PREPARATION AND CHARACTERIZATION OF PP/HDPE/NANOCLAY/SHORT FIBER HYBRID COMPOSITES USING RESPONSE SURFACE METHODOLOGY

Indira V, Anjana R and K E George*

Department of Chemical Engineering, Government Engineering College, Thrissur

*Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology

ABSTRACT

Polymer composites reinforced with either short fiber or nanoclay are popular in the field of polymers and nanotechnology. The objective of this work is to study the combined effect of glass fiber and nan kaolinite clay in polymer matrix. The polymer blend selected in this study is 80/20 blend of polypropylene and high density polyethylene. The hybrid composites of polymer/short fiber/nanoclay were prepared by melt compounding. The effect of process parameters like temperature, time, clay content and glass fiber content on the properties of the hybrid composites were analysed using Box Behnken Design of Response Surface Methodology. Mechanical properties of the composites investigated were tensile strength, tensile modulus, elongation at break, impact strength, flexural strength and flexural modulus. Morphological behaviour of the composites were analysed using scanning electron microscopy of the fracture surface of hybrid composite samples. Thermal characterization was done using thermo gravimetric analysis. The studies show that glass fiber and nanoclay can introduce synergism in the polymer matrix. The hybrid composite has potential applications in the manufacture of aircrafts, ships and submarines.

***Key words**:* Nano kaolinite clay, e- glass fiber, hybrid composite, melt compounding and Box Behnken Design.

INTRODUCTION

Polymer nanocomposites are a unique new class of materials with an ultrafine dispersion of nano materials in a polymeric matrix. They have recently gained a great deal of attention because of the much superior properties in terms of increased strength and modulus, improved heat resistance, decreased gas permeability and flame retardancy at very low loadings of < 5-wt% of nano fillers (Box and Draper, 1987). Similarly, fiber-reinforced composites are very widely used because; they have high specific tensile and compressive strength, controllable electrical conductivity, low coefficient of thermal expansion, good fatigue resistance and suitability for the production of complex shape materials. Hybrid nanocomposite can be made from different combination of fibers (glass fiber, carbon fiber, and natural fibers etc.), polymers (thermosets/thermoplastics) and nano fillers/layered silicates (at least one dimension is in nano meter). These new class of composite materials are known for improved mechanical and thermal properties for structural applications. Even less work has been published on variation of mechanical properties with mixed nanocomposites of glass fiber. The objective is to develop hybrid composites that exhibit overall optimized performance. Optimization is done using Response surface methodology (RSM). Design of experiment (DoE) is a well-accepted statistical technique able to design and optimize the experimental process that involves choosing the optimal experimental design, model and estimate the effect of the several variables independently and also the interactions simultaneously (Lazi, 2004 and Montgomery, 2005). It has the advantage of avoiding repetition of experiment for multiple factors experiments (Amiri *et al.,* 2008). RSM also allocates more comprehensive analysis of the interactions between the experimental variables than other experimental design methods (Keshav and Gopalakrishna. 2011). Therefore, utilizing RSM in optimization gives more accurate and complete data with a minimal number of experiments (Tan *et al.,* 2009). Fiber reinforced polymer nanocomposites possess improved mechanical properties than fiber reinforced polymer composites due to the synergistic effect of both the fillers (Grima *et al.,* 1994). In the present work, glass fiber and nanoclay are incorporated into the 80/20 PP/HDPE blend and its properties are determined. The mechanical properties are optimized using Box-Behnken method of RSM. The thermal and morphological characterization of the composites is also performed. The addition of nanoclay to glass fiber reinforced polymer matrix gives better performance than fiber reinforced plastics. The variables chosen for study are mixing temperature, nanoclay loading, glass fiber content and mixing time.

MATERIALS AND METHODS

Polypropylene homo polymer (PP): (REPOL H110MA)and high density polyethylene (HDPE) (REPOL H110MA) were supplied by M/s Reliance Industries Ltd., Hazira, Gujarat, Unmodified Nanoclay (Nanocaliber 100) supplied by M/s English Clay Ltd, Vely, Thiruvananthapuram and E-glass fiber (RP10 grade) supplied by M/s Reliance Industries Ltd., Hazira, Gujarat.

