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RESEARCH ARTICLE

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Statistical analysis of the effect of varying material and manufacturing conditions on the mechanical properties of high-density polyethylene/layered double hydroxide composites

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Abstract

Polymers are used in various industrial applications due to their ease of production, light weight, and ductility. Fillers such as clays are added to polymers to improve a range of factors such as material processing, thermal properties, fire retardance and cost. However, adding clays may negatively impact the mechanical performance of the composite. In addition, manufacturing parameters, for example, number of extrusions, press time, and so forth may also have an influence on the resulting composite system. This study performs a statistical analysis on a set of previously obtained experimental results, which investigated the influence of various manufacturing, material, and testing parameters on the composite mechanical properties. Exploratory data and statistical analysis techniques are applied to the historical tensile test data to gain insight into the influence on mechanical properties as well as the relationships and interactions between the parameters. Specifically, it is shown that clay loading does not have a statistically significant effect on the composite mechanical properties, which is contrary to literature. Another surprising result is the poor performance of the clay that is compatible with high-density polyethylene compared to the clay that is compatible with poly vinyl chloride. The contribution of this paper is to demonstrate the usefulness of applying statistical analysis on a large volume of data to understand the diverse correlations between the different variables.

KEYWORDS

analysis of variance, exploratory data analysis, polymer-clay composites, tensile properties

1 | INTRODUCTION

In recent years, both in research and industry, polymer-clay composites have received considerable attention. This is mainly due to their ability to manipulate the base polymer material by adding small micro- or nano-sized clay fillers (platelets, fibers or particles) to improve the thermo-mechanical properties.[1–11] By adding these clay fillers the final composite material may have improved material, thermal and electrical properties, as well as a high strength to weight ratio at lower costs, all desirable traits for various industrial applications.[1,2,4,6–10,12–14] However, even when clay is added with the intention of improving a certain set of properties for a specific application area, there is still a need to understand the effect on the mechanical properties. A number of authors have indicated that by adding a small amount of filler (≤5 wt %), significant improvements in the mechanical properties are obtained.[2,3,5,6,8–14] However, material properties can start to degrade when the filler content exceeds 10 wt %.[15] The influence of the polymer-clay material system (e.g., clay and polymer type, clay loading, dispersion and the interaction between the clay and polymer) on the mechanical properties have been the subject of much research.[3–5,12,16]

In addition to the material system, the manufacturing process has an influence on the composite morphology and consequently the thermo-mechanical properties.[6,7,12,17] Albdiry et al.[12] 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. This is largely due to the change in polymer-clay morphology (i.e., degree of dispersion, polymer chain formation, crystallinity, ductility, etc.), which is dependent on the manufacturing procedure.[6,7,12] This was illustrated in Albdiry et al.[12] where they compared various experimental studies. Each study considered different manufacturing methods, which ultimately changed the composite morphology and consequently influenced the mechanical properties. It is theoretically possible to tailor the mechanical properties of polymer-clay composites by controlling the manufacturing process and hence change the composite morphology. However, before the desired manufacturing process can be successfully controlled it is first necessary to understand the effects of manufacturing on the composite morphology and mechanical properties.

In a previous study,[18] we performed a simple statistical analysis on a set of historical tensile data. In this paper, we extend this work to gain further insight into the effect of various manufacturing and composite material parameters on the mechanical properties based on historical tensile data. This will be done in two stages:

1. Investigate and understand the data set to identify any main characteristics, patterns, or anomalies. This process is referred to as an exploratory data analysis (EDA).
2. Once we have a better understanding of the data, a statistical analysis will be conducted to quantify the observed effects.

The contribution of this paper to the field of polymer composites is to demonstrate the usefulness of applying statistical analysis methods to a large volume of data. This allows for the understanding of diverse correlations between the different variables.

2 | METHODS

The experimental data considered were collected from 2016 to 2018 as part of a larger study to better understand the composite material system and manufacturing procedure and how the mechanical properties are affected by these. This was done by focusing on different aspects of the system as part of the final year undergraduate mechanical engineering research projects at the University of Pretoria. In 2016, the aim was to investigate the influence of the number of extrusion passes and clay loading on HDPE A7260 and Alcamizer 1.[19] With the number of extrusions fixed, in 2017 the aim was to find the mechanism which causes changes in the mechanical properties by investigating different polymer grades, clay types, clay loading and varying the vertex hot press time.[20] Following this, in 2018 the number of extrusions and press time were fixed along with the clay type and polymer grade. Two research projects were defined. The first investigated the effects of higher clay loadings and again considered the influence of the number of extrusions at these higher loads.[21] The second investigated the effects of the sample cooling method and the strain rate during tensile testing.[22] Clay loading as a design variable is the only commonality between the experimental studies, except for the second study in 2018, which only considered neat HDPE.

