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Response Surface Based Optimization of Thermal Stability of Nano Composite PA6/MMT/MH

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The thermal stability properties of polyamide nano composites (nylon 6/montmorillonite/magnesium hydroxide) were investigated using differential scanning calorimetry, thermogravimetric analysis. In order to study the morphological structure of the materials by TEM, XRD and FTIR analysis were also carried out. The nano composites were prepared using the melt mixing technique in twin screw extruder. Particular attention was given to studying the influence of different processing condition (barrel temperature profile and screw rate) and compositions of PA6, nano clay and nano magnesium hydrate blends. The results show that all the properties analysis were strongly influenced by the nano composite composition, instead of processing conditions. Using response surface system optimal mathematical models to determine and quantify the relation between values and to find out the setting of experimental factors that produce the best value or the best set of values of the response.

Key Words: Thermal stability, Nylon 6, Nano montmorillonit, Nano magnesium hydrate, Response system method.

INTRODUCTION

PA6 (Nylon 6) as an engineer thermoplastic is playing a more and more important role in modern industrial fields. However, this material with low limiting oxygen index (easily burn), so, maintenance flame retardancy of nylon 6 material become an important research topic.

Organically modified layered silicate nano composite materials have attracted both scientific & industrial interest after the introduction of melt interaction method to produce nanocomposite because they exhibit improved physical properties such as modulus, tensile, strength, heat distortion temperature and barriers properties at very low filler loading[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 hydroxide (MH) extensively used, nevertheless they have some disadvantages (high loading, which deteriorate the mechanical properties and low flame retardant efficiency), to solve the problems two methods used *i.e.*, surface treatment and decrease particle size[3].

In recent years, nano metal hydroxides (NMH) have aroused great attention[4-9]. This paper seeks to contribute the understanding of nano particles of montmorillonite and magnesium hydroxide on thermal stability characterization of the nano composites. It is determined using X-ray (XRD), thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier Transform Infrared (FTIR).

EXPERIMENTAL

The polyamide 6 used in this study was obtained 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 modifying used methyle tallow *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. Nylon 6, montmorillonite and magnesium hydroxide were dried at 110 ºC for 24, 12 h, respectively.

Dual response surface (DRS) method used for three response surface as shown in Table-1: ST: Spend time for weight changing on the other word slant in TGA curve, It's ideal when increased. WC *i.e.*, weight change: 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 is minimum.

Response surface methodology was used to design experiments and analyze the effects of considered parameters. Nano powder (montmorillonite, magnesium hydroxide) 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.

TABLE-1
FORMULATION DESIGN OF PREPARING SAMPLES AND RESPONSES RESULTS

WC/ST	Weight change (%)	Spent time (min)	Speed (rpm)	Temp. (ºC)	Magnesium hydroxide (%)	Montmorillonite (%)	Run No.
3.089744028	90.409	29.261	125	260	3.00	3.00	1
3.156400402	91.160	28.881	125	260	3.00	3.00	2
2.947933333	88.438	30.000	110	265	4.00	4.00	3
3.057015620	90.613	29.641	140	255	2.00	4.00	4
3.170934875	92.122	29.052	125	260	3.00	3.00	5
3.000424739	91.834	30.607	125	260	1.30	3.00	6
2.773751037	86.946	31.346	110	255	4.00	4.00	7
3.114893910	90.578	29.079	150	260	3.00	3.00	8
3.124105094	91.202	29.193	125	260	3.00	3.00	9
3.119339445	90.857	29.127	100	260	3.00	3.00	10
2.994363956	90.319	30.163	125	260	3.00	4.70	11
3.134422154	90.776	28.961	125	252	3.00	3.00	12
3.148449293	91.771	29.148	110	265	2.00	2.00	13
3.133754914	91.678	29.255	110	255	2.00	2.00	14
3.104282220	90.108	29.027	125	260	4.70	3.00	15
3.062871254	91.782	29.966	140	265	4.00	2.00	16
3.313999860	94.734	28.586	125	260	3.00	1.30	17
3.185832374	91.341	28.671	125	270	3.00	3.00	18
3.043666522	91.380	30.023	140	265	2.00	4.00	19
3.131993049	91.198	29.1182	125	260	3.00	3.00	20
3.088925223	92.572	29.969	140	255	4.00	2.00	21

