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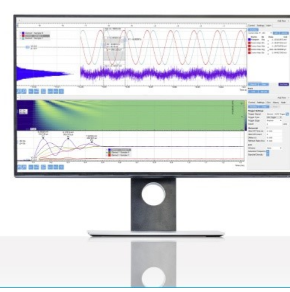

Understanding the Influence of Manufacturing and Material Parameters on the Mechanical Properties of Polymer-Clay Composites: An Exploratory Statistical Analysis

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Abstract. Polymers are used in various industrial applications due to their ease of production, light weight and ductility. Adding fillers, such as clays, improves a range of thermo-mechanical properties, however manufacturing parameters may have an influence on the composite system. This paper provides a statistical analysis on a set of previously obtained experimental tensile data with various clay fillers added to high density polyethylene (HDPE). The composite material was compounded using an extrusion process and manufactured into tensile test samples by means of hot pressing. Various manufacturing parameters (number of extrusions, press time, sample cooling method), material (polymer grade, clay type, clay weight loading) and testing parameters (strain rate) were investigated to determine their influence on the mechanical properties, specifically strength (ultimate tensile strength) and ductility (percentage elongation at failure), of the composite system. The results showed wide variability, necessitating a statistical approach. The statistical analysis concluded that all parameters, except for press time, have a statistically significant influence on the mechanical properties of interest. The conclusions and insights gained from these analyses will be used to inform a statistical design of experiments to quantify the manufacturing variability and reliability in future work.

Introduction

Polymer-clay composites have received considerable attention in recent years, both in research and industry, as they allow for the manipulation of the base polymer material to improve the thermo-mechanical properties by adding small micro- or nano-sized clay fillers [1, 2, 3, 4, 5, 6, 7]. By adding a small amount of filler ($\leq$ 5 wt%) there is an improvement in the mechanical properties compared to neat polymer [2, 3, 5, 6, 8]. However, our previous work has shown that when the filler content exceeds 10 wt% the material properties begin to degrade [9].

In addition to the material system, the manufacturing process has an influence on the composite morphology and consequently the thermo-mechanical properties [6, 7, 8]. This is largely due to the change in polymer-clay morphology (i.e. type of dispersion, ductility, etc.) which is dependent on the manufacturing procedure [6, 8]. Albdiry *et al.* [8] compared various experimental studies, each using different manufacturing methods, and concluded that the mechanical properties of the resulting polymer-clay composites are affected by the manufacturing method. Gaining more insight and understanding into the effects of the manufacturing process on the mechanical properties will allow for improved composite design practices [8].

The aim of this study is therefore to gain insight into the effect of various manufacturing and composite material parameters on the mechanical properties. This will be done by investigating and understanding a historical data set (collected between 2016 and 2018) to identify any main characteristics, patterns or anomalies using statistical analysis techniques.

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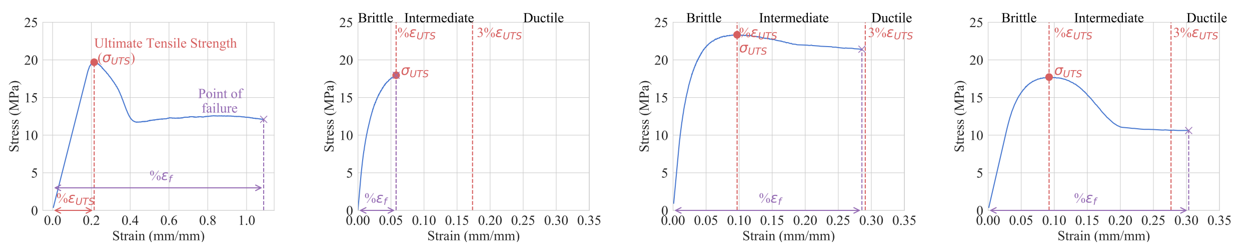
Materials and Methods

The polymer-clay composite systems in this study were compounded using a twin-screw extruder followed by compression moulding to manufacture the tensile test samples [10, 11, 12, 13]. The composite material, manufacturing and testing system parameters considered in this study are: (1) different grades of HDPE, (2) different clay types, (3) clay loading, (4) number of extrusions, (5) press time, (6) sample cooling method and (7) strain rate. The reader is referred to [14] for a more detailed description of the manufacturing, testing and data processing.