The composite material, manufacturing and testing system parameters considered in the historical studies are summarized in Table 1. The total number of samples include the five repeated test specimens for each case investigated as per the requirements of ASTM D638 to ensure statistical significance.[23] Strain rate, press time, number of extrusions and sample cooling method are constant variables in at least three of the four experimental studies.

2.1 | Materials

One of the most versatile and widely used thermoplastics is polyethylene because of its toughness, near-zero moisture absorption, chemical inertness, low coefficient of friction, ease of processing and electrical properties.[7,24] High density polyethylene (HDPE) was chosen for the polymer matrix, with different grades considered during the different experimental studies. The polymer was procured in pellet form by Safripol, South Africa.

TABLE 1 Summary of the historical experimental studies conducted by the students indicating the design and constant variables considered.

Year	Experiment	Design variable	Constant variable	Total samples
2016	Influence of the number of extrusions and clay loading	Clay loading: 0, 5, 10 wt% No. of extrusions: 1, 2, 3	Press time: 20 min Sample cooling: Air Strain rate: 5 mm/min Clay type: Alcamizer 1 Polymer type: HDPE A7260	79
2017	Influence of the material system and press time	Polymer type: HDPE B7750, C7260, D7255 Clay type: Alcamizer 1, DHT4-A, Uncoated Alcamizer 1 Clay loading: 0, 2.5, 5, 7.5 wt% Press time: 25, 30, 35, 45 min	No. of extrusions: 2 Sample cooling: Air Strain rate: 5 mm/min	538
2018	Influence of extrusions and higher clay loadings	Clay loading: 10, 15, 20 wt% No. of extrusions: 1, 2	Press time: 25 min Sample cooling: Air Strain rate: 5 mm/min Clay type: DHT4-A Polymer type: HDPE B7750	20
2018	Influence of sample cooling method and strain rate	Sample cooling: Air, Quenched, Furnace Strain rate: 5, 100, 500 mm/min	Polymer type: HDPE C7260 Clay type: None Clay loading: 0 wt% No. of extrusions: 2 Press time: 25 min	65

To better understand the effects of the clay filler, three fillers were considered; (1) Alcamizer 1, which is developed for polyvinyl chloride (PVC) compatibility; (2) DHT4-A, which is designed for poly-olefin compatibility; and (3) an uncoated Alcamizer 1 to determine the effect of surface coating, which was obtained by removing the surfactant using a solvent. All clays were obtained from Kisuma Chemicals, The Netherlands. Literature has shown that we can expect an improvement in mechanical properties at relatively low levels of clay loading (≤5 wt%).[2,5,8–11,13,14] For this reason, the historical experimental studies mainly focused on clay loadings of 2.5, 5, and 7.5 wt%. However, as we are interested in better understanding the relationship between clay loading and degradation of mechanical properties, higher clay loadings of 10, 15, and 20 wt% were considered in a later study.

2.2 | Manufacturing

The manufacturing process is divided into two phases. The first phase is the compounding process. HDPE is pulverized into a fine powder and tumble mixed with the required clay loading in a bag for 45 min to ensure dispersion.[6] The polymer-clay mixture is then extruded into a long wire using a TK28P CFAM (28 mm 18 L/D) twin-screw extruder after which the wire is fed through a chipper to obtain pellets. This process was repeated a second time when two extrusions were required and a third time for three extrusions. The heating zone temperatures for the extruder were set to 105°C (heating zone 1), 165°C (heating zone 2), 195°C (heating zone 3), and 185°C (die heating zone).

In the second phase, the tensile testing samples are created by stacking the polymer composite pellets into specimen molds designed and manufactured by Parschau,[19] based on the ASTM D638 Type I[23] dimensions. The specimens were then compression molded using a vertex hot press at a fixed temperature of 180°C and a pressure of 15 MPa, applied in increments for the total press time specified in Table 1. The pressure increments were applied from 0 to 7.5 MPa and held for 30 s before increasing the pressure to 15 MPa for 5 min. The pressure is then dropped back to 0 MPa where it is increased to 7.5 MPa and held for 30 s before increasing it to 15 MPa, at which it is fixed for the remainder of the press time. The pressure is released back to 0 MPa before removing the mold from the vertex hot press. This incremental pressure increase, and reduction, are done to ensure that any air trapped in the mold is released to prevent air bubbles from forming in the final sample.