TABLE-2
DESIGN SUMMARY BASED ON QUADRATIC MODEL WITH 21 RUNS

Factor	Name	Type	Low actual	High actual	Low coded	High coded
A	Montmorillonite (%)	Numeric	2.00	4.00	-1.000	1.000
B	Magnesium hydroxide (%)	Numeric	2.00	4.00	-1.000	1.000
C	Temperature (ºC)	Numeric	255.00	265.00	-1.000	1.000
D	Speed (rpm)	Numeric	110.00	140.00	-1.000	1.000
Response	Name	Obs	Analysis	Minimum	Maximum	Mean
Y1	Spent time	21	Polynomial	28.586	31.346	29.480
Y2	Weight change	21	Polynomial	86.946	94.734	91.039
Y3	ST/WC	21	Polynomial	2.774	3.314	3.091

TABLE-3
ANOA SUMMERY OF EACH SURFACE

Response	Design model	Sum of squares	Df	Mean square	F value	*P*-value	Suggested model
Spent time	Quadratic	2.88	4	0.72	4.91	0.0422	Ok
Weight change	Linear *vs* mean	32.85	4	8.21	10.5	0.0002	Ok
WC/ST	Quadratic	0.04	4	0.01	3.09	0.1056	Ok

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 showed the formulation design according to the 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[10].

Tables 1 and 2 is employed the RMS experimental design and Table-3 show ANOVA summery of each surfaces.

RESULTS AND DISCUSSION

Follow up to Table-2, chosen quadratic Model for spent time surface (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 (standard deviation 0.38) and model analysis has shown amount of montmorillonite and magnesium hydroxide P-value have significant effect (montmorillonite = 0.0441, magnesium hydroxide = 0.0269).

The best effective function for weight change 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).

As shown in Table-2, for WC/ST surface quadratic model (P-value 0.1056) has suggested, this model implies 3.09 as F-value. There is only 3.09 % chance that a model F-value could

TABLE-4
FINAL EQUATIONS OF DIFFERENT RESPONSE

Response	Equation
ST	= 28.99+0.47+0.47B-.011C-0.012D-0.11AC-0.87AD-0.2BC+0.13BD+0.23CD+0.22AA+0.38BB+0.027CC+0.13DD
WC	= 91.04+1.31A+0.63B+0.18C+0.52D
WC/ST	= 3.15+0.095A+0.031B+0.019C-0.029AB+0.025AC+0.091AD+0.022BC-0.22BD-0.032CD-0.011AA-0.047BB-0.024DD

occur due to noise (standard deviation 0.057) and model analysis has shown amount of montmorillonite P-value have significant effect (montmorillonite=0.0074).

Table-3 shows the final equation of each surfaces, for checking the model navigating ability measured signals to noise ratio. (ratio $\leq$ 4 desirable), 7.171, 9.914 were spent time and WC/ST ratios respectively.

Follow up to these equation, 30 solutions setting present,in Fig. 1 you can find standard error of design according to solutions with different amount of montmorillonite and magnesium hydroxide.

