Response Surface Based Optimization of Toughness of Hybrid Polyamide 6 Nanocomposites

E. Hajizadeh, and H. Garmabi

Abstract—Toughening of polyamide 6 (PA6)/ Nanoclay (NC) nanocomposites with styrene-ethylene/butadiene-styrene copolymer (SEBS) using maleated styrene-ethylene/butadiene-styrene copolymer (mSEBS)/ as a compatibilizer were investigated by blending them in a co-rotating twin-screw extruder. Response surface method of experimental design was used for optimizing the material and processing parameters. Effect of four factors, including SEBS, mSEBS and NC contents as material variables and order of mixing as a processing factor, on toughness of hybrid nanocomposites were studied. All the prepared samples showed ductile behavior and low temperature Izod impact toughness of some of the hybrid nanocomposites demonstrated 900% improvement compared to the PA6 matrix while the modulus showed maximum enhancement of 20% compared to the pristine PA6 resin.

Keywords—Hybrid nanocomposites, PA6, SEBS rubber, toughness.

I. INTRODUCTION

AMONG the various polymer-clay nanocomposites, the polyamde6-based clay nanocomposite has received substantial attention in recent years [1-3].

However, to achieve a successful polymer/clay nanocomposite, the most important matter is to disperse the inorganic fillers throughout the polyamide6 matrix. Unless a uniform dispersion is achieved, agglomerates of inorganic clay will be a limiting property improvement. Chemistry of the clay surface and conditions of compounding process are two vital parameters that affect the intercalation and dispersion of clay throughout the PA6-matrix [4].

PA6 based nanocomposites are typical example of a significant enhancement of all properties by platelet like nanoclay. The only short-coming of these systems is low toughness. In recent years some researchers have studied methods on toughening of nanocomposites[5]. Nazabal et. all have studied microstructure and mechanical properties of rubber-modified PA6-clay nanocomposites [6 - 7]. They investigated the effect of clay, rubber and compatibilizer levels on toughening behavior of their systems.

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TABLE I
FORMULATIONS BASED ON RESPONSE SURFACE METHOD

No	SEBS %	mSEBS %	CLAY %	Order of mixing
1	12.5	7.25	5	-1
2	12.5	7.25	1	-1
3	22.5	5.25	3	0
4	17.5	5.25	3	0
5	22.5	3.25	1	-1
6	22.5	3.25	1	1
7	12.5	7.25	5	1
8	12.5	3.25	5	-1
9	22.5	3.25	5	-1
10	17.5	5.25	3	0
11	12.5	5.25	3	0
12	17.5	5.25	5	0
13	17.5	5.25	3	-1
14	17.5	3.25	3	0
15	12.5	3.25	1	-1
16	22.5	7.25	1	1
17	12.5	3.25	5	1
18	17.5	5.25	3	1
19	17.5	5.25	3	0
20	12.5	7.25	1	1
21	17.5	5.25	3	0
22	22.5	7.25	1	-1
23	17.5	5.25	1	0
24	17.5	5.25	3	0
25	12.5	3.25	1	1
26	22.5	3.25	5	1
27	22.5	7.25	5	-1
28	17.5	5.25	3	0
29	17.5	5.25	3	0
30	17.5	7.25	3	0
31	22.5	7.25	5	1

An increase of the compatibilizer content generally led to a decrease in the rubber particle size, but the presence of organo -modified clay reduced the fracture toughness. They achieved improvement in the modulus of hybrid nanocomposites, while maintaining the ductile nature of the hybrid systems. Tjong and Bao [8] also studied these hybrid systems. They have used the essential work of fracture (EWF) approach under impact drop-weight conditions to evaluate the impact fracture toughness of the mentioned hybrid nanocomposite systems. They have found that the addition of mSEBS enhances both the impact essential and nonessential works of PA6. Kelnar and his co-workers [9] have studied the effect of elastomer type and functionality on the fracture behavior of toughened hybrid nanocomposites. According to them, the best-balanced mechanical behavior was found for nanocomposite containing

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finely dispersed non-reactive polar elastomers. In this study we used response surface method of experimental design to optimize the material and processing parameters in twin-screw compounding of PA6/SEBS/NC hybrid nanocomposites and studied the effect of rubber, compatibilizer and clay contents and order of mixing of components on low temperature Izod impact toughness and tensile modulus and strength of these systems.

II. EXPERIMENTAL

The PA6 used in this work was B5 from BASF, and the styrene-ethylene/butadiene-styrene copolymers were Kraton G 1651 and G 1901X (maleated SEBS) both from GLS Corp. The nanofiller Nanofil®9 was provided kindly by Sudchemie which is organically modified montmorillonite (OMMT) with good adhesion to PA6. A lab scale co-rotating twin-screw extruder (ZSK25, L/D = 40) manufactured by Coperion Co. was used for the compounding operations.