Preparation of hybrid composites: All composites were prepared in an internal mixer Torque Rheometer (Thermo Haake Rheocord 600). The rotor speed was set at 50 rpm. The components of 40 g were loaded to the mixing chamber through the hopper and compounded at temperature and time given by RSM, with rotor speed of 50 rpm. Box-behnken method of RSM suggested an experimental design consisting of 27 runs, each with varying clay and glass fiber content, mixing time and temperature and composites are prepared accordingly. Nano clay used was preheated to about 75^0C for 45 minutes and glass fiber in the form of short fiber of uniform length of 6mm.

The composites so prepared were hot pressed in a hydraulic press, cut into pieces and moulded using a semi-automatic plunger type injection moulding machine.

Testing of hybrid composites: The specimens obtained after moulding were tested for tensile and flexural properties in a Shimadzu Autograph Universal Testing Machine (UTM)), impact strength in Resil Impact Testing Machine. Thermal analysis is done in TA-Q 500 series instrument in nitrogen atmosphere for a temperature range of 40^0C to 1020^0C at 20^0C/min and SEM images were taken with JSM 6390 with an accelerator voltage 20 kV on a vacuum atmosphere.

Experimental design: A three level- four factor Box-Behnken design containing 27 experiments under response surface methodology was chosen as experimental method to evaluate the effect of blending, shear rate and nanoclay addition on the mechanical properties of the nanocomposite. The levels and variables with code values in parenthesis is given in Table 1 and the design data and the resultant mechanical properties in Table 2. Analysis of the experimental data obtained from Box-Behnken design runs was done on MINITAB 15 software using full quadratic response surface model (2nd order polynomial equation) as given by.

$$y - \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i x_i + \sum_{i<j=1}^{3} \beta_{ij} x_i x_j$$

RESULTS AND DISCUSSION

Mechanical properties: The formulated hybrid composite showed considerable increase in mechanical properties and is listed in table 2. The model equation for the mechanical properties is given in Table III. The R^2 value which is the degree of agreement between the experimental results with those predicted by the model are obtained in the range of 0.78-0.99 for all the responses (Table 3). The range achieved for R^2 in this study is an indication of very good fitting of experimental data by the model equations. Contour plots are two dimensional series of curves based on the model equations and show different combinations of variables for the response. The circle shape indicates that a maximum lies in the selected range of operation and the selected range of process parameters. It is observed that the tensile strength and modulus first increases and then decreases with increase in time, temperature, clay content, fiber content. Initially strength increases due to proper mixing and thereby better dispersion and interaction between the nanoclay and glass fiber. Further increase in temperature and time causes the degradation of polymers, which lead to decrease in tensile strength (Fig 1).

The p values obtained from the analysis using are given in the Table 4. The p value is an indication of significance of each variable and their combined effect on the mechanical properties. The analysis has been done with 95% confidence level; hence the p value obtained should be less than 0.05 for the particular variable to be significant for the property under consideration. The results show that the most significant independent variable is temperature and some extend of interaction effect is present. The clay and fiber content also exerts synergistic effect on the properties. Optimum parameters for better mechanical properties was obtained using RSM, that is 160^0C, 8min. 2 wt% clay, 20 wt% glass fiber. The optimization plot for the mechanical properties is given in Figure 2.

Scanning electron microscopy: The fracture surface SEM images of polymer-fibre composite and optimum hybrid composite are given in Figure 3. The pictures give a much better feel of the particles in 3 D space. SEM images shows that glass fiber and nanoclay particles are evenly distributed in the polymer matrix. Hence the stress applied is evenly distributed resulting in higher strength. The broken surface of fibers can be seen in the SEM image which further shows that complete breakage of hybrid composite takes place only after the fiber breaks.