The mechanical properties of interest were determined from the processed stress-strain graphs as shown in Fig. 1a where the Ultimate Tensile Stress (σ_{UTS}) is the maximum stress the material can achieve and the percentage elongation to failure ($\%\varepsilon_f$) is the strain measured at the recorded point of failure. In each of the studies the tensile testing conditions were different and as a result the variability in $\%\varepsilon_f$ is large. The failure mode was therefore grouped into three categories resulting in 17 Brittle (if $0 < \%\varepsilon_f \leq \%\varepsilon_{UTS}$, cf. Fig. 1b), 323 Intermediate (if $\%\varepsilon_{UTS} < \%\varepsilon_f \leq 3(\%\varepsilon_{UTS})$, cf. Fig. 1c) and 157 Ductile samples (if $\%\varepsilon_f > 3(\%\varepsilon_{UTS})$, cf. Fig. 1d).



(a) Defining variables (HDPE B7750/10 wt% DHT4A)

(b) Brittle Failure (HDPE B7750/2.5 wt% Alcamizer)

(c) Intermediate Failure (HDPE B7750/2.5 wt% Alcamizer)

(d) Ductile Failure (HDPE B7750/2.5 wt% Alcamizer)

FIGURE 1: Stress-strain curve defining the different variables and failure types in this study.

Statistical Analysis

The reader is referred to [14] for further details pertaining to the statistical analysis, including the summary statistics for the σ_{UTS} and $\%\varepsilon_f$ responses. The number of observations for the different combinations of experimental conditions is very different, which indicates that the experiments were not performed according to a statistical experimental design, i.e. the experimental conditions are unbalanced. The effects of polymer grade, clay type, clay loading, number of extrusions, press time and strain rate on the responses, σ_{UTS} and failure mode, were of interest. For the statistical analysis sample cooling was not considered as there were fewer data points (9 furnaced and 12 quenced) compared to 555 air cooled data points. Due to the unbalanced nature of the experimental study, only the main or linear effects of the variables could be statistically quantified, but no two-order interactions.

Statistical Analysis for σ_{UTS}

The effects of the variables on σ_{UTS} are quantified through analysis of variance (ANOVA) [16] with the results shown in Table 1. ANOVA is a statistical procedure to determine whether several population means are equal where the p-value (Pr(>F)) indicates the probability that the effect of the variable on the response is only by chance. For example, a p-value smaller than 0.05 indicates that the variable has a significant effect on the response with more than 95% confidence. From Table 1, it is clear that polymer grade, clay type, number of extrusions and strain rate have a statistically significant effect on σ_{UTS} with at least 97% confidence. Clay loading and press time don't have any significant effect on σ_{UTS}.

Table 2 provides the linear model for σ_{UTS} as a function of the experimental variables. The low adjusted $R^2 = 0.4515$ indicates that the model cannot be used for predicting σ_{UTS}. The standard error of the model (2.6) is very small compared to the overall mean of 20.25 ((Intercept) first entry in Table 2) which indicates that statistically significant effects of the variables on σ_{UTS} can be quantified. The values in the Estimate column for the variables are the average change in σ_{UTS} for the specific level of the variable compared to its first level. For example, clay loading has on average a negative effect on σ_{UTS} which decreases by 0.09 units for a 1 wt% increase in loading. All the effects of the variables are statistically significant with 95% confidence except for polymer grade C7260 and A7260 at a 5 wt% level, neat HDPE and Alcamizer 1 and press time which have no statistically significant effect.

TABLE 1: Analysis of variance for σ_{UTS}. A significant effect is when Pr(>F)< 0.05.

