Interaction of Mixing Factors with Mechanical Properties of PP/ENR Blend via Response Surface Methodology

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ABSTRACT

This research is carried out to establish interaction between mixing parameters with mechanical properties of polypropylene (PP) incorporated with epoxidized natural rubber (ENR). The blends of PP/ENR were prepared by melt compounding using an internal mixer and vulcanized through sulfur curing system. The experiment was designed using two-level factorial design via response surface methodology by Design Expert software. Mechanical testing such as tensile test and impact test were performed to characterize the properties of PP/ENR blends. It was clearly observed that high ENR to PP ratio increases the toughness and flexibility of the PP/ENR blends. In comparison to the pure PP, PP/ENR blend with 40% ENR showed improvement of elongation at break and impact strength up to 68% and 56%,

respectively. In contrary, the tensile strength and hardness decreases as the amount of PP decreases. The changes were associated to the properties imparted by the elastic chains of cross-linked ENR. The obtained properties showed good correlation with fracture surfaces observed in microscopy analysis performed by Field Emission Scanning Electron Microscope at magnifications of 500 and 5000-x.

Keywords: *Polypropylene; epoxidized natural rubber; blend; factorial design, mechanical properties*

Introduction

Blending of thermoplastic and elastomeric polymer generates a new class of material termed thermoplastic elastomer (TPE) with combined properties of its constituent. It is a common technology that frequently applied in order to develop products with superior mechanical properties from inexpensive polymer material [1].

TPEs received attention from researchers all over the world due to their versatile function in various automotive parts, household appliances, electrical equipments, industrial supplies, food contact systems and medical apparatus [2]. TPEs can be classified into two groups: block copolymers and rubber-plastic blend. Thermoplastic vulcanizates (TPV) or dynamic vulcanizates (DV) is a class of TPE based on rubber and thermoplastic compositions where the rubber which is later crosslink under dynamic conditions. The one based on natural rubber and thermoplastic blends are classified as 'thermoplastic natural rubber' (TPNR) blends. There are two types of TPNRs; 1) The thermoplastic polyolefin (TPO) which is prepared by blending NR with thermoplastic such as polyolefin to obtain co-continuous phase morphology, 2) The 'thermoplastic vulcanizate (TPV)' which is prepared by blending NR with polyolefins where the rubber phase is vulcanized during the mixing process at high temperature by a process known as 'dynamic vulcanization (DV)' [3].

Polypropylene (PP) is a polymer with large molecular weight distribution [4]. There are three types of PP, i.e., atatic (aPP), isotactic (iPP) and syndiotactic (sPP) [5]. PP has wide range of application due to its unique properties such as high melting temperature, low density, high chemical resistance, and resistance to heat. On the other hand, PP exhibits poor impact strength which gives limitation to several other applications [6].

Epoxidized natural rubber (ENR) is a material of great interest; exhibiting a double functionality for crosslinking (double bonds and epoxy site) while retaining most of the properties of natural rubber [7]. The

epoxidation of natural rubber can be performed using peracid which is generated from the reaction of formic acid and hydrogen peroxide [8]. The properties of ENR are gradually changed with increasing degree of epoxidation [8]. The presence of epoxy groups in rubber chains imparts great properties to natural rubber such as oil resistance, low gas permeability, good wet grip and high damping characteristics [9-12].

Melt compounding via internal mixer is a widely used technique to prepare polymer compounds and blends [10]. Uniform compounding is achieved when the materials are sheared in control manner between two circulating rotors. Besides rotational speed, other processing parameters such as mixing temperature and mixing time are important factors to improve blends miscibility as well as its properties. The interactions between these parameters should be established to understand its contribution towards process optimization. Statistical and mathematical approach is a useful technique to correlate between factors and response due to less time consuming and has the ability of detecting the true optimum of the factor [10]. Response surface methodology (RSM) is commonly used technique due to its reliability [13, 14, and 15]. It allows simultaneous evaluation number of factors and eliminates the need for a large number of independent experiments that are otherwise required in a conventional one-factor-at-a-time or trial-and-error approach [16].

