OPTIMISATION ON PROPERTY ENHANCEMENT OF POLYPROPYLENE/ORGANOCLAY NANOCOMPOSITES

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Abstract

Three grades of polypropylene (PP) with different melt viscosities and three types of organomodified montmorillonite (MMT) clays with varied interlayer spacings were used to prepare PP/organoclay nanocomposites in the presence of maleated PP(MAPP). Taguchi design of experiments (DoE) was employed as an effective engineering statistical method to investigate the enhancement of mechanical properties of nanocomposites in relation to the selected materials. Individual optimum factors to promote each of tensile, flexural and impact properties were then determined using a Pareto analysis of variance (ANOVA). PP grade was found to be the most significant factor to improve the overall mechanical properties with the lowest PP viscosity demonstrating the best performance. Clay content appeared to play the second important role for the enhancement of tensile and flexural properties. Although clay type and MAPP content were determined as two non-significant factors for the tensile and flexural properties, MAPP content greatly influenced the impact strengths of nanocomposites.

1 Introduction

The enhancement of mechanical properties of PP/organoclay nanocomposites normally lies in two categories of factors, namely processing parameters such as temperature profile, screw speed, feed rate, die pressure in twin screw extrusion and injection moulding processes as well as grades of polymers, additives, compatibilisers and their respective contents. However, a great number of influential factors can lead to the complexity of the experimental work. In this study, Taguchi DoE method was used to concentrate on the evaluation of the effects on the use of different combinations of PP/organoclay nanocomposites in the presence of MAPP as the compatibiliser. The processing parameters were kept the same in the entire DoE work to keep it simple. Finally, Pareto analysis of variance (ANOVA) was employed to identify optimum factors for enhancing the mechanical properties of prepared nanocomposites.

2 Experimental Details

2.1 Materials

Three polypropylenes with various melt flow indices (MFI), denoted as PP-Co M710, PP-Hom Y130 and PP-Hom H380F, were provided by Clariant (New Zealand) Ltd. PP-Co M710 is a high molecular weight PP copolymer (MFI=0.6g/10min) with the excellent impact property. PP-Hom Y130 and PP-Hom H380F are medium and low molecular weight PP homopolymers (MFI=4.0 and 25g/10min, respectively). MAPP Exxelor™ PO 1020 as the compatibiliser was obtained from ExxonMobil Chemical (Germany) with a high maleic anhydride (MA) content (MFI=~430g/10min). All PP and MAPP had the nominal density of 0.9g/cm^3.

Three organomodified montmorillonite (MMT) NANOLIN™ clays were supplied from Zhejiang Feng Hong Clay Chemicals Co., Ltd, China, denoted as DK1N, DK2 and DK4 with the nominal density of 1.8 g/cm^3 and the interlayer spacings of about 2.29, 2.25 and 3.56 nm, respectively.

2.2 Melt Processing

Twice-direct compounding (TDC) was used for the prepared nanocomposites by extending the residence time in twin screw extrusion in order to facilitate the good organoclay dispersion within PP matrices. PP and MAPP pellets were first separately melt compounded and organoclay powders were fed downstream into the melted mixture at 185-210^{o}C and 200rpm in a co-rotating intermesh twin screw extruder DSE 20 (D=20 mm, L:D=40, BRABENDER OHG, Germany). All prepared nanocomposite batches were then recompounded at 100 rpm in the same conditions. At the first step of TDC, MAPP and PP pellets were fed simultaneously using two granule feeders, Plasticolor 1000 and 2200 (WOYWOD GmbH& Co. Vertriebs KG, Germany). Organoclay powders were then fed with a SCHENCK AccuRate model 300 powder feeder (SCHENCK AccuRate, Wisconsin, USA) in a fixed agitation setting of 600. Furthermore, an engraver (Ideal Industries Inc., Illinois, USA) was attached to the central rod of the powder feeder, working as a vibrator, to allow the better material flow and break up clay agglomerates. At the second step, the initially prepared nanocomposite pellets were again fed into the extruder using a Plasticolor 2200 feeder with PP and nanocomposite pellets both being fed at 3.0 kg/hr.