	Df	Sum Sq	Mean Sq	F-value	Pr(>F)	
Polymer.Grade	3	1084	361.4	53.419	<2e-16	***
Clay.Type	3	581	193.6	28.617	<2e-16	***
Clay.Loading	1	20	20.5	3.023	0.0826	.
Extrusions	2	47	23.7	3.505	0.0307	*
Strain.Rate	1	1539	1539.2	227.485	<2e-16	***
Press.Time	1	4	4.5	0.663	0.416	
Residuals	564	3816	6.8			

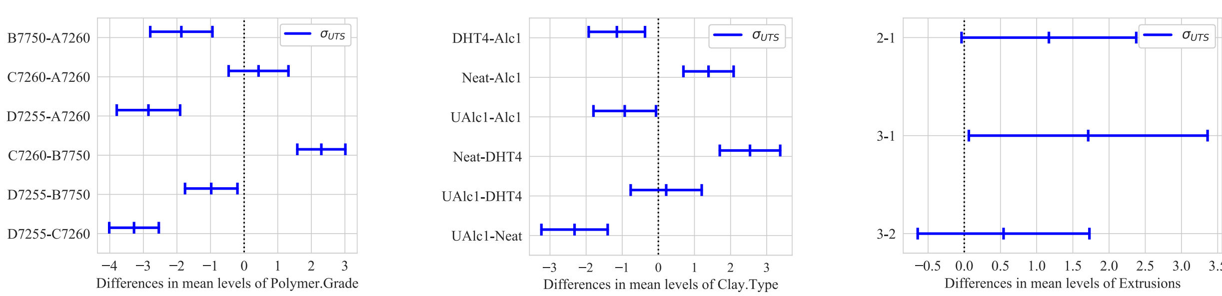
Significance Codes: '***': 0-0.001, '**': 0.001-0.01, '*': 0.01-0.05, '.':0.05-0.1, ' ': 0.1-1.0

TABLE 2: Linear model for σ_{UTS} (Type2: Alc1 = Alcamizer 1; DHT4 = DHT4-A; Neat = Neat; UAlc1 = Uncoated Alcamizer 1). A significant effect is when Pr(> |t|)< 0.05.

	Estimate	Std. Error	t-value	Pr(> |t|)	
(Intercept)	20.254431	0.737995	27.445	< 2e-16	***
Polymer.GradeB7750	-1.792339	0.55417	-3.234	0.00129	**
Polymer.GradeC7260	-0.921277	0.545691	-1.688	0.09191	.
Polymer.GradeD7255	-2.97388	0.572045	-5.199	2.81E-07	***
Type2DHT4	-1.033413	0.328535	-3.146	0.00175	**
Type2Neat	0.021626	0.385145	0.056	0.95524	
Type2UAlc1	-0.930066	0.352656	-2.637	0.00859	**
Clay.Loading	-0.092029	0.045094	-2.041	0.04174	*
Extrusions2	1.45562	0.628646	2.315	0.02094	*
Extrusions3	1.720001	0.708387	2.428	0.01549	*
Strain.Rate	0.022229	0.001478	15.043	< 2e-16	***
Press.Time	0.015219	0.018697	0.814	0.41602	

Significance Codes: '***': 0-0.001, '**': 0.001-0.01, '*': 0.01-0.05, '.':0.05-0.1, ' ': 0.1-1.0
Residual standard error: 2.601 on 564 degrees of freedom
Multiple R-squared: 0.462, Adjusted R-squared: 0.4515
F-statistic: 44.03 on 11 and 564 DF, p-value: <2.2e-16

The Tukey Honest Significant Difference (HSD) test is used to provide multiple comparisons between all the levels of the variable of interest [16]; and is based on the Studentized Range Statistic to provide a family-wise true significant difference test. The Tukey HSD test results are shown in Fig. 2 where the intervals represent 95% confidence intervals (CI) for the mean difference in σ_{UTS} between the two levels of interest. If the CI does not contain zero, the two levels are statistically significantly different. All levels are statistically significantly different except grade C7260 and A7260 (cf. Fig. 2a), Uncoated Alcamizer 1 and DHT4-A (cf. Fig. 2b); and 2-1 and 3-2 extrusions (c.f. Fig. 2c).



(a) σ_{UTS} for Polymer Grade **(b)** σ_{UTS} for Clay Type **(c)** σ_{UTS} for Number of Extrusions

FIGURE 2: Tukey HSD test considering the statistical significance for different material and manufacturing variables on the σ_{UTS}.