Most of the studies [17] conducted on PP/ENR or ENR/PP blends were focusing on dynamic vulcanization [4, 12, and 18] or irradiation effects [19] to the properties of blends. Unfortunately, there are limited studies which focusing on the effect of mixing parameters to the properties of blends. In this paper, we investigate the effect of mixing parameters as well as material ratio on the mechanical properties of polypropylene/epoxidized natural rubber blends via RSM. The findings are further supported by morphological analysis on the tensile fracture surfaces.

Experimental

Materials

Table 1 shows the formulation used in this study. Polypropylene (PP) was supplied by Titan PP Polymers (M) Sdn. Bhd. PP under the trade name of TITANPRO 6531. It is an isotactic type with melt flow index of 3.5 g/10 minutes. ENR was supplied by the Malaysian Rubber Board under the trade name of ENR 50 with 53% epoxidization. The average Mooney viscosity [measured at ML (1+4) 100°C] was 85.5, and the average specific gravity at approximately 25°C was 0.9366. Sulfur was used as vulcanizing agent whereas zinc oxide and stearic acid were used as activators in the sulfur curing system. They were purchased from Sin Rubtech®.

Table 1: Formulation of PP/ENR blend

Materials/Chemicals	**(phr)**
Polypropylene Epoxidized Natural Rubber	100.0
Zinc oxide	5.0
Stearic Acid	2.5
Sulfur	2.0

Mixing and preparation of sample

The blending process of PP/ENR blends was performed according to ASTM D 3192 and carried out using a Haake internal mixer working with combination of parameters determined by the design of experiment. Firstly, PP and ENR were blended together in mixing chamber before all ingredients were added in sequential. Finally, sulphur was added and mixed for about 2 minutes to complete the dynamic vulcanization process. Then, the mixture was dumped and left to cool to room temperature for 24 hours. Subsequently, the produced TPV blend was pressed using hot press (GT7014-A, Gotech) for about 5 minutes at 185°C and 176 MPa before undergone cutting process. Samples prepared according to ASTM standard were conditioned at room temperature for 24 hours before testing.

Experimental design

Experimental design to correlates mixing parameters with mechanical properties of PP/ENR blend was based on two level factorial designs generated using the *Design Expert 6.0.10* software. Four factors were investigated; ENR content, X_1 (%), mixing temperature, X_2 (^oC), rotor speed, X_3 (rpm) and mixing time, X_4 (minutes). Three replications at center point were performed to increase the confidence level. This design matrix is shown in Table 2. Meanwhile, the actual value of the factor codes is shown in Table 3. The interactions between all factors were established for three responses; 1) tensile strength, 2) elongation at break and 3) impact strength.

Table 2: Combination of parameters internal mixer machine for 2^4 factorial designs for screening factor

Std	ENR X_1 (%)	Temperature X_2 (°C)	Rotor Speed X_3 (rpm)	Time X_4 (min)
1	-1	-1	-1	-1
2	1	-1	-1	-1
3	-1	1	-1	-1
4	1	1	-1	-1
5	-1	-1	1	-1
6	1	-1	1	-1
7	-1	1	1	-1
8	1	1	1	-1
9	-1	-1	-1	1
10	1	-1	-1	1
11	-1	1	-1	1
12	1	1	-1	1
13	-1	-1	1	1
14	1	-1	1	1
15	-1	1	1	1
16	1	1	1	1
17	0	0	0	0
18	0	0	0	0
19	0	0	0	0

Table 3: Level of variables for the screening factor

ENR (X_1; %)	Temperature (X_2; °C)	Rotor Speed (X_3; rpm)	Time (X_4; min)
0(-1)	170(-1)	50(-1)	6(-1)
30(0)	185(0)	75(0)	10.5(0)
60(+1)	200(+1)	100(+1)	15(+1)

Mechanical testing and morphological analysis

Tensile test was carried out according to ASTM D638. It is the most common plastic strength specifications and covers the tensile properties of unreinforced and reinforced plastics. This test conducted on standard "dumbbell" or "dogbone" shaped samples with 3 mm thickness. Dumbbell samples of PP/ENR blends were cut from moulded sheets using a cutter machine (Gotech). The tensile test was performed using Universal Testing Machine (Autograph AG-IC, Shimadzu Scientific Instruments) at a cross head speed of 2.0 mm/min and 25± 5 °C. Samples prepared according to ASTM D 256 were tested for impact strength using Izod pendulum impact

tester. In the test, un-notched specimen was held as a vertical cantilevered beam and impacted by a pendulum.