The final dried nanocomposite pellets were further injection moulded using a BOY 50A injection moulder (DR. BOY GmbH, Neustadt, Germany) at 190-210^{o}C with a die temperature of 25^{o}C and injection pressure of about 60-80 bars. All the raw materials and compounded nanocomposite pellets were dried in a vacuum oven at 80 ^{o}C for over 16 hrs.

2.3 Mechanical Testing

Injection moulded nanocomposite samples were subjected to mechanical testing to determine their tensile, flexural and impact properties according to ASTM D638, D790 and D6110, respectively. Tensile and flexural tests were conducted on a universal tensile machine (Instron 1185) and charpy impact tests were performed on a RESIL 25 pendulum impact testing machine (CEAST SpA, Torino, Italy). All the test samples were placed in a vacuum desiccator for over 24 hrs prior to the mechanical testing. Note that the reported results are based on the average data of five samples with calculated standard deviations.

3 Experimental results and Data Analysis

3.1 L_9 DoE layout

Taguchi method is a well-known engineering statistical design of experiments to optimise the product and process conditions with the minimal sensitivity to the various causes of variation and also produces high-quality products with low development and manufacturing costs [1]. Taguchi method normally consists of the signal-to-noise ratio and orthogonal arrays to measure the variation emphasised quality and accommodate many design factors simultaneously.

The goal of this Taguchi DoE work was to detect the significant factors for achieving the maximum enhancement of mechanical properties of the described nanocomposites. The effects of using different combinations of PP and organoclays with varied types and contents in the presence of MAPP were evaluated. As mentioned earlier, all the process conditions remained the same in twin screw extrusion and injection moulding processes.

Four factors of clay type and content, MAPP content and PP type with three different levels of low, medium and high settings have been selected in the DoE work, Table 1. This setup results in a typical three-level four factors L_9 Taguchi DoE layout compared to a traditional full-factorial 81 trials to complete the entire experimental programme. The factorial interactions have not been considered to keep the analysis simple. The details of L_9 DoE layout in 9 trials are also displayed in the sequence of random order trial numbers, Table 2. Furthermore, final results for all the mechanical properties are depicted in Figs. 1(a)-(e).

A “larger-the-better” characteristic formula [1-2] has been used to identify the combination of optimum factors to enhance the mechanical properties of formulated nanocomposites:

$$S/N = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \qquad (1)$$

where S/N is the signal-to-noise ratio, n is the number of samples in each trial and y is the measured response value, namely the normalised moduli or strengths over those of corresponding neat PP.

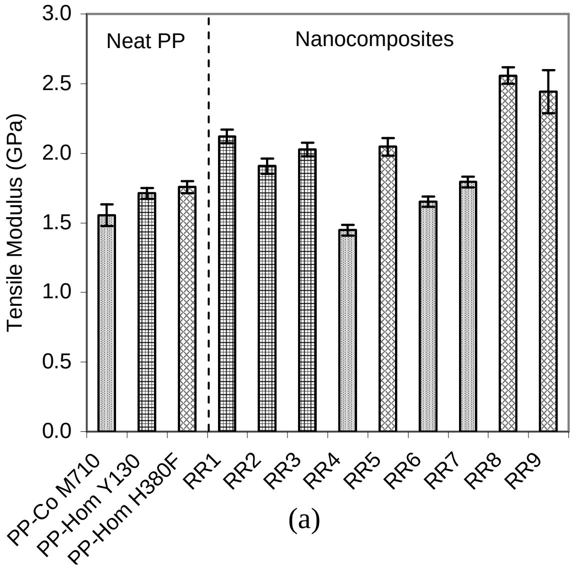
Table 1. Four factors and three levels in L_9 DoE