Finally, specimens were cured using one of three sample cooling methods: (1) air cooled at room temperature, by placing the mold in the laboratory until the mold was cool enough to touch; (2) quenched, by placing the mold immediately after removal from the press into cold water; or (3) furnaced, by placing the molds into a furnace, which was heated to 60°C before switching it off. Once the molds were cooled, the samples were removed, and the surfaces finished using a carpenter's knife and fine grade sanding paper. This is done to remove any excess material or impurities due to the pressing procedure that could potentially influence the tensile testing results.

2.3 | Tensile testing characterization

To obtain the desired mechanical properties a tensile test was conducted using a Lloyd Instruments LRX Plus 5 kN Tensile Machine according to ASTM D638.[23] For each case investigated an average of five repeated samples were tested. Tensile tests were conducted at a strain rate of 5, 100 or 500 mm/min depending on the study as described in Table 1.

The mechanical properties of interest are the first peak stress the material can achieve (σ_{FPS}), and percentage elongation to failure (ε_f), which is the strain measured at the recorded point of failure. These are illustrated in Figure 1. As the tensile testing conditions for each of the experimental studies were different, ε_f is merely considered to give an indication of the material ductility and potential material property degradation. To this end, ε_f is normalized using ε_{FPS} (the percentage elongation at the first peak stress) to obtain the normalized ε_f which can be compared across the different experimental studies. An example of the normalized ε_f calculation is shown in Figure 1. A normalized ε_f of 1 would indicate a sample that failed at the ultimate tensile stress (ε_{FPS}). Based on this definition, it is not possible to obtain a normalized ε_f value below 1. This would assume that ε_{FPS} is higher than ε_f, which is an unlikely occurrence in any material as the first peak stress will, at the very least, equal the point of failure if failure was reached before yield.

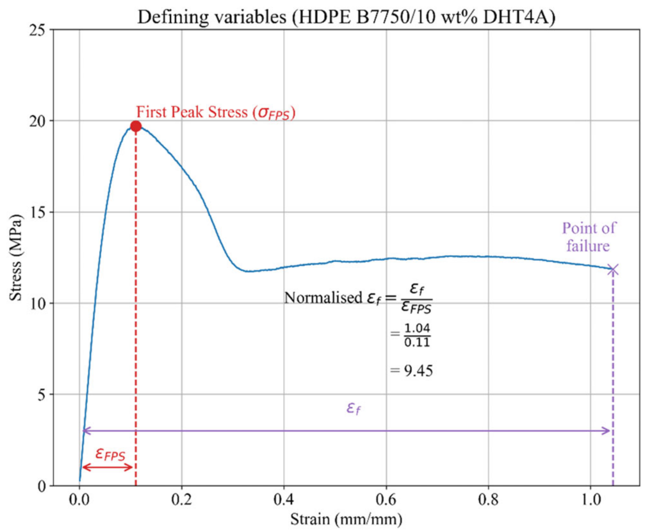

FIGURE 1 Defining tensile properties considering HDPE B7750/10 wt% DHT4A as an example.

2.4 | Statistical analysis

In any manufacturing process we expect a degree of variability and uncertainty, and the aim of the statistical analysis is to quantify the sources of this variability. That is, the percentage of variability attributable to the material system, the manufacturing methodology or random error.

For the statistical analysis, normalized ε_f is considered due to the large variability observed for ε_f in the EDA. Sample cooling is not considered as there are fewer data points for furnaced and quenched samples (9 furnaced and 12 quenched) compared to the 555 air cooled data points. For the normalized ε_f analysis, the 2016 data are excluded as results are only up to FPS.

Due to the unbalanced nature of the historical experimental study, only the main or linear effects of the variables could be statistically quantified, and no two-order interactions are considered. The statistical analysis was conducted using Python's statistical modeling module, *statsmodels*.[25]

We will provide the summary statistics for the different combinations of the experimental variables, reporting the mean, standard deviation (SD) and the standard error of the mean (SEM) for each of the experimental conditions. The SD indicates the variation in the data from the mean. Therefore, a lower SD indicates that the data are clustered about the mean, where a high SD indicates that the data are spread out. The SEM provides an indication of how far the sample mean of the data is from the true population mean, and will always be smaller than SD. A SEM value close to 0 will indicate that the sample mean is equal to the population mean, approximately.

2.4.1 | Analysis of variance (ANOVA)

Let y denote the response variable, which is either σ_{FPS} or normalized ε_f. ANOVA is a statistical procedure used to determine whether several population means are equal. This is done using an F-test, which simply compares the variability between two or more groups[26]:

$$F = \frac{\mathrm{SS_{between}}/\mathrm{Df_{between}}}{\mathrm{SS_{within}}/\mathrm{Df_{within}}}, \tag{1}$$

TABLE 2 Summary statistics of the σ_{FPS} and normalized ε_f responses for the different combinations of experimental variables, where SD is the standard deviation and SEM is the standard error of the mean.