The examination of the impact fracture surfaces were carried out using a scanning electron microscope (ZEISS EVO 50) at magnifications of 500x and 5000x under variable pressure. For every sample, a minimum of three micrographs at each magnification were taken to ensure a high confidence level in the analysis. The fractograph was observed and the morphology was analyzed qualitatively.

Results and Discussions

Mechanical properties

Table 4 tabulates the regression model for tensile strength (TS), elongation at break (EB) and impact strength of the PP/ENR blends. Regression model is a mathematical relationship which represents the quantitative effects of the independent variables and their interaction effects to the response. Positive values reflect an effect that leads to optimization whereas negative values are factors that give opposite effect on the response. The R^2 values indicate the degree of agreement between the experimental results with those predicted by model. The R^2 values for all responses are obtained in the range of 0.90–0.99 which were very close to union ($R^2 = 1$); almost 100% of the variation in the overall system was presented by the model. This indicates that the regression model is accurate in describing and predicting the pattern of significance for each factors [14].

Table 4: Regression model for every response

Response	Coefficient of determination, R^2	Adjusted R^2	Regression Model
Tensile Strength, Y_5	0.9858	0.9848	$Y_5 = 16.27 - 12.03X_1 - 0.19X_2 - 0.35X_3 + 0.049X_1X_2 + 0.44X_1X_3 - 0.84X_2X_3 + 0.66X_1X_2X_3$
Elongation to Break, Y_6	0.9242	0.9194	$Y_6 = 13.35 + 3.35X_1 - 0.19X_2 + 0.021X_3 + 0.15X_4 - 5x10^{-3}X_1X_2 + 0.19X_1X_3 - 5x10^{-3}X_1X_4 - 0.21X_2X_3 - 0.34X_2X_4 + 0.27X_3X_4 + 0.4X_1X_2X_3 - 0.17X_1X_2X_4 + 0.23X_1X_3X_4 - 0.44X^2X^3X^4 - 0.35X_1X_2X_3X_4$
Impact Strength, Y_4	0.9312	0.9220	$Y_4 = 2.09 + 0.46X_1 + 0.056X_2 + 0.031X_3 - 0.13X_4 + 0.023X_1X_2 + 0.040X_1X_3 + 0.056X_1X_4 - 0.027X_2X_3 + 0.056X_2X_4 - 2.083x10^{-3}X_3X_4 + 6.25x10^{-3}X_1X_2X_3 + 0.048X_1X_2X_4 - 2.083x10^{-3}X_1X_3X_4 - 0.01X^2X^3X^4 - 0.035X_1X_2X_3X_4$

Three dimension interactions between rotor speed-ENR and rotor speed-temperature towards tensile strength are shown in Figure 1 (a) and (b), respectively. It can be seen that the tensile strength decreases with increasing rubber content in the blends. Meanwhile, rotor speed in the range of 50 to 100rpm show trivial effect to tensile strength. In contrast, interaction between rotor speed and temperature at constant ENR value decreased the maximum stress experienced by the blend (Figure 1(b)). This is due to the fact that polymeric materials are heat sensitive and increasing both mixing factors (rotor speed and temperature) at the same time could generate excessive heat which may expose the blend to degradation.