Thermo gravimetric analysis: The thermo gravimetric analysis curves are given in Figure 4 as % loss in weight vs temperature. In the case of fiber composite containing 20 wt% glass fiber onset of thermal degradation is obtained at 326.370C and it is completely degraded at a temperature of 437.330C. For hybrid composite containing 20 wt% glass fiber and 2 wt% unmodified clay onset of thermal degradation is at 343.730C and it is completely degraded at a temperature of 446.440C. It shows that clay addition increases thermal stability of composite

CONCLUSIONS

In summary, addition of nanoclay improves the performance of fiber reinforced polymer blends. Here, clay addition increases tensile strength and modulus by 35 & 59%, impact strength and elongation at break decreases by 61 & 65% and flexural strength and modulus increases by 30% and 50% as compared to the blend with fiber alone. Hybrid composite is also having better thermal stability. The good interaction of nanoclay and glass fiber as evident in the morphological characterization explain the reason for the betterment of thermal an mechanical properties The optimum parameters obtained are 160^0C, 8min. 2 wt% clay, 20 wt% glass fiber. Thus nano kaolinite clay addition can provide overall best performance.

It incorporates synergistic effect in polymer fiber composites and hence an economical and effective modifier to the PP/HDPE/glass fiber composites

REFERENCES

Amiri, M., Najafi A and K. Gheshlaghi, 2008. Response surface methodology and genetic algorithm in optimication od cement clinkering process. J. of Appl. Sci. 8 (15): 2732-2738.

Box. G and N. Draper, 1987. Empirical Model-Building and Response Surface, John Wiley and Sons, New York.

Grima, E. M. Medina, A. R. Giménez, A. G. Sánchez Pérez, J. A. Camacho, F. G and J. L. García Sánchez, 1994. Comparison between extraction of lipids and fatty acids from microalgal biomass,"*Journal of the American Oil Chemists' Society*, 71(9): 955–959.

Keshav.M and H.D.Gopalakrishna. 2011. Development of design to manufacture tubing methodology in dmu environment. *Global J. of Mech., Engg. & Comp. Sciences,* 1 (**3**): 45-47.

Lazi, Z. 2004. Design of Experiments in Chemical Engineering: A Practical Guide, Wiley-VCH Verlag GmbH&Co., Morristown.

Montgomery, D. 2005. Design and Analysis of Experiments, John Wiley and Sons, New York.

Tan, K. T. Lee, K and A. R. Mohamed, 2009. "Production of FAME by palm oil transesterification via supercritical methanol technology," *Biomass and Bioenergy*, 33(8): 1096–1099.

Table 1: Ranges of the independent variables and experimental design levels

Variables	Notation	Unit	Design Levels		
			Low (-1)	Medium(0)	High(1)
Temperature	X_1	^0C	150	160	170
Time	X_2	Min	4	8	12
Clay content	X_3	Wt%	1	2	3
Fiber content	X_4	Wt%	10	20	30