Clay loading	Strain rate	Extrusions	Clay type	Polymer grade	Press time	Sample cooling	No. of observations	σ_{FPS}			Normalized ε_f		
								Mean	SD	SEM	Mean	SD	SEM
0	5	1	Neat	A7260	20	Air	7	18.801	1.533	0.579	-	-	-
0	5	2	Neat	A7260	20	Air	11	21.538	2.812	0.848	-	-	-
0	5	2	Neat	B7750	25	Air	5	22.275	3.43	1.534	2.152	0.787	0.352
0	5	2	Neat	B7750	30	Air	8	21.086	1.497	0.529	1.709	0.874	0.309
0	5	2	Neat	B7750	35	Air	5	23.874	2.954	1.321	2.662	0.953	0.426
0	5	2	Neat	B7750	45	Air	5	22.491	2.992	1.338	2.903	1.086	0.485
0	5	2	Neat	C7260	25	Air	20	22.395	1.964	0.439	11.316	5.604	1.253
0	5	2	Neat	C7260	25	Furnace	9	16.729	7.713	2.571	6.504	5.885	1.962
0	5	2	Neat	C7260	25	Quenched	11	18.778	2.669	0.805	10.719	3.346	1.009
0	5	2	Neat	C7260	30	Air	5	21.563	3.478	1.555	2.522	0.728	0.326
0	5	2	Neat	C7260	35	Air	5	21.24	1.992	0.891	3.431	0.407	0.182
0	5	2	Neat	C7260	45	Air	5	20.395	2.977	1.331	2.543	1.42	0.635
0	5	2	Neat	D7255	25	Air	5	20.145	2.13	0.952	3.153	0.696	0.311
0	5	2	Neat	D7255	30	Air	5	19.913	2.428	1.086	2.551	0.651	0.291
0	5	2	Neat	D7255	35	Air	5	18.758	3.56	1.592	2.195	0.825	0.369
0	5	2	Neat	D7255	45	Air	5	19.643	3.437	1.537	2.892	0.127	0.057
0	5	3	Neat	A7260	20	Air	10	21.725	3.086	0.976	-	-	-
0	100	2	Neat	C7260	25	Air	14	26.486	3.436	0.918	2.478	0.774	0.207
0	100	2	Neat	C7260	25	Quenched	1	25.373	-	-	6.818	-	-
0	500	2	Neat	C7260	25	Air	15	31.73	1.236	0.319	1.067	0.073	0.019
2.5	5	2	Alcamizer 1	B7750	25	Air	5	20.822	3.343	1.495	3.047	0.32	0.143
2.5	5	2	Alcamizer 1	B7750	30	Air	5	19.36	1.7	0.76	3.025	0.148	0.066
2.5	5	2	Alcamizer 1	B7750	35	Air	5	20.545	1.15	0.514	2.976	0.029	0.013
2.5	5	2	Alcamizer 1	B7750	45	Air	5	19.122	2.644	1.183	2.371	1.004	0.449
2.5	5	2	Alcamizer 1	C7260	25	Air	5	22.147	2.361	1.056	2.936	0.565	0.253
2.5	5	2	Alcamizer 1	C7260	30	Air	5	22.581	2.941	1.315	2.991	1.041	0.466
2.5	5	2	Alcamizer 1	C7260	35	Air	5	23.491	1.224	0.547	3.199	1.175	0.526
2.5	5	2	Alcamizer 1	C7260	45	Air	5	22.393	1.233	0.551	3.245	0.181	0.081
2.5	5	2	Alcamizer 1	D7255	25	Air	5	17.708	1.802	0.806	3.28	0.54	0.242

TABLE 2 (Continued)