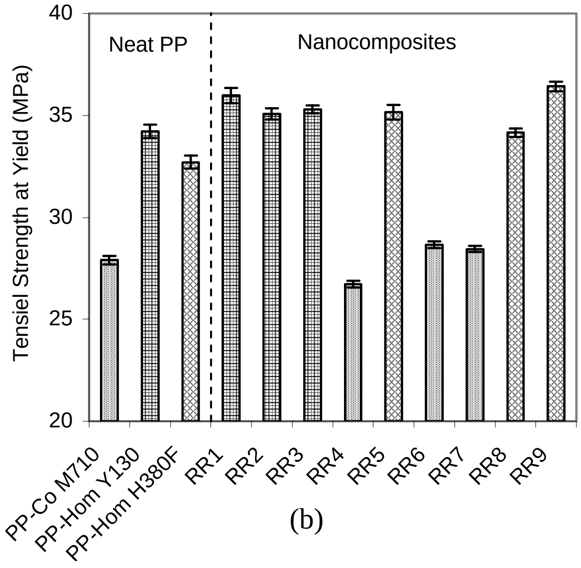
Factor	Level 1	 2	 3
A: Clay type	DK1N	DK2	DK4
B: Clay content (wt%)	3	5	10
C: MAPP content (wt%)	5	10	20
D: PP type	PP-Co M710	PP-Hom Y130	PP-Hom H380F

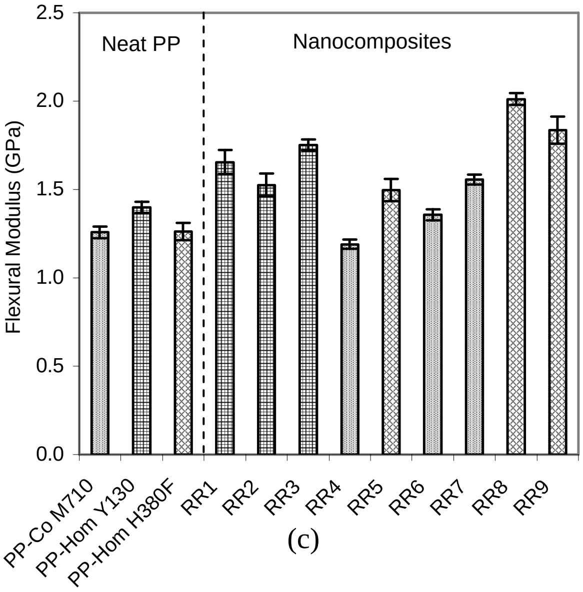
Table 2. L$_9$ DoE table for twice-direct compounding

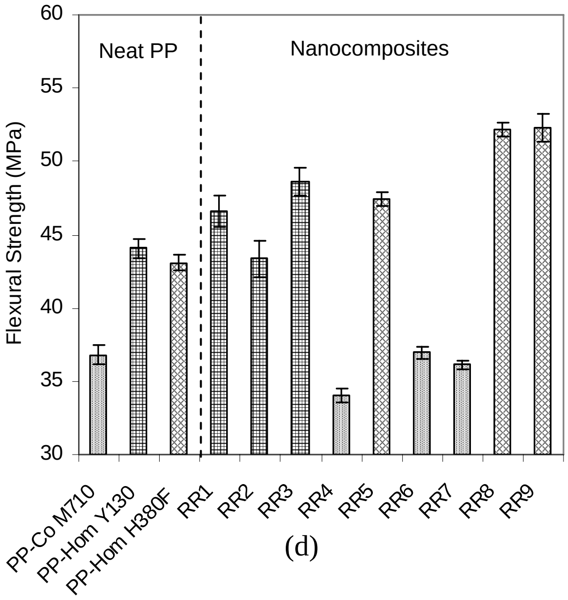
Random number	Standard number	Symbol
1	2	*RR1: DK1N/MAPP/PP-Hom Y130 (5/10/85)
2	7	RR2: DK4/MAPP/PP-Hom Y130 (3/20/77)
3	6	RR3: DK2/MAPP/PP-Hom Y130 (10/5/85)
4	1	RR4: DK1N/MAPP/PP-Co M710 (3/5/92)
5	4	RR5: DK2/MAPP/PP-Hom H380F (3/10/87)
6	5	RR6: DK2/MAPP/PP-Co M710 (5/20/75)
7	9	RR7: DK4/MAPP/PP-Co M710 (10/10/80)
8	3	RR8: DK1N/MAPP/PP-Hom H380F (10/20/70)
9	8	RR9: DK4/MAPP/PP-Hom H380F (5/5/90)