Table 2. Box-behnken experimental design data and mechanical properties

Run	X_1	X_2	X_3	X_4	Tensile Strength (N/mm^2)	Tensile Modulus (N/mm^2)	Elongation break (%)	Impact Strength (J/m)	Flexural Strength (N/mm^2)	Flexural Modulus (N/mm^2)
1	170	12	2	20	44.08	1577.06	3.38	237.86	58.01	2417.63
2	160	12	2	10	41.12	1295.56	5.10	235.91	47.71	2135.38
3	150	12	2	20	40.49	1296.01	4.83	230.70	44.16	1545.93
4	160	12	3	20	42.09	1065.96	3.65	165.43	50.25	2820.07
5	170	8	3	20	38.65	610.93	3.60	190.85	47.38	2127.41
6	150	8	1	20	38.04	355.55	6.32	332.19	46.73	2592.11
7	160	4	2	10	42.56	1265.80	5.58	370.68	49.29	3172.42
8	160	4	1	20	50.20	499.801	5.21	207.14	50.83	2967.81
9	160	12	2	30	51.31	329.278	4.85	197.18	52.92	2848.75
10	160	8	3	10	37.07	282.774	6.21	292.57	46.46	1894.35
11	160	8	2	20	53.67	1626.08	2.94	132.24	68.27	3848.75
12	170	8	2	30	41.78	701.036	4.33	206.34	48.94	2763.11
13	160	8	1	10	42.06	1284.93	4.99	269.34	46.08	1298.42
14	150	8	2	30	38.63	487.165	5.21	308.28	48.04	2827.29
15	160	8	3	30	45.50	611.707	4.03	145.00	47.94	2841.78
16	170	4	2	20	42.92	488.95	3.32	222.39	49.13	2041.44
17	170	8	1	20	32.40	458.509	4.63	266.14	47.22	2775.05
18	150	8	3	20	34.03	449.413	6.52	377.35	45.04	2279.48
19	160	8	1	30	44.65	1482.96	4.85	195.30	53.35	3072.06
20	150	4	2	20	34.54	488.95	4.56	345.49	41.23	1393.61
21	160	8	2	20	53.82	1626.25	2.97	132.49	68.54	3848.43
22	160	4	3	20	42.34	1295.77	5.18	242.82	44.27	2558.09
23	160	12	1	20	44.18	421.599	4.89	221.56	49.94	3104.69
24	160	8	2	20	53.97	1626.57	2.91	132.55	68.83	3848.92
25	170	8	2	10	39.46	1319.47	4.37	296.17	42.76	1194.59
26	150	8	2	10	40.75	489.67	5.92	375.00	42.98	1020.77
27	160	4	2	30	40.00	477.289	4.23	192.01	49.35	3174.42

Table 3. Model equations and R^2 value for the mechanical properties

Property	R^2 (%)	Model Equations for the mechanical properties
Tensile strength	85.89	$-2472.71+31.45X_1+6.31X_2-21.09X_3-0.29X_4-0.10X_1^2-0.23X_2^2-6.69X_3^2-0.05X_4^2-0.03X_1X_2+0.26X_1X_3+0.01X_1X_4+0.36X_2X_3+0.08X_2X_4+0.15X_3X_4$
Tensile modulus	93.84	$-223484+2765X_1+112X_2+2245X_3+21X_4-9X_1^2-16X_2^2-130X_3^3-2X_4^2+X_1X_2-12X_1X_4-X_2X_3+5X_3X_4$
Elongation at break	87.35	$233.227-2.7X_1-0.359X_2+1.537X_3-0.726X_4+0.008X_1^2+0.035X_2^2+1.217X_3^2+0.012X_4^2-0.001X_1X_2-0.031X_1X_3+0.002X_1X_4-0.076X_2X_3+0.007X_2X_4-0.051X_3X_4$
Impact strength	93.14	$28341.4-339.5X_1-182.3X_2+385.3X_3-26.3X_4+X_1^2+2.5X_2^2+36.6X_3^2+0.6X_4^2+0.8X_1X_2-3X_1X_3-X_1X_4-5.7X_2X_3+0.9X_2X_4-0.3X_3X_4$
Flexural strength	97.62	$-3350.41+41.14X_1+12.12X_2+30.38X_3+3.72X_4-0.13X_1^2-0.60X_2^2-9.85X_3^2-0.10X_4^2-0.02X_1X_2+0.05X_1X_3+0.43X_2X_3+0.03X_2X_4-0.14X_3X_4$
Flexural modulus	78.71	$-309023+3780X_1+184X_2+3592X_3+463X_4-12X_1^2-33X_2^2-502X_3^2-8X_4^2+X_1X_2-8X_1X_3-X_1X_4+8X_2X_3+4X_2X_4-21X_3X_4$