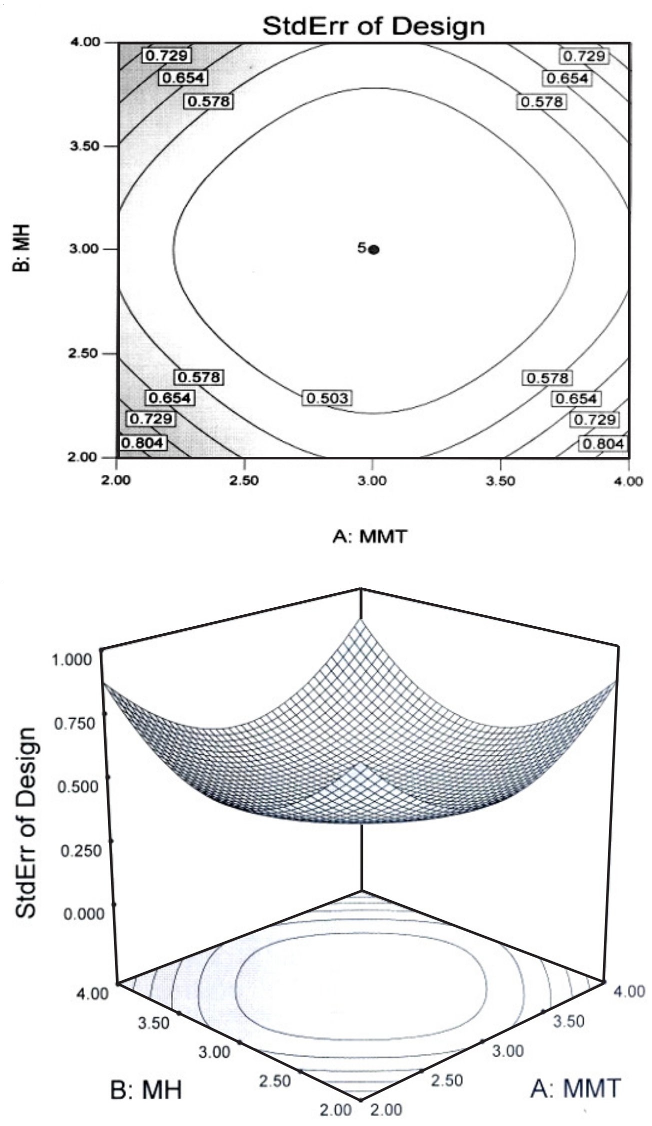


Fig. 1. Show Standard error follow up changing montmorillonite, magnesium hydroxide amounts

In Fig. 2 check desirability with different amount of montmorillonite, magnesium hydroxide.

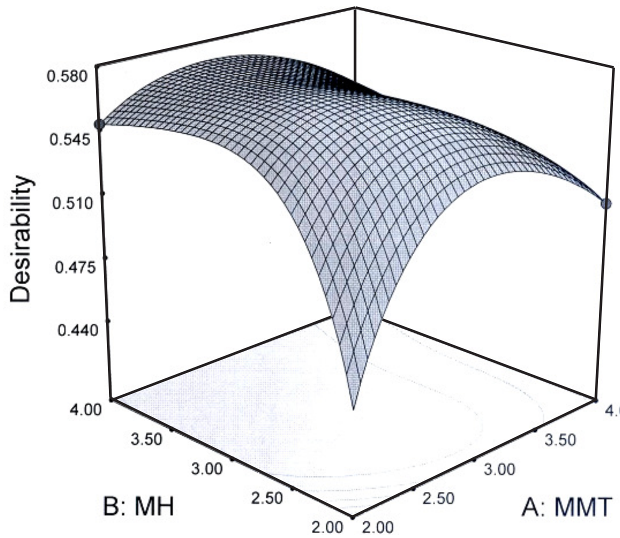


Fig. 2. Show desirability of solutions.

Table-5 shows low and higher values of each surface in third row compare these runs data with pure poly amide 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 our date analyzing,we recognized Run 7 (montmorillonite = 4 %, magnesium hydroxide = 4 %, Temp = 255, Sp = 110) is the best one, but our DRS model solution is composite include these items (montmorillonite = 2.61%, magnesium hydroxide = 2.85 %, Temp = 265, Sp = 140)

Infrared spectra were recorded in the spectral zone 0- 4000 cm^{-1} using NEXUS-870 FT-IR-(Thermo Nicolet, USA), mirror velocity: 0.6329. The FTIR spectrum of the decomposition products reveals in fact the absorbance of MgO (Fig. 3) shows a board at 3635 cm^{-1} for isolated OH groups, $Mg(OH)_2$ pick shown on 1460 cm^{-1} where as adsorbed water is observed on the surface of the hydroxide.

The FTIR graphs indicate montmorillonite pick occur between 3696-3697 cm^{-1} carbonates are also found on the surface.