Note: *RR1 represents random trial 1 in twice-direct compounding. Figures in parentheses such as (5/10/85) indicate the contents (wt%) of organoclays, MAPP and PP in nanocomposites, respectively.









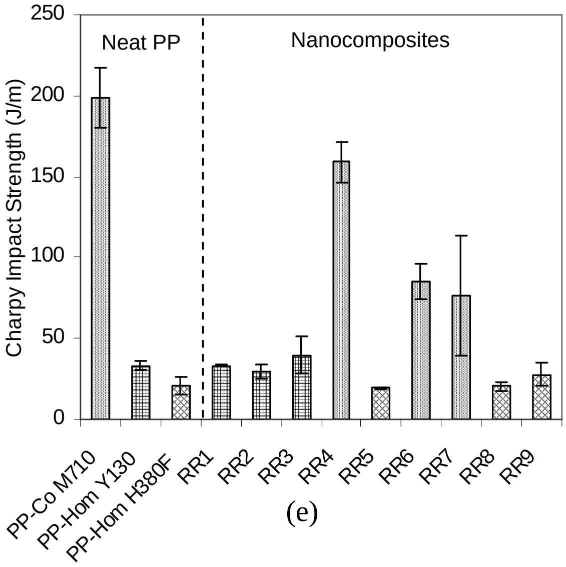
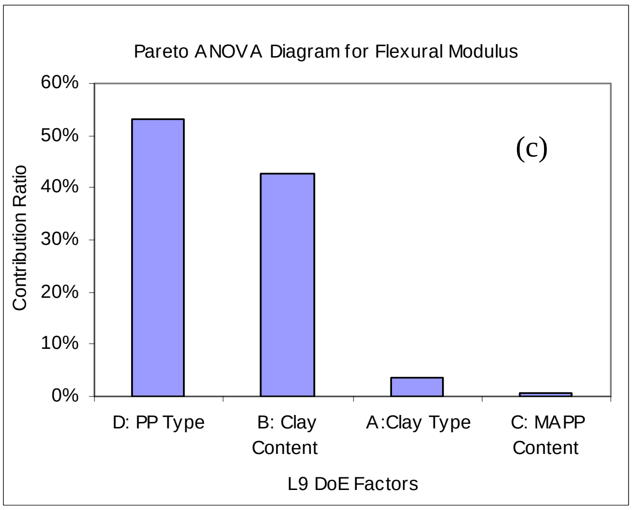


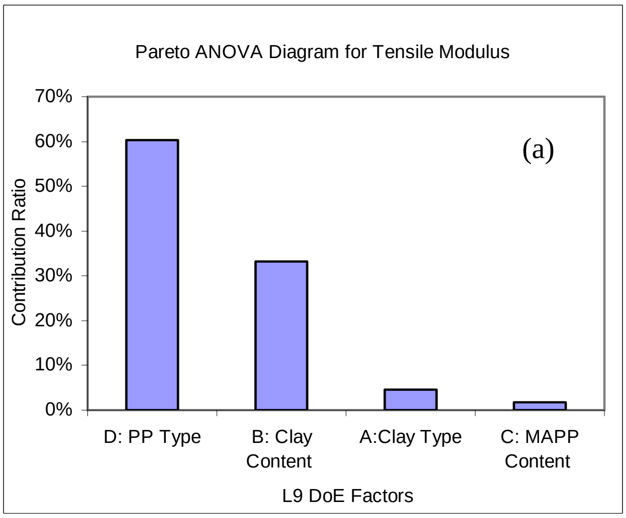
Fig.1. Mechanical properties of nanocomposites and corresponding neat PP