All the materials were dried before processing. The drying was performed at 80 °C and 24 h for PA6, and 12 h for the SEBSs, and in the case of the OMMT,the drying was done at 80°C for 4 h.

Formulations design according to the response surface method is shown in Table I.

In Table I, in the column of order of mixing, -1 was defined as mixing of PA6 and NC in twin-screw extruder in the first stage and then SEBS/mSEBS mixture was added to the PA6/NC mixture in the second stage in the twin-screw extruder. While, 0 was defined for the mixing of PA6/SEBS/mSEBS in the first stage and then addition of the NC was done in the second stage, and 1 was defined for the mixing of PA6 and NC and also SEBS and mSEBS in separate operations in the twin-screw and then final mixing of these two granules in the twin-screw extruder. The rotation speed of the screws for all the samples were held constant at 600 rpm and a die temperature of 245ºC were used. Injection molding was carried out on the obtained granules to get specimens for tensile and impact tests.

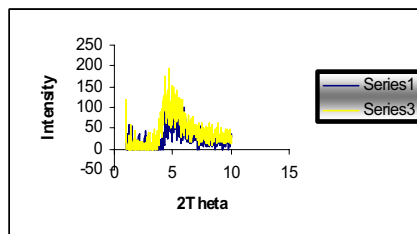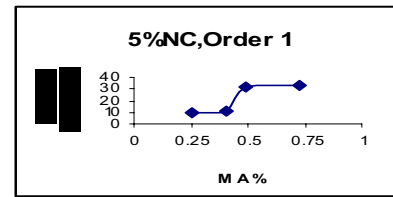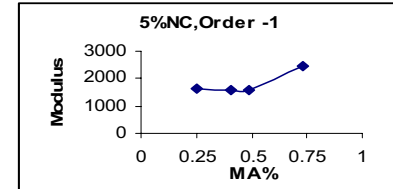SEM images were taken in TESCANA equipment at 1, 3 and k magnifications with and without etching at Toulon for 20 minutes.
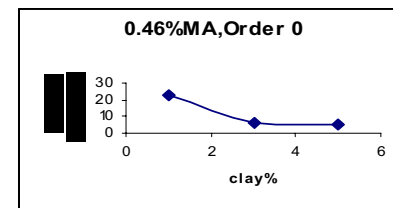

Fig. 1 XRD patterns of the NC and sample 1
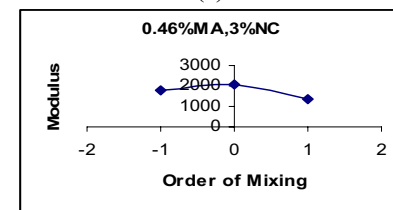

(a)

(b)

(c)
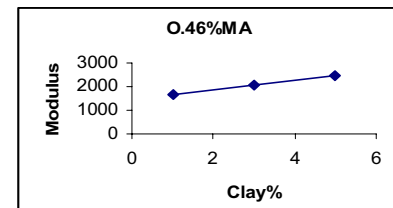
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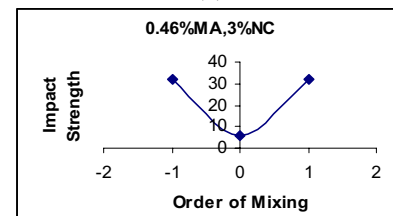
(e)

(f)

Fig. 2 Effects of different parameters on mechanical properties

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TABLE II
TENSILE AND IMPACT RESULTS OF FORMULATIONS

No	Strength Σ_B(N/MM^2)	Ductility ε_b(%)	Modulus (N/mm^2)	Fracture energy (J)	Impact strength (KJ/m^2)
PA6	63.41	198.03	2581.56	195.488	3.21
P6/3%NC	72.23	126.94	3530.01	206.26	1.43
1	43.40	93.43	2442.23	115.59	10.97
2	40.97	197.46	1815.58	224.49	26.90
3	44.84	46.86	2256.83	44.04	7.3
4	40.56	110.85	2014.99	181.35	5.01
5	39.22	237	1445.73	251.84	10.68
6	38.58	150.88	2014.99	181.35	5.01
7	44.59	106.67	2353.19	118.17	N.B*
8	41.34	208.20	1593.19	245.44	8.95
9	39.98	218.37	1609.84	296.40	11.97
10	35.81	171.22	2074.44	165.39	5.96
11	49.51	59.35	3004.62	76.26	5.51
12	50.75	56.34	2470.34	72.26	5.14
13	39.38	237.23	1790.13	253.75	N.B
14	43.51	60.65	2185.17	74.56	4.75
15	54.40	211.09	1782.05	257.87	8.72
16	38.35	224.5	1374.40	216.37	N.B
17	39.79	174.35	1822.79	197.34	11.22
18	39.59	244.66	1361.81	232.86	N.B
19	41.78	111.89	2057.36	122.18	6.45
20	45.54	227.14	1524.84	252.28	N.B
21	40.39	164.70	1524.84	152.94	6.32
22	42.38	264.39	1005.85	257.58	N.B
23	48.90	217.01	1676.14	247.41	22.7
24	46.41	108.86	2046.57	122.15	6.22
25	42.76	268.05	1756.48	328.63	8.72
26	39.09	132.58	1916	166.67	10.29
27	35.46	252.67	1252.70	217.55	N.B
28	38.59	169.52	2106.31	137.56	6.39
29	40.11	140.04	2060.96	143.77	6.09
30	42.43	158.29	2134.30	190.88	8.22
31	39.32	247.09	1431.61	212.93	N.B