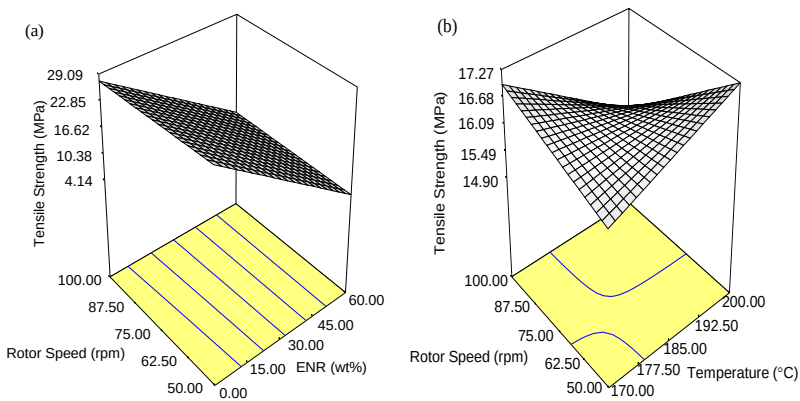

Figure 1: Three dimension interaction of (a) rotor speed-ENR content and (b) rotor speed-temperature with tensile strength.

Tensile strength measures the ability of the material to sustain maximum stress before the material undergoes plastic deformation. The decrease in tensile strength with increasing ENR content was postulated. Elastomeric behaviour prevailed at high ENR content due to rubber phase's continuity. It allows the blend to experience greater plastic deformation at lower maximum stress value. In comparison, at low rubber content than 50%, the elastomer phases remained as dispersed bodies in polypropylene matrices. As rubber phase increases, it increased the particle–particle interaction of the rubber phases, hence results in occlusion and accounts for the decrease in tensile strength. The molecular entanglements in the rubber chains prevent rapid flow and disturb the ability of PP to move [20] and to be strain-crystallized in response to the applied stress. The decrease in tensile strength could also possibly due to the decrease in crytallinity as reported by George et al. [21]. According to them [21], rubber particles present in inter- and

intra-spherulitic region of the crystalline phase plastic. It is supposed that the presence of rubber particles in the blend interrupts the formation of crystallite and decreases the crystallinity, which consequently results in lower tensile strength of the PP/ENR blend when compared to pure PP.

As presented in Figure 2, the elongation at break (EB) value increases with the increase of ENR in PP/ENR blends. The result shows that addition of ENR contributes for better elasticity, toughness and flexibility of the material. The ability of the material to absorb energy improves as the rubber content increases since crosslinking in rubber phases (ENR-50) will impart the elastic behaviour to the blend [22]. Besides, it is reported that the addition of ENR into PP increases the inter-planar distance (d value), which indicates the presence of rubber particles in the intra-spherulitic structure of PP [23]. The system experienced reversal as concentration of ENR increased more than 50 wt% due to the occlusion of rubber particles.

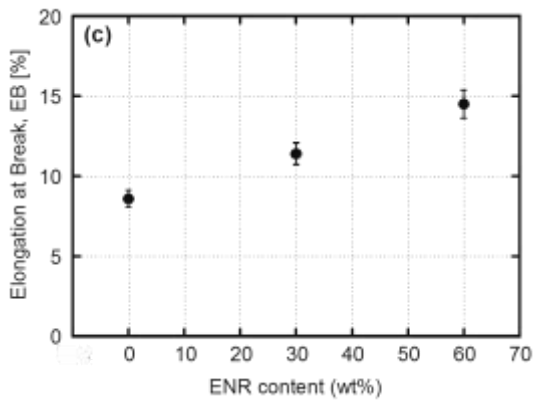

Figure 2: Elongation at break versus ENR content of PP/ENR blends.

Figure 3 shows the perturbation plot of factor X_1 (ENR content) and X_4 (mixing time) towards impact strength of PP/ENR blends. It can be observed that ENR content has positive contribution whereas mixing time shows negative contribution towards the impact strength. Higher impact strength represents higher resistance of the material to fracture under impact loading. This is related to toughness of the material whereby it measures the ability of the material to withstand both plastic and elastic deformations. It depicts the amount of energy required by the material to break the bonds before fracture. The blend with 60 wt% ENR showed the highest impact strength in the range of 2.1 to 2.7 J/m. It is improvement of 56 % if compared to pure PP. The result suggests that ENR is a good candidate to increase the toughness and flexibility of thermoplastic material. The decrease in impact

strength with mixing time may due to the tendency of polymeric chains to break down into shorter chains with time and limit the blend's ability to absorb higher energy.