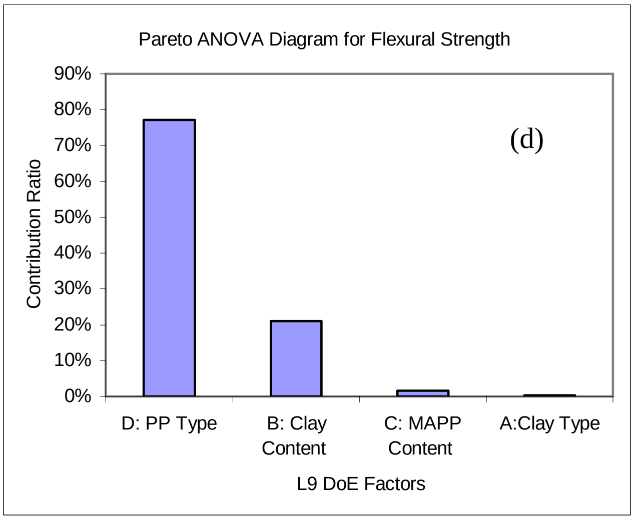
3.2 Pareto ANOVA

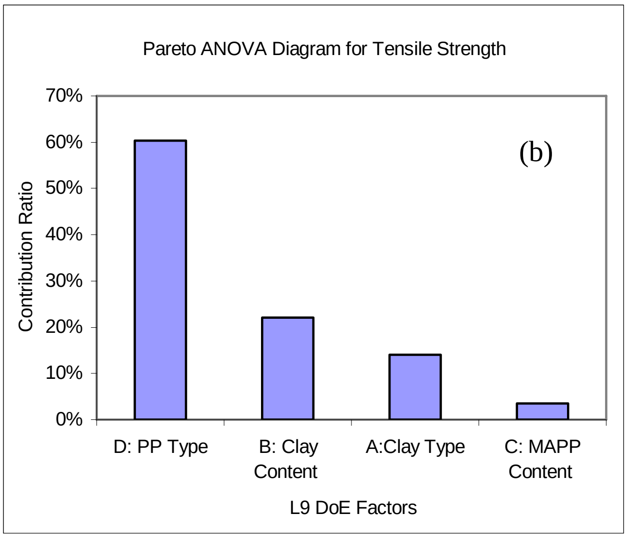
3.2.1 Evaluation of Significant Factors

Pareto ANOVA [1,3], as a simplified ANOVA analysis, uses Pareto principle (i.e. the 80/20 rule) to evaluate the results of parameter design without the employment of ANOVA table and F-tests. Moreover, significant factors and interactions as well as the relevant optimum level of factors could be easily detected by this special Pareto-type analysis. The general criterion to determine the significant factors in this study is based upon the cumulative contribution ratio (expressed in %) to be about 90%. Economical and technical issues are considered for the other non-significant factors.









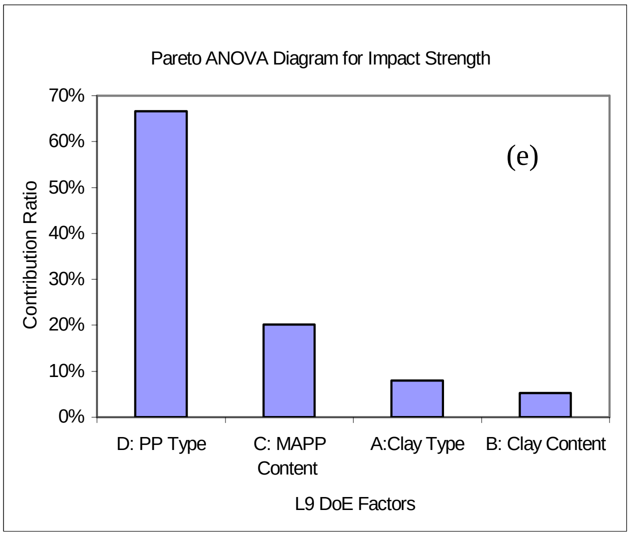


Fig. 2. Pareto ANOVA analysis for the enhancement of mechanical properties of nanocomposites