N.B: No Breakage occurred in sample.

III. RESULTS AND DISCUSSION

A. Characterization of Nanostructure

The characterization of the nanostructure of the hybrid nanocomposite was carried out using XRD method. XRD Plots of the OMMT and formulation 1 are shown in Fig.1. As can be seen from Fig. 1, the OMMT showed the expected peak at 2θ of 5.38 corresponding a basal spacing: 34.21° A. While, for the hybrid systems there were peaks at 2θ: 3.41, 4.37, 4.46, 4.62 and 4.86 for formulations 1,11,14,7 and 12, respectively which can be considered as an indication of intercalation of NC layers in the system. Formulation 1 which showed 60% of basal spacing, showed maximum modulus as expected. Formulation 7 showed lower intercalating in comparison to formulation 1, which could be due to the different order of mixing in these two systems. Probably order of mixing -1 is better for intercalating rather than order of mixing of 1. A comparison between the basal spacing of formulations 11 and 14 shows that increased compatibilizer content in formulation 11 imparts a positive effect on intercalating.

B. Tensile and Impact Properties

The mechanical properties of the samples were studied by means of both tensile and impact tests. Table II presents the results. To study the impact behavior of the samples, Izod impact (notched) test was done at -20℃. The effect of varying material and processing parameters on tensile and impact properties of the samples are shown in Fig. 2. Some of the remarks which may be concluded from the results presented in Fig. 2 and Table II are as follows:

- By reducing the MA (maleic anhydride) content in the system, modulus was decreased and ductility and fracture energy was increased significantly (e. g , formulations 1 & 8). It is important to notice that in these formulations, order of mixing is -1 and probably, there is no chance for the NC layers to migrate to the rubber-matrix interface and, therefore, they are most likely localized in the PA6 matrix. Also, one could see that in these formulations (1 and 8), by reducing the compatibilizer level, impact strength reduces, which was expected in advance. In contrary to formulations 1 and 8, comparison between formulations 3 and 4 shows that, by increasing the rubber content and also reducing the MA content, ductility reduces. It seems that due to the using order of mixing of 0 in these formulations, there was a chance for

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the NC layers to react with MA groups of mSEBS and inter into the rubber particles and consequently cavitation capability of the system monotonically is reduced and, therefore, the ductility and fracture energy are decreased as well. But due to the increased rubber content in the system, one could see minor increase in the impact strength.

- According to Fig 2.a and 2.b, it seems that there is a saturation level for the MA content, above it, the impact strength of the modulus values are maintained constant.

- It seems that for a specific clay level, there is a specific MA content that is a key factor to control the balance between the elastic modulus and the impact strength. For example, comparing formulations 1 and 13 shows that, MA and NC content was different but in both formulations a good balance between these two important formulation parameters could be observed. It is believed that, this phenomenon arises from a balance between organo groups at the surface of the organoclay, MA groups and amide and amine end groups of the PA6 and it could be possible to control the microstructure by localizing the clay layers in the preferred region, i.e. in the PA6 matrix. Therefore, it is possible to increase the modulus by increasing clay content without significant decrease in impact strength for NC content above 3%.

-According to Fig. 2.c and 2.d, by increasing the clay content modulus increased monotonically and impact strength decreases and shows a plateau for NC content above 3wt% therefore, it is possible to increase the modulus by increasing clay content without significant decrease in impact strength for NC content above 3wt%.

- According to the obtained results in Table II and Fig. 2.e and 2.f, order of mixing of -1 is the best order for blending the components in the twin-screw extruder. As can be seen, order of mixing of 0 is the worst order to achieve high impact strength, but there is no significant differences between impact results for order 1 and -1. On the other hand, modulus for order -1 is higher than order of 1, witch keeps the clay layers in the PA6 matrix.

