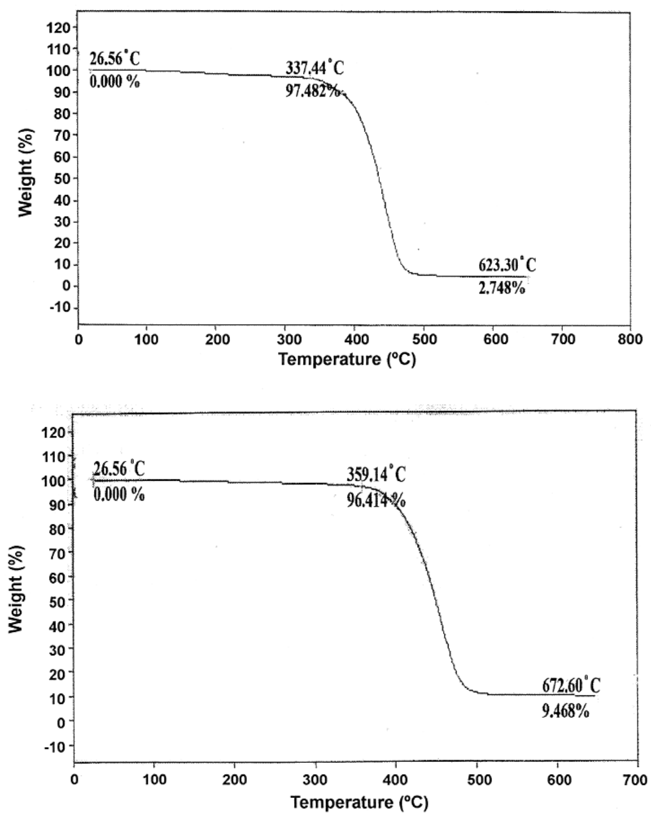

Fig. 3. TGA graph of run 7 and 17 (max and min)

The FTIR spectrum of the decomposition products reveals in fact the absorbance of MgO (Fig. 4) shows a broad band at 3635 cm^{-1} for isolated OH groups, peak at 1460 cm^{-1} whereas adsorbed water is observed on the surface of the hydroxide. The FTIR indicate MMT peak occurs at 3697 cm^{-1}, it means that carbonates are also found on the surface.

RESULTS AND DISCUSSION

Table-1 is employed the DRS experimental design and Tables 2-4 show ANOVA summery of each surfaces.

Follow up to Table-2, chosen quadratic Model (P-value 0.0422) has suggested, this model implies 4.18 as F-value. there is only 4.41 % chance that a "Model F-value" could occur due to noise (Std. Dev. 0.38) and model analysis has shown amount of MMT and MH P-value have significant effect (MMT = 0.0441, MH = 0.0269).

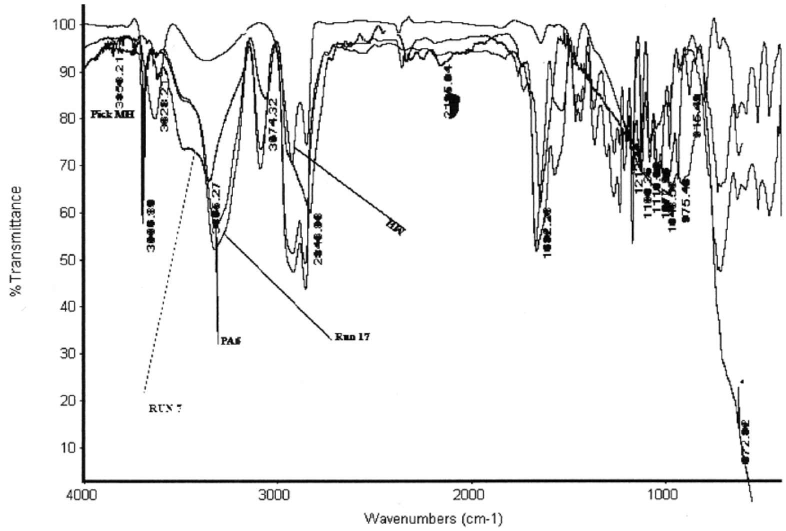

Fig. 4. Infrared bands

TABLE-2
SPEND TIME SURFACE ANOA SUMMERY

Source	Sum of squares	df	Mean square	F-value	P-value	Suggested model
Mean *vs.* Total	18250.140	1	18250.14	–	–	Ok
Linear *vs.* Mear	2.280	4	0.57	1.27	0.3224	–
2FI *vs.* Linear	3.420	6	0.57	1.51	0.2681	–
Quadratic	2.880	4	0.72	4.91	0.0422	Ok
Cubic *vs.* Quad	0.800	2	0.40	18.67	0.0094	Aliased
Residual	0.085	4	0.021	–	–	–
Total	18259.600	21	869.50	–	–	–