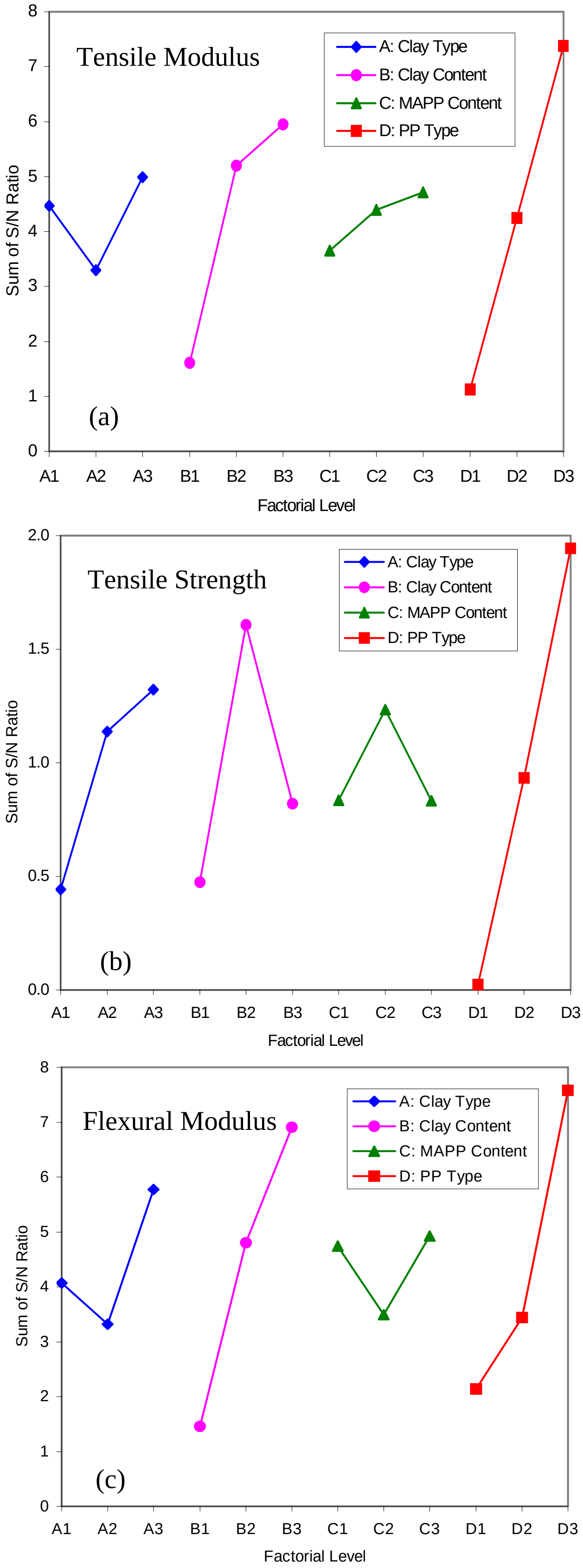
The Pareto ANOVA technique was performed for each of mechanical parameters and the related Pareto ANOVA diagrams are demonstrated in Fig. 2. In order to achieve the maximum tensile modulus, PP type (factor D) and clay content (factor B) appear to have the significant effects with the contribution ratios of 60.4% and 33.2%, respectively, Fig. 2(a). The effects of clay type (factor A) and MAPP content (factor C) are trivial with the sum of the contribution ratios less than 10%. Consequently, it is suggested that PP type and clay content greatly influence the enhancement of tensile modulus according to computed cumulative contribution ratio beyond 90%. Similar tendency of Pareto ANOVA diagram to improve tensile strength is depicted in Fig. 2(b) despite the addition of clay type (factor A) becoming the third significant factor.