X-ray diffraction (XRD): X-ray 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 1-40º (2θ). As shown in

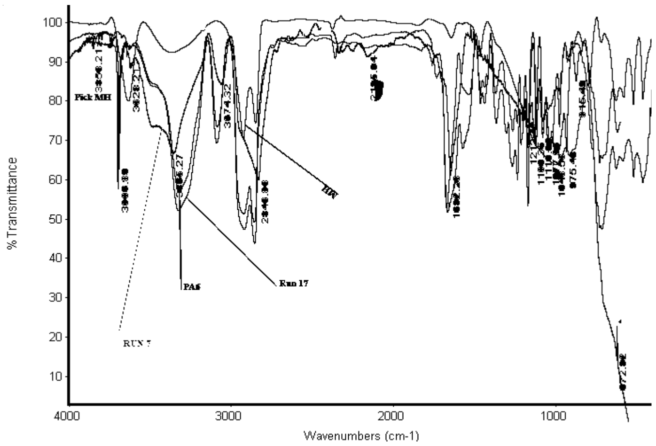


Fig. 3. Picks of different bonds

Fig. 1 peak of montmorillonite 4.80° (2θ) and Peak of magnesium hydroxide occurred in 28° (2θ).

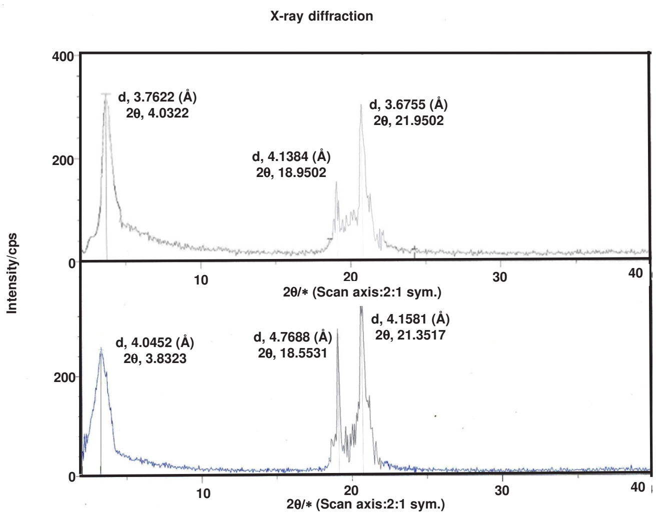
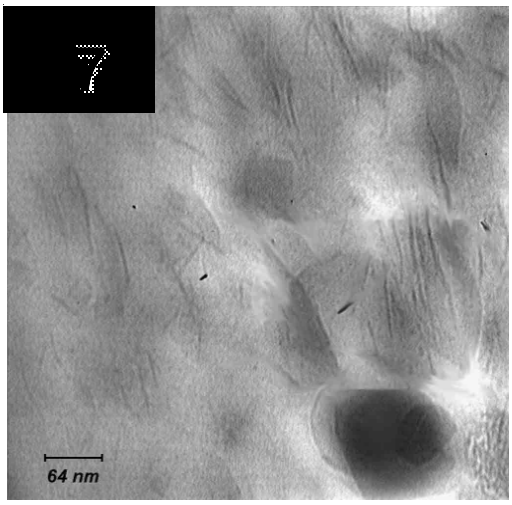


Fig. 4. X-Ray Comparison between Run 7,17.

Transmission electron microscopy (TEM): Transmission electron microscopy was performed without using cryogenic cooling to more comprehensively investigate the nano scale dispersion of the nano composites produced in this work, follow up sample schedule higher shear forces and temperature cause greater exfoliation and alignment.



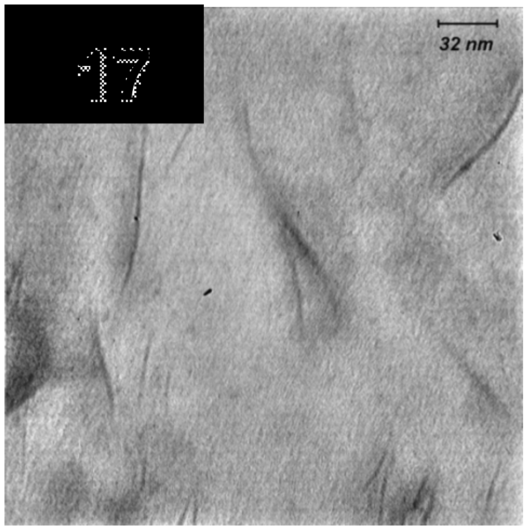


Fig. 5. TEM picture show nano clay and magnesium yydrate.