Clay loading	Strain rate	Extrusions	Clay type	Polymer grade	Press time	Sample cooling	No. of observations	σ_{FPS}			Normalized ε_f		
								Mean	SD	SEM	Mean	SD	SEM
2.5	5	2	Alcamizer 1	D7255	30	Air	5	19.583	1.515	0.677	2.424	1.06	0.474
2.5	5	2	Alcamizer 1	D7255	35	Air	5	17.077	0.832	0.372	2.783	0.887	0.397
2.5	5	2	Alcamizer 1	D7255	45	Air	5	18.177	1.034	0.463	2.409	0.82	0.367
2.5	5	2	DHT4-A	B7750	25	Air	5	17.374	1.344	0.601	1.713	0.553	0.247
2.5	5	2	DHT4-A	B7750	35	Air	5	20.054	1.418	0.634	2.016	0.244	0.109
2.5	5	2	DHT4-A	C7260	25	Air	5	20.86	1.452	0.649	2.437	0.825	0.369
2.5	5	2	DHT4-A	C7260	35	Air	5	20.134	0.878	0.393	4.103	2.288	1.023
2.5	5	2	DHT4-A	D7255	25	Air	5	18.111	2.32	1.038	2.537	0.799	0.357
2.5	5	2	DHT4-A	D7255	35	Air	5	17.806	2.076	0.928	2.728	0.1	0.045
2.5	5	2	Uncoated Alcamizer 1	B7750	25	Air	5	19.345	1.048	0.469	2.146	0.539	0.241
2.5	5	2	Uncoated Alcamizer 1	B7750	35	Air	5	19.904	3.108	1.39	1.692	0.282	0.126
2.5	5	2	Uncoated Alcamizer 1	C7260	25	Air	5	18.934	3.09	1.382	1.406	0.245	0.109
2.5	5	2	Uncoated Alcamizer 1	C7260	35	Air	5	21.414	2.41	1.078	1.385	0.42	0.188
2.5	5	2	Uncoated Alcamizer 1	D7255	25	Air	5	18.886	1.31	0.586	1.075	0.124	0.055
2.5	5	2	Uncoated Alcamizer 1	D7255	35	Air	5	17.429	1.557	0.696	1.729	0.445	0.199
5	5	1	Alcamizer 1	A7260	20	Air	8	22.284	0.596	0.211	-	-	-
5	5	2	Alcamizer 1	A7260	20	Air	9	22.693	0.803	0.268	-	-	-
5	5	2	Alcamizer 1	B7750	25	Air	5	19.121	0.816	0.365	2.73	0.53	0.237
5	5	2	Alcamizer 1	B7750	30	Air	5	19.079	2.365	1.058	2.65	0.879	0.393
5	5	2	Alcamizer 1	B7750	35	Air	5	18.625	1.869	0.836	2.561	1.316	0.588
5	5	2	Alcamizer 1	B7750	45	Air	5	20.976	2.21	0.989	2.196	1.025	0.458
5	5	2	Alcamizer 1	C7260	25	Air	4	20.431	3.025	1.512	3.053	0.658	0.329
5	5	2	Alcamizer 1	C7260	30	Air	6	20.027	1.318	0.538	3.463	1.228	0.501
5	5	2	Alcamizer 1	C7260	35	Air	5	21.037	1.308	0.585	3.427	0.386	0.173
5	5	2	Alcamizer 1	C7260	45	Air	5	20.809	1.345	0.602	3.188	0.868	0.388
5	5	2	Alcamizer 1	D7255	25	Air	5	20.56	1.803	0.806	2.773	0.993	0.444
5	5	2	Alcamizer 1	D7255	30	Air	5	20.64	3.205	1.433	3.249	0.348	0.156
5	5	2	Alcamizer 1	D7255	35	Air	5	18.935	2.455	1.098	2.279	0.826	0.369
5	5	2	Alcamizer 1	D7255	45	Air	5	17.872	1.667	0.745	2.741	1.254	0.561
5	5	2	DHT4-A	B7750	25	Air	5	19.361	1.298	0.581	2.131	1.068	0.478

(Continues)

TABLE 2 (Continued)