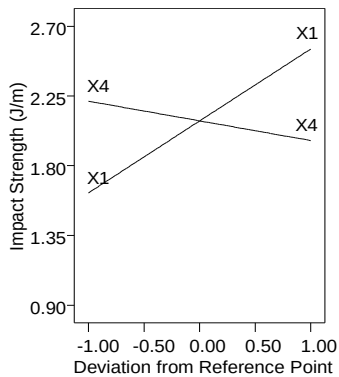

Figure 3: Perturbation plot of ENR content and mixing time to impact strength of PP/ENR blends.

Morphological Analysis

Figure 4 shows the tensile fracture surfaces of PP, PP/ENR with 30% ENR and PP/ENR with 60% ENR. The dark and bright phases represent ENR and PP, respectively. Most of the fracture surfaces show spherical shaped dimples from pulled-out of PP domains or ENR domains except for the fractograph of unfilled PP, as shown in Figure 4(a). The fractograph of the unfilled PP shows characteristics of ductile fracture under uniaxial tensile loads with the obvious pattern of shear yielding on the surface. In Figure 4(b), fracture surface of PP/ENR (70/30) blend reveals that the ENR were dispersed as domains in a continuous PP phase. This is the stage where ENR is present in the intra-spherulitic structure of PP. In Figure 4(c), the ENR phase started to enlarge its size and formed bigger ENR domains in PP matrix. In addition, there were smaller PP domains (PP particles) situated in ENR phases as depicted in Figure 4(d). It clearly shown the condition where occlusions of ENR phase started to form as the concentration of rubber matrix higher than 50 wt% in the blend; with the presence of PP particulates trapped in the ENR regions.

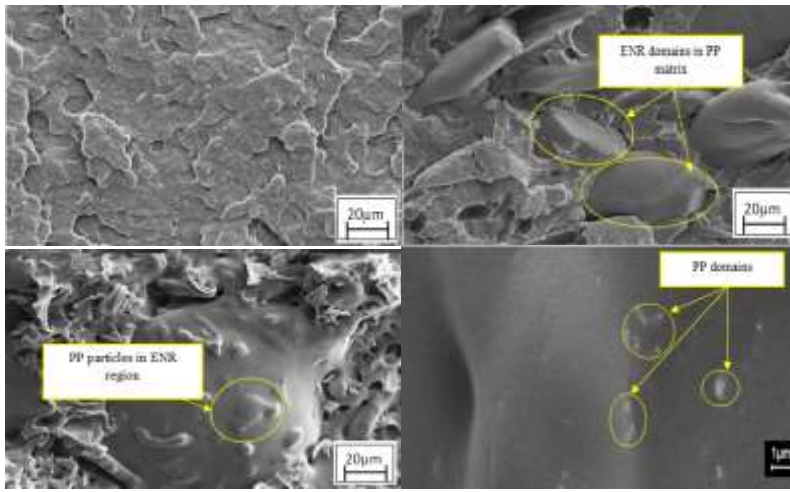

Figure 4: Scanning electron micrograph of (a) unfilled PP, (b) 70/30 PP/ENR and (c) 40/60 PP/ENR at magnification of 500x (d) 40/60 PP/ENR at magnification of 5000x

Conclusion

As a conclusion, mixing parameters as well as formulation play major roles in the mechanical properties of PP/ENR blend. Suitable combination of mixing parameters could increase miscibility of the blend and avoid chains degradation during processing. Besides, it was found that PP/ENR at high rubber content shows an improvement in its toughness and flexibility. In contrast, the addition of rubber content lowers the tensile strength of the blend due to the reduction in rigidity associated to the PP chains. These properties are also contributed by PP ability to be strain-crystallized. The presence of cross linking in the rubber matrix of PP/ENR blends imparts elastic behavior to PP matrices due to rubber-like properties introduced by the ENR.

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