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 ºC (rate 10 ºC/min).

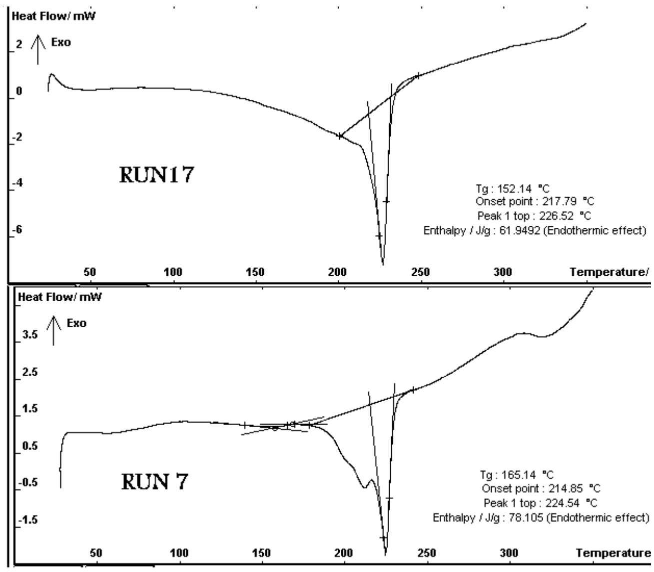


Fig. 6. Shown of run 7 and 17 (max & min)

Follow up to Fig. 6 thermogravimetric and endothermic effect are increased. It is *ca.* 26.07 % form minimum to maximum. It shows 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 ºC/min from room temperature to 680 ºC.

Conclusion

Dual response surface (DRS) methodology was used to investigate thermal stability by amount of nanoparticles (montmorillonite, magnesium hydroxide) and processing parameters (barrel temperature profile and screw rate). In this work introduce

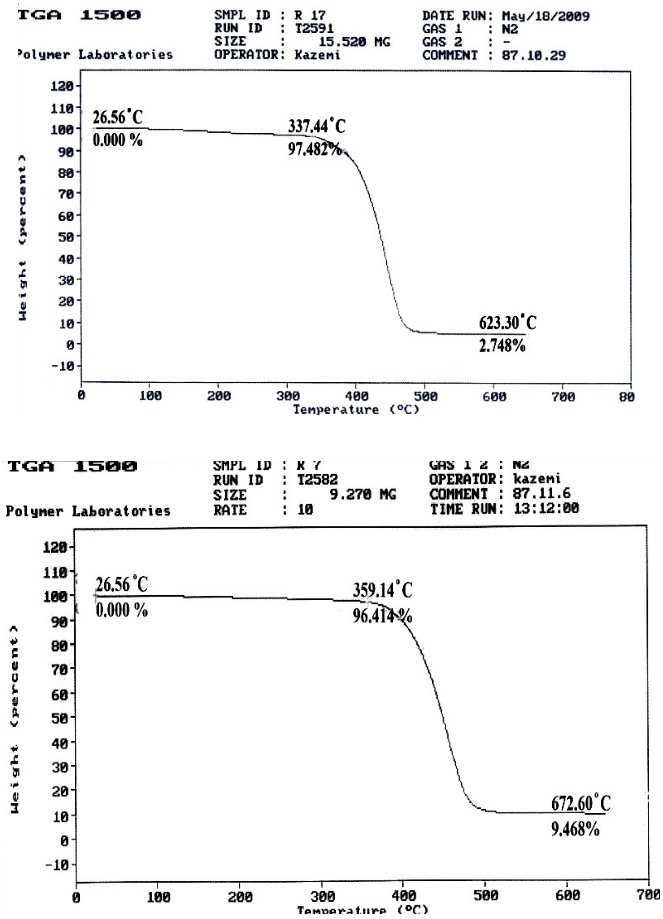


Fig. 7. TGA graph of run 7 and 17 (max and min)

three surface (ST, WC, WC/ST), finally, analysis of variance was used to find relative significance of parameters and the bset 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 (temperature and product speed) were less noticeable.

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

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