Clay loading	Strain rate	Extrusions	Clay type	Polymer grade	Press time	Sample cooling	No. of observations	σ_{FPS} Mean	SD	SEM	Normalized ε_f Mean	SD	SEM
5	5	2	DHT4-A	B7750	35	Air	5	18.917	2.375	1.062	2.954	0.085	0.038
5	5	2	DHT4-A	C7260	25	Air	5	17.427	1.193	0.534	2.963	0.557	0.249
5	5	2	DHT4-A	C7260	35	Air	4	17.074	1.321	0.661	4.282	4.997	2.499
5	5	2	DHT4-A	D7255	25	Air	5	18.521	2.381	1.065	2.595	0.749	0.335
5	5	2	DHT4-A	D7255	35	Air	5	19.738	1.133	0.507	2.842	0.343	0.153
5	5	2	Uncoated Alcamizer 1	B7750	25	Air	5	16.878	5.03	2.249	1.037	0.052	0.023
5	5	2	Uncoated Alcamizer 1	B7750	35	Air	4	20.563	1.24	0.62	1.026	0.436	0.218
5	5	2	Uncoated Alcamizer 1	C7260	25	Air	5	20.295	3.019	1.35	1.682	0.697	0.312
5	5	2	Uncoated Alcamizer 1	C7260	35	Air	5	21.346	2.104	0.941	1.624	0.554	0.248
5	5	2	Uncoated Alcamizer 1	D7255	25	Air	5	15.267	3.612	1.615	1.851	0.41	0.183
5	5	2	Uncoated Alcamizer 1	D7255	35	Air	5	18.987	2.161	0.966	2.277	0.798	0.357
5	5	3	Alcamizer 1	A7260	20	Air	8	22.844	0.79	0.279	-	-	-
7.5	5	2	Alcamizer 1	B7750	25	Air	5	19.21	1.28	0.573	3.41	2.216	0.991
7.5	5	2	Alcamizer 1	B7750	30	Air	5	19.385	1.593	0.712	2.214	1.388	0.621
7.5	5	2	Alcamizer 1	B7750	35	Air	5	20.847	1.656	0.74	3.412	0.241	0.108
7.5	5	2	Alcamizer 1	B7750	45	Air	5	19.463	1.442	0.645	1.937	1.721	0.769
7.5	5	2	Alcamizer 1	C7260	25	Air	4	20.92	0.94	0.47	2.342	3.359	1.679
7.5	5	2	Alcamizer 1	C7260	30	Air	5	21.47	0.597	0.267	1.681	1.315	0.588
7.5	5	2	Alcamizer 1	C7260	35	Air	5	20.094	2.495	1.116	2.497	1.026	0.459
7.5	5	2	Alcamizer 1	C7260	45	Air	5	20.232	2.975	1.33	5.424	4.983	2.228
7.5	5	2	Alcamizer 1	D7255	25	Air	5	16.999	1.537	0.687	3.024	0.552	0.247
7.5	5	2	Alcamizer 1	D7255	30	Air	5	18.024	2.353	1.052	2.747	0.61	0.273
7.5	5	2	Alcamizer 1	D7255	35	Air	5	18.762	1.132	0.506	2.504	0.921	0.412
7.5	5	2	Alcamizer 1	D7255	45	Air	5	17.515	0.737	0.33	2.61	0.487	0.218
7.5	5	2	DHT4-A	B7750	25	Air	5	18.295	1.161	0.519	1.652	0.3	0.134
7.5	5	2	DHT4-A	B7750	35	Air	5	16.64	2.885	1.29	1.987	1.045	0.467
7.5	5	2	DHT4-A	C7260	25	Air	5	19.258	1.43	0.639	1.595	0.385	0.172
7.5	5	2	DHT4-A	C7260	35	Air	5	19.854	1.33	0.595	1.995	0.294	0.132
7.5	5	2	DHT4-A	D7255	25	Air	5	18.901	2.297	1.027	2.635	0.812	0.363
7.5	5	2	DHT4-A	D7255	35	Air	5	18.88	2.495	1.116	2.971	0.294	0.132

TABLE 2 (Continued)

Clay loading	Strain rate	Extrusions	Clay type	Polymer grade	Press time	Sample cooling	No. of observations	σ_{FPS} Mean	σ_{FPS} SD	σ_{FPS} SEM	Normalized ε_f Mean	Normalized ε_f SD	Normalized ε_f SEM
7.5	5	2	Uncoated Alcamizer 1	B7750	25	Air	4	16.469	3.887	1.943	2.434	2.178	1.089
7.5	5	2	Uncoated Alcamizer 1	C7260	25	Air	4	20.505	4.973	2.486	2.62	1.592	0.796
7.5	5	2	Uncoated Alcamizer 1	C7260	35	Air	4	21.082	2.869	1.435	1.621	0.449	0.224
7.5	5	2	Uncoated Alcamizer 1	D7255	25	Air	5	17.096	1.689	0.755	1.38	0.428	0.191
7.5	5	2	Uncoated Alcamizer 1	D7255	35	Air	5	18.747	3.967	1.774	1.108	0.159	0.071
10	5	1	Alcamizer 1	A7260	20	Air	7	18.736	0.636	0.241	-	-	-
10	5	1	DHT4-A	B7750	25	Air	5	17.747	0.358	0.16	3.581	1.326	0.593
10	5	2	Alcamizer 1	A7260	20	Air	9	21.337	0.435	0.145	-	-	-
10	5	2	DHT4-A	B7750	25	Air	5	19.001	0.587	0.263	3.589	3.761	1.682
10	5	3	Alcamizer 1	A7260	20	Air	10	21.425	0.754	0.238	-	-	-
15	5	2	DHT4-A	B7750	25	Air	5	18.448	0.344	0.154	1.07	0.059	0.027
20	5	2	DHT4-A	B7750	25	Air	5	18.001	0.237	0.106	1.078	0.085	0.038

TABLE 3 Analysis of variance for σ_{FPS}.