Pareto ANOVA diagram for flexural modulus is exhibited in Fig. 2(c), again resulting in a similar trend for significant factors to those for tensile modulus. In particular, clay content (factor B) demonstrates even stronger effects (contribution ratio: 42.6%) than the same factor for tensile modulus (contribution ratio: 33.2%) shown in Fig. 2(a). The enhancement of flexural modulus mainly relies on PP type (factor D) and clay content (factor B). Pareto ANOVA diagram for flexural strength in Fig. 2(d) presents more distinct reflection from the previous counterparts even though the significant factorial effects are still dependent upon PP type (factor D) and clay content (factor B). The effect of PP type here is more predominant with the contribution ratio up to 77.1% compared to 21.0% for that of clay content.

Nevertheless, the enhancement of impact strength may lie in PP type (factor D), MAPP content (factor C) and clay type (factor A), Fig. 2(e). It appears that MAPP content, as the second significant factor, plays a more important role to promote the impact property in contrast to tensile and flexural properties.

3.2.2 Determination of Optimum Conditions

It is well understood for the “larger-the-better” characteristic in Taguchi design of experiments method that mathematically the higher the sum of S/N ratio is, the better response for the factorial effects can be obtained. Hence, the sum of S/N ratio diagrams to enhance each of the mechanical properties of nanocomposites are depicted in Fig. 3. It is worth noting that this study focuses solely on the optimisation to obtain individual maximum properties since the global optimisation to maximise all the properties of nanocomposites together would be too difficult to achieve and might be compromising some important properties.



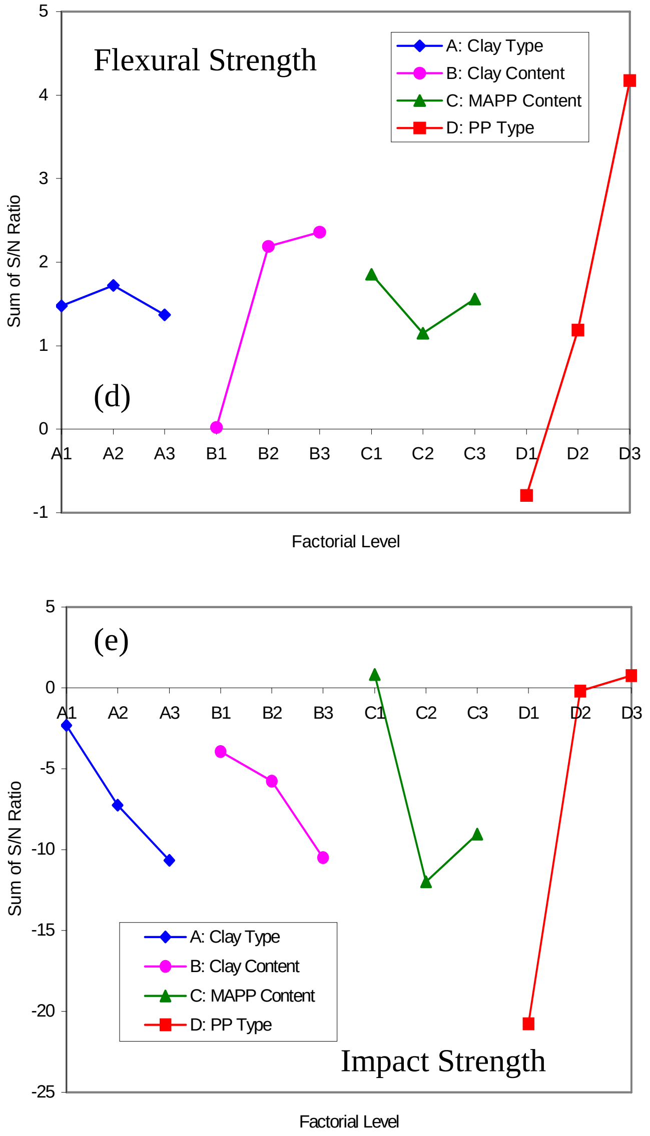


Fig. 3. Sum of S/N ratio diagrams for the enhancement of mechanical properties of nanocomposites