TABLE-3
WEIGHT CHANGE SURFACE ANOVA SUMMERY

Source	Sum of squares	df	Mean square	F value	P-value	Suggested model
Mean *vs.* Total	1.74E+05	1	1.74E+05	–	–	–
Linear *vs.* Mean	32.85	4	8.21	10.5	0.0002	Ok
2FI *vs.* Linear	5.01	6	0.84	1.11	0.419	–
Quadratic	4.79	4	1.21	2.64	0.1383	–
Cubic *vs.* Quad	1.24	2	0.62	1.68	0.2948	Aliased
Residual	1.48	4	0.37	–	–	–
Total	1.74E+05	21	8290.25	–	–	–

Fig. 4 showed the normal probability graph and spend time quadratic model plot. According to the above result of spend time, they are near normal probability line as shown in left graph, R-squared 0.9070 it's near ideal regression (one).

TABLE-4
WC/ST SURFACE ANOVA SUMMERY

Source	Sum of squares	df	Mean square	F-value	P-value	Suggested model
Mean *vs.* Total	200.68	1	200.68	–	–	–
Linear *vs.* Mear	0.11	4	0.027	3.97	0.0201	Ok
2FI *vs.* Linear	0.049	6	8.129E-003	1.36	0.3184	–
Quadratic	0.04	4	0.01	3.09	0.1056	Ok
Cubic *vs.* Quad	0.016	2	7.830E-004	8.00	0.04	Aliased
Residual	3.914E-003	4	9.785E-004	–	–	–
Total	200.9	21	9.57	–	–	–

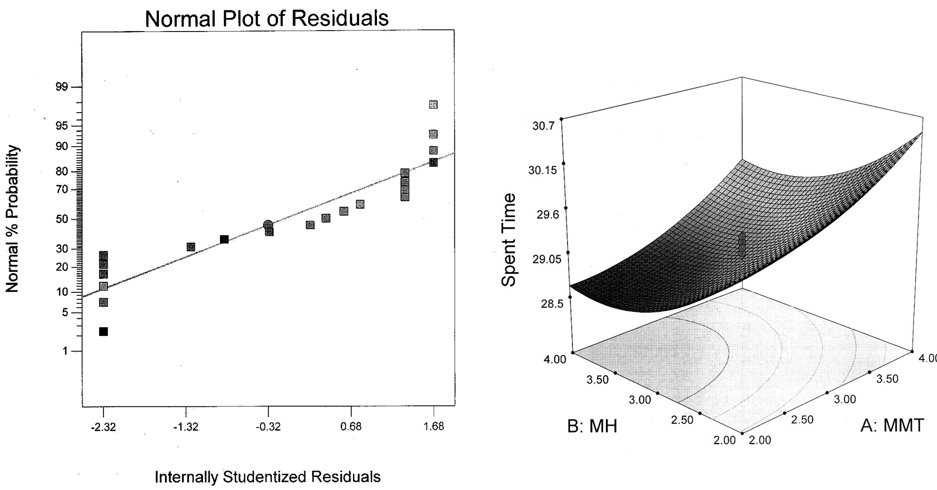

Fig. 5. Surface plot of spent time as function of MMT and MH amount and normal probability (left plot)

Results of Table-3 were analyzed, follow up to a/m table, the best effective function was linear *vs.* mean with 0.0002 as P-value.

Significance probabilities (P-value) were calculated and parameters with P-value higher than 0.1 were eliminated. A parameter has a significant effect on the objective response whenever the corresponding P-value be lower than 0.1, the model F-value of 10.50 is significant. there is only 0.02 % chance that a "model F-value" this large could occur due to noise, the lack of fit F-value of 2.49 implies that it's not significant relative to pure error 19.56 % chance that a "lack of fit F-value" could occur due to noise (it's good and show that the model is fit).

According to the surface plot of WC as a function of Nano MH and MMT amounts, temperature and screw rate have insignificant effects.

There is only a 19.56 % probability that this large model F-value could be due to noise. selected model have insignificant lack of fit.