	Df	Sum Sq	*F*-value	Pr (>*F*)
Intercept	1.0	839.24	512.54	$5.43e^{-38}$***
Polymer grade	3.0	77.35	15.75	$3.03e^{-08}$***
Clay type	3.0	24.98	5.09	$2.74e^{-03}$**
Extrusions	2.0	7.36	2.25	0.112
Clay loading	1.0	4.44	2.71	0.103
Strain rate	1.0	92.91	56.74	$4.62e^{-11}$***
Press time	1.0	0.027	0.017	0.90
Residual	86.0	140.82		

Note: A significant effect is when Pr (>*F*) (*p*-value) <0.05. Significance codes: "***": 0–0.001, "**": 0.001–0.01, "*": 0.01–0.05, ".": 0.05–0.1, " ": 0.1–1.0.

where, $SS_{\text{between}} = \sum_{i=1}^{k} n_i (\bar{y}_i - \bar{y})^2$, the sum of squares between groups and is indicated by the variable name in the ANOVA table (cf. Table 3) for each variable. Here, k is the number of groups or levels of the variable, n_i is the number of observtions per level, $Df_{\text{between}} = k-1$, and $\bar{y}_i, \bar{y}$ are the mean for level i and the overall mean, respectively. $SS_{\text{within}} = \sum_{i=1}^{k} \sum_{j=1}^{n_i} \left(y_{ij} - \bar{y}_i\right)^2$, the variability within the groups and is indicated by the "Residual" row in the ANOVA table. $Df_{\text{within}} = N - k$, where $N = \sum_{i=1}^{k} n_i$. To yield significance, SS_{between} must be greater than SS_{within}. Note the Df denotes the degrees of freedom and is dependent on the number of levels within each variable (e.g., clay type has three levels: Alcamizer 1, DHT4-A, and Uncoated Alcamizer 1), and the number of repeated sample points (i.e., the number of observations listed in Table 2). The total variability in the data is given by $SS_{\text{total}} = SS_{\text{between}} + SS_{\text{within}}$, with $Df_{\text{total}} = N - 1$.

The *p*-value is the probability of obtaining an *F*-value with the specified degrees of freedom, that is, $k-1$ and $N-k$, that is greater than the calculated *F*-value. Specifically, the probability that the calculated value follows the *F*-distribution under the null hypothesis, which indicates the means of the groups are equal. It is therefore represented as $Pr(\geq F)$ in the ANOVA table (cf. Table 3) and indicates the probability that the effect of the variable on the response is only by chance. Therefore, the smaller the *p*-value the greater the probability that the variable influences the response. 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.

The different computations mentioned here are used to populate the ANOVA tables that will be discussed in this subsection. The significance level or *p*-value is indicated with a set of codes below the table, where only those with a "*" indicate statistical significance (e.g., "*," "**" or "***").

In the tables the first row refers to Intercept, which is the value of the intercept for a linear model, as the ANOVA is performed for the linear model discussed in the following subsection.

2.4.2 | Linear (or regression) model

The linear model fitted on the data is defined as:

$$\hat{y} = \hat{\beta}_0 + \hat{\beta}_1 z_{1,B7750} + \hat{\beta}_2 z_{1,C7260} + \hat{\beta}_3 z_{1,D7255} + \hat{\beta}_4 z_{2,DHT4-A} + \hat{\beta}_5 z_{2,Neat} + \hat{\beta}_6 z_{2,Unc\,Alc} + \hat{\beta}_7 z_{3,extr2} + \hat{\beta}_8 z_{3,extr3} + \hat{\beta}_9 x_{loading} + \hat{\beta}_{10} x_{strain} + \hat{\beta}_{11} x_{press\ time}. \tag{2}$$

The response variable is represented by y, with the fitted or predicted value denoted by $\hat{y}$, and is either σ_{FPS} or normalized ε_f. The estimated regression coefficients are represented by $\hat{\beta}_i$, which is shown in the "Estimate" column in the linear regression table (cf. Table 5). Parameter estimates are obtained with least squares minimisation of the residuals, that is, $\sum_u (y_u - \hat{y}_u)^2, u = 1,2,...,N$. Categorical variables are denoted by dummy variables with $z_{i,level}$, indicating the level of the variable, except the first level since $\hat{\beta}_0$, the intercept, captures the first levels. The dummy variable is set to either 0 or 1 depending on which level is active. Continuous variables are denoted with $x_{variable}$.