As is evident from Fig. 3(a), the best combination for the significant factors to get the highest value of tensile modulus is at level 3 of clay content (10 wt% of organoclays) and level 3 of PP type (PP-Hom H380F). Thus, the overall optimum condition for all factors becomes $A_3B_3C_3D_3$, namely at level 3 for both clay type (i.e. DK4 organoclays) and MAPP content (20 wt% of MAPP) for non-significant factors. To maximise the tensile strength, the corresponding best combination shown in Fig. 3(b) is at level 3 of clay type (DK4 organoclays), level 2 of clay content (5 wt% of organoclays) as well as level 3 of PP type (PP-Hom H380F), which overall leads to $A_3B_2C_2D_3$ including MAPP content (10wt%) as the non-significant factor.

In terms of enhancing the flexural modulus, the best combination is at level 3 for both clay content (10 wt% of organoclays) and PP type (PP-Hom H380F), Fig. 3(c). Therefore, the overall optimum condition for all factors becomes $A_3B_3C_3D_3$. On the other hand, in order to get the highest flexural strength, the best combination for the significant factors should be at both level 3 of clay content (10 wt% of organoclays) and PP type (PP-Hom H380F), Fig. 3(d). Considering the non-significant effects of MAPP content (factor C) and clay type (factor A), the overall optimum condition of all factors is indicated as $A_2B_3C_1D_3$.

In contrast, Fig. 3(e) displays the majority of negative values calculated as the sum of S/N ratios at each factor level for the impact strength. This implies that the inclusion of organoclays in PP matrices could deteriorate the impact properties, particularly for PP-Co M710 based nanocomposites. Hence, the best combination to get the highest impact strength is at level 1 of MAPP content (5 wt% of MAPP), level 3 of PP type (PP-Hom H380F) and level 1 of clay type (DK1N organoclays) for the significant factors. Thus, the overall optimum condition for all factors becomes $A_1B_1C_1D_3$.

The final optimum factors for enhancing each of the mechanical properties of nanocomposites are summarised in Table 3, along with the respective compositions. Although MAPP content shows the non-significant effect for tensile and flexural properties in this study, the presence of MAPP is still very important for the strong interaction between organoclay particles and PP matrices through the functioning maleic anhydride groups. This can lead to the better organoclay dispersion. Furthermore, it is also suggested that the manufacturers and designers can use a relatively small amount of MAPP in nanocomposite compounding to reduce the total material cost.

Table 3. Summary of optimum factors in L_9 DoE

L_9 DoE response	Optimum factors	Composition (wt%)
Tensile modulus	$A_3B_3C_3D_3$	DK4/MAPP/PP-Hom H380F (10/20/70)
Tensile strength	$A_3B_2C_2D_3$	DK4/MAPP/ PP-Hom H380F (5/10/85)
Flexural modulus	$A_3B_3C_3D_3$	DK4/MAPP/ PP-Hom H380F (10/20/70)
Flexural strength	$A_2B_3C_1D_3$	DK2/MAPP/ PP-Hom H380F (10/5/85)
Impact strength	$A_1B_1C_1D_3$	DK1N/MAPP/ PP-Hom H380F (3/5/92)

4 Conclusions

Taguchi design of experiments method along with the Pareto ANOVA technique was found to be an effective approach for the optimisation of enhancing mechanical properties of PP /organoclay nanocomposites. Evidently, PP type played the most significant role in the enhancement of overall mechanical properties, particularly low molecular weight PP-Hom H380F being the most favourable grade. In addition, clay content was detected to be the second significant factor for enhancing the tensile and flexural properties. MAPP content and clay type were determined as two non-significant factors for tensile and flexural properties. However, MAPP content showed a strong effect on the impact property as the second significant factor (after PP type) and a high MAPP content could worsen the impact strengths of nanocomposites. Consequently, this study provides some insight to the selection of appropriate materials and their proportions in order to achieve the optimum performances (guided by the end usages) of nanocomposites produced by the melt processing method.

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