Table 4. p values of mechanical properties

Term	Tensile strength	Tensile modulus	Elongation at Break	Impact strength	Flexural strength	Flexural modulus
Temperature	0.000	0.000	0.004	0.000	0.000	0.000
Time	0.364	0.733	0.754	0.013	0.004	0.872
Clay	0.446	0.107	0.738	0.147	0.048	0.436
Fiber	0.915	0.874	0.131	0.311	0.020	0.320
Temp*Temp	0.000	0.000	0.004	0.000	0.000	0.000
Time*Time	0.024	0.003	0.035	0.009	0.000	0.044
Clay*Clay	0.000	0.076	0.000	0.015	0.000	0.052
Fiber*Fiber	0.004	0.032	0.000	0.001	0.000	0.006
Temp*Time	0.472	0.661	0.849	0.050	0.274	0.838
Temp*Clay	0.137	0.163	0.276	0.067	0.588	0.760
Temp*Fiber	0.562	0.762	0.546	0.706	0.742	0.828
Time*Clay	0.388	0.976	0.284	0.151	0.061	0.909
Time*Fiber	0.071	0.903	0.328	0.037	0.147	0.519
Clay*Fiber	0.383	0.540	0.083	0.864	0.107	0.456

Figure I: Contour plots of tensile strength, flexural strength , impact strength, elongation at break, tensile modulus and flexural modulus.

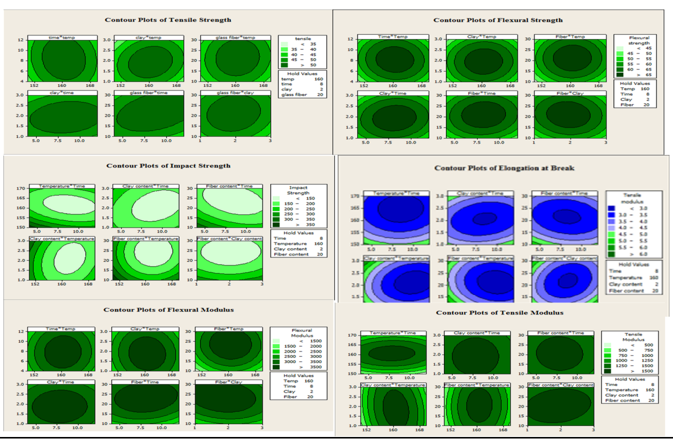


Figure 2: Optimization plot for the mechanical properties

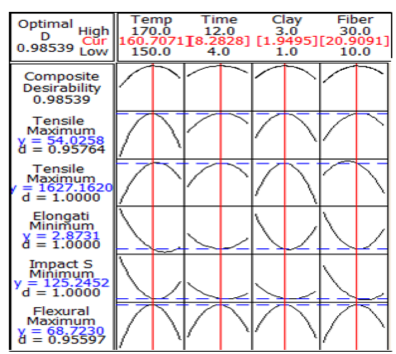


Figure 3. SEM of fractured surface of (a) PP/HDPE/20GF and (b) PP/HDPE/20GF/2UC

a. b.

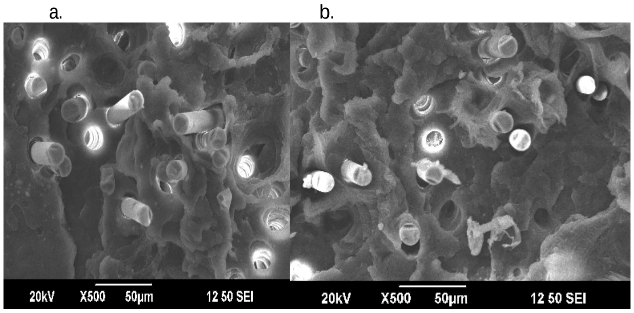
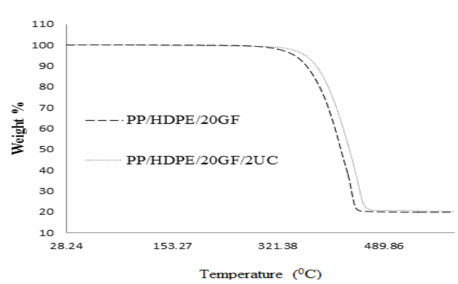


Figure 4: TGA Curves of PP/HDPE/GF and PP/HDPE/GF/2UC



****