Statistical Analysis for Failure Mode

A Linear Discriminant Analysis (LDA) technique is used which constructs linear functions of the variables to separate the groups using a linear boundary [17]. The boundary is fixed by coefficients (LD1, LD2) and the value of these coefficients indicates the degree of influence of a design variable on the defined groupings. The 2016 data was omitted as the reported $\%\varepsilon_f$ was only available up to UTS and therefore not a meaningful measure. The number of observations for the number of extrusions (1 extr: 5, 2 extr: 492, 3 extr: 0) and strain rate (5 mm/min: 546, 100 mm/min: 15, 500 mm/min: 15) was skewed and therefore omitted from the analysis.

LDA Considering All Three Groups

An LDA model was developed by modelling the failure mode grouping as a function of the polymer grade, clay type, clay loading and press time considering all three failure mode groups. The model struggled to accurately predict the Brittle and Ductile classes and only achieved an accuracy of 71.35% for the training data set and 65.49% for the test data set. The poor performance of the model to accurately predict the Brittle and Ductile groups may be due to the few observations available for these groups (only 17) compared to the Intermediate group (323 observations). The reader is referred to [14] for further details regarding this analysis.

LDA Omitting the Brittle Group

In the second LDA analysis, the Brittle group is omitted due to the smaller number of observations and the model struggling to predict an observation as Brittle. The failure mode group means are provided in Table 3. The prior probabilities for the Ductile (0.318) and Intermediate (0.682) groups are determined as the proportion of observations in the dataset. HDPE B7750 and Alcamizer 1 are used as the baseline for the categorical variables polymer grade and clay type and therefore don't appear in Table 4.

Based on the linear discriminant coefficient (LD1), clay type has the highest value which indicates that it has the largest influence on the material failure mode. The dataset was divided into a training (randomly selecting 80% of the data) and test data set (remaining 20%) for testing of the model. The resulting confusion matrices are shown in Tables 5 and 6. Both the training and test data set had a 72.92% accuracy. Considering the test data in Table 6, the model is able to correctly predict 52 observations as Intermedate, with only 17 Ductile observations predicted as Intermediate. Similarly, 18 Ductile observations were correctly grouped and 9 were incorrectly grouped as Intermediate.

TABLE 3: Means for the different groups of failure mode omitting the Brittle group.

	Intermediate	Ductile
Polymer.GradeC7260	0.324	0.574
Polymer.GradeD7255	0.317	0.189
Clay.TypeDHT4-A	0.298	0.115
Clay.TypeNeat	0.221	0.369
Clay.TypeUncoated Alcamizer 1	0.218	0
Clay.Loading	4.323	3.381
Press.Time	30.706	31.393

TABLE 4: Coefficients for the linear discrement model for failure mode omitting the Brittle group.

	LD 1
Polymer.GradeC7260	-0.935304341
Polymer.GradeD7255	0.13178971
Clay.TypeDHT4-A	1.757747774
Clay.TypeNeat	0.473677118
Clay.TypeUncoatedAlcamizer1	2.587720605
Clay.Loading	-0.018098249
Press.Time	0.005923164

TABLE 5: Confusion matrix for the training data set with a 72.92% accuracy when omitting the Brittle group.

		Observed	
		Ductile	Intermediate
Predicted	Ductile	63	45
	Intermediate	59	217

TABLE 6: Confusion matrix for the testing data set with a 72.92% accuracy when omitting the Brittle group.

		Observed	
		Ductile	Intermediate
Predicted	Ductile	18	9
	Intermediate	17	52

Conclusion

Over the past few years a number of experiments were performed which considered different polymer-clay composite systems and manufacturing parameters. This has largely been a one-factor-at-a-time experimental approach trying to understand the material system and manufacturing process and its influence on the mechanical properties of interest.

Initial observations in the statistical analysis indicated that proper experimental design approaches were not considered as data was either skewed or insufficient for comparison. The ANOVA results indicated that polymer grade, clay type, number of extrusions and strain rate were statistically significant for σ_{UTS}. The linear regression model indicated polymer grade, clay type and clay loading had a negative effect on σ_{UTS}, while the number of extrusions and strain rate had a positive effect. Linear Discriminant Analysis (LDA) was considered to analyse material failure (based on $\%\varepsilon_f$) which indicated that clay type has the largest influence.

In any future study, a proper statistical design of experiments is required to fully characterise, understand and quantify any effects on the properties of polymer-clay composites.

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