- In formulations 4, 10, 19, 21, 24, 28 and 29, all the material and processing factors were maintained constant and the compounds were prepared at various dates. According to the results it is evident that the obtained results are reproducible and reliable.

C. SEM Micrographs of Fractured Surfaces

All the samples for SEM test were etched in Toulon for 20 min and images were taken in 1, 3 and 5 k magnifications. In Fig. 3, pictures of samples at 5000 magnification were shown. As can be seen, there is large differences between the dispersed phase size and shape for different samples. In comparison between samples 7 and 12 (Fig. 3.a and 3.b), it is shown that by reducing MA group content in the system; unexpected reduction of rubber particle size is observed. Probably, this is due to the lack of compatibilizing effect in existence of organo clay and possible reaction between MA group of the compatibilizer and surfactant at the nanoclay surface. Also, it seems that interfacial tension in these two systems is not a key factor i.e. both systems placed above the saturation level of MA. However, the main difference between

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In samples 11 and 14 (Fig. 3.c and 3.d) larger particles having non-spherical shape are observed. In both samples the order of mixing was 0 and it seems that nanoclay particles had chance to inter the rubber particles and also probability of existing two types of particles.

According to the literatures here is the highest optimum inter-particle distance or particle size that gives the best toughening action. In our systems where SEM images of samples 7 and 12 shows, although the MA content have been decreased in sample 12 and there were smaller rubber particles but impact strength has been decreased, indicates particle size is out of optimum range for toughening.

IV. CONCLUSION

Rubber-toughened PA6/NC nanocomposites were prepared via melt compounding in a co-rotating twin-screw extruder. Using response surface method of experimental design, it was concluded that, order of mixing of -1 is the preferred method for mixing of the component, in which intercalation/exfoliation of NC is possible. While, it seems that in other orders of mixing, especially in order of 0, some NC layers enters the rubber particles and results in reduced cavitation and lower impact strength. The presence of NC increases the yield stress much more than the stress at break, indicating that NC affects mostly the shear yielding mechanism. By increasing the compatibilizer (mSEBS) content, the impact strength and modulus increases significantly.
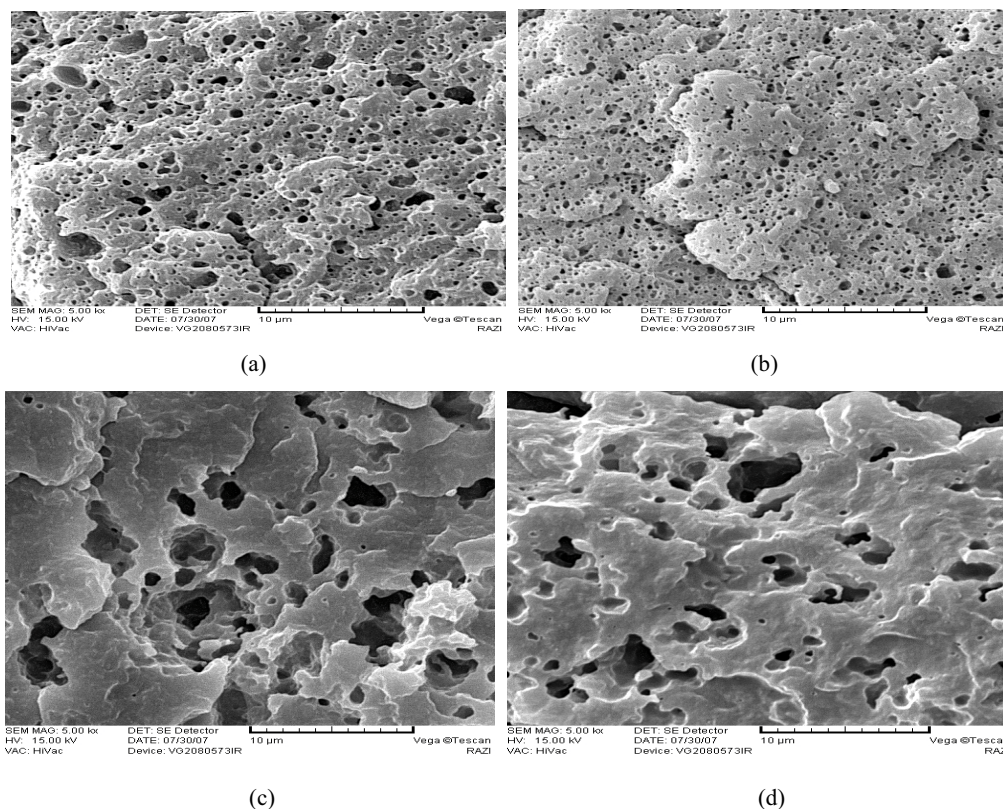
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Fig. 3 SEM images of some samples a) sample 7, b) sample 12, c) sample 11, d) sample 14

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