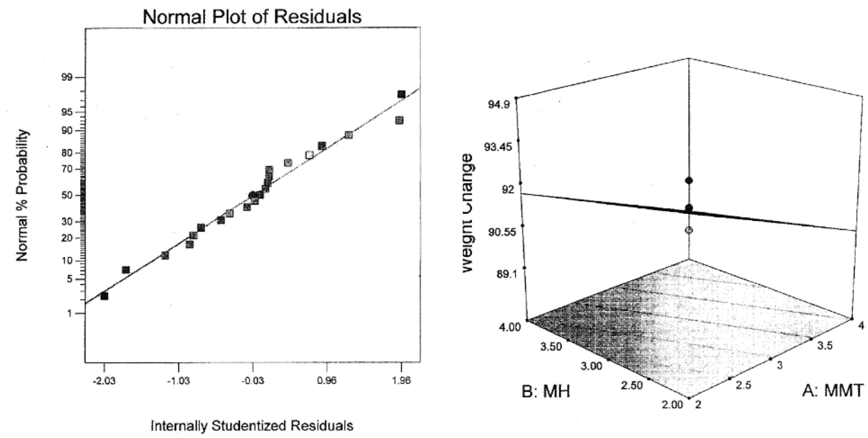

Fig. 6. Surface plot of weight change as function of MMT and MH amount and normal probability plot

The chosen quadratic model (P-value 0.1056) (Table-4) has suggested, this model implies 3.09 as F-value. There is only 3.09 % chance that a "model F-value" could occur due to noise (Std. Dev. 0.057) and model analysis has shown amount of MMT P-value have significant effect (MMT = 0.0074).

As matter of fact, normal probability plot show normality of residuals for WC/ST quadratic model data (R-squared 0.9095).

As shown in Fig. 7, there are significant differences in shapes of plot when MMT and MH amount varies.

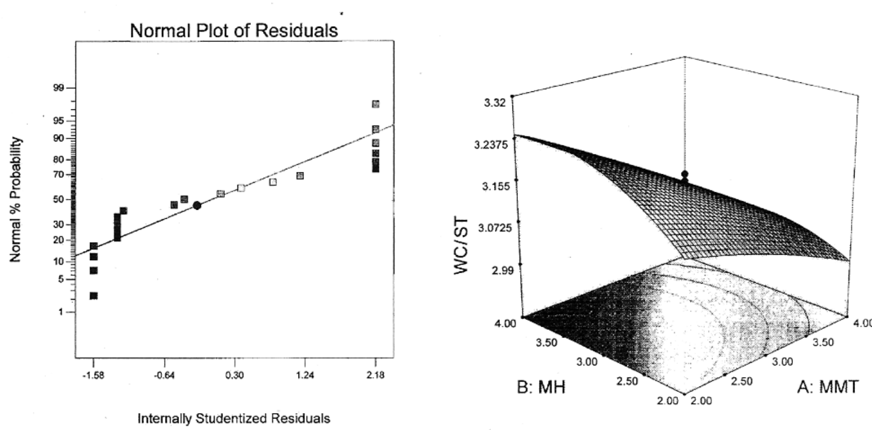

Fig. 7. Surface plot of WC/ST as function of MMT and MH amount and normal probability plot

In Table-5 shows low and up value of each surface in third row compare these runs data with pure polyamide 6 and from calculated models, the best solution is shown in last column.

TABLE-5
COMPARE RUN 7 WITH PA6

Surface	Min-Run	Max-Run	Solution	Maintenance (%)
Spent Time	28.586-Run 17	31.346-Run 7	29.5611	24.38888889
Weight change	86.946-Run 7	94.734-Run 17	92.3408	10.25234053
WC/ST	2.774-Run 7	3.314-Run 17	3.08648	37.12934391

According to present data analysis, we recognized Run 7 (MMT = 4 %, MH = 4 %, Temp = 255, Sp = 110) is the best one, but our DRS model solution is composite include these items (MMT = 2.61 %, MH = 2.85 %, Temp = 265, Sp = 140).

Conclusion

Dual response surface (DRS) methodology was used to investigate thermal stability by amount of Nano particles (MMT, MH) and processing parameters (Barrel temperature profile and screw rate). In this work, three surface (ST, WC, WC/ST) were introduced and finally, analysis of variance was used to find relative significance of parameters and the best model. Montmorillonite was found to be the most effective parameter on thermal stability. On the other hand, thermal stability increased by amount of magnesium hydrate as expected. Influences of melt mixing parameters (tempreture and product speed) were less noticeable.

Amount of Nano particles cause increasing in crystallinity, It show great effect on thermal stability as shown in study. It cause 37 % increase with compare Run 7 (MMT = 4 %, MH = 4 %, Temp = 255, Sp = 110) by pure polyamide 6.

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