For a linear regression model the R^2 value provides an indication of the proportion of total variability in the response variable explained by the model. The adjusted R^2 is a variation on the R^2 value, which adjusts the R^2 for the number of terms in the regression model. This value decreases as the number of statistical non-significant terms in the model is increased.[27] A value close to 1 is indicative of good model predictability. For this study, a minimum adjusted R^2 value of 0.7 is arbitrarily considered to denote a good model. Residual standard error indicates the standard error of the model and provides an indication of the model's ability to quantify statistically significant effects. This value should ideally be very small when compared to the overall mean of the model. The linear regression model considers the t-statistic to determine the p-value for the parameter estimates. In regression, the t-value is determined from[26]:

$$t = \frac{\hat{\beta}_i - \beta_i}{\mathrm{SE}\left(\hat{\beta}_i\right)}. \tag{3}$$

Under the null hypothesis $\beta_i = 0$, and the numerator is just the estimated regression coefficient, $\hat{\beta}_i$. The denominator is the standard error (SE) of the parameter estimate, which is specified by the "Std. Error" in the linear model table (cf. Table 5). Similar to the ANOVA, the p-value is the probability to obtain a t-distribution value with specified degrees of freedom which is greater than the calculated t-value. It is therefore represented as $Pr(\geq |t|)$ in the linear model table (cf. Table 5) and indicates the probability that the effect of the variable on the response is only by chance. The significance level of the p-value is indicated with a set of codes below the table, where only those with a "*" indicate statistical significance (e.g., "*", "**" or "***").

2.4.3 | Tukey Honest Significant Difference (HSD)

The linear model does not provide a statistical comparison of all the variable levels with each other, only to the first level (listed alphabetically for each variable). The Tukey Honest Significant Difference (HSD) test is used to provide multiple comparisons between all the levels of the variables of interest[27]; and is based on the studentized range distribution to provide a family-wise true significant difference test. Specifically, the $(1-\alpha)100\%$ Tukey simultaneous confidence intervals for all pairwise comparisons between the group means $\bar{y}_i - \bar{y}_j, i \neq j$, are calculated as follows:

$$\bar{y}_i - \bar{y}_j \pm Q_{\alpha,k,N-k} \sqrt{\frac{S_p^2}{2}\left(\frac{1}{n_i} + \frac{1}{n_j}\right)}, \tag{4}$$

where, $Q_{\alpha,k,N-k}$ is the upper tail α critical value of the studentized range distribution with k, the number of groups, and $N-k$ degrees of freedom. $S_p^2 = \frac{1}{N-k}\sum_u (y_u - \hat{y}_u)^2$, which is the pooled variance or mean squared error (MSE) of the model. If the confidence interval does not contain zero, then the two means are significantly different at significance level α.

3 | RESULTS AND DISCUSSION

3.1 | Summary statistics

The summary statistics for σ_{FPS} and normalized ε_f are presented in Table 2. For the historical data the SD for σ_{FPS} ranges from 0.237 to 7.713, which indicates that the means of some groups are more accurately estimated compared to others. Note this is also a function of the number of replications per experimental condition. We observe similar results for normalized ε_f with a range of 0.029–5.885. In both instances the SEM is rather small compared to the SD and provides a good indication that the sample mean is accurate. The mean for σ_{FPS} ranges between 15.267 and 31.730 MPa and for normalized ε_f between 1.026% and 11.316%. In both instances, this is quite a large variation across the data set, which provides an initial indication that the variables do have an influence on the mechanical responses. The number of observations for the different combinations of experimental conditions are very different, which is partly because the experiments were conducted over a period of 3 years. Consequently, the experimental conditions are unbalanced. In a balanced design, the number of observations is the same for all the different conditions considered.

3.2 | Exploratory data analysis

The exploratory data analysis (EDA) investigates the effect of the different manufacturing (number of extrusions, press time, and sample cooling method), testing (strain rate) and material parameters (polymer grade, clay type, and clay weight loading) on the mechanical properties of interest, that is, σ_{FPS} and ε_f.

According to literature, we expect to observe an increase in σ_{FPS} if there is a good interaction between the filler and polymer,[4–6] and a decrease if the interaction between the filler and polymer is poor.[2,4] HDPE is a semi-crystalline polymer[24] and it has been reported that, in general, with the addition of clay particles a decrease in ε_f is observed regardless of the interaction between the clay and polymer.[2]

3.2.1 | Material system influence

The influence of the material system on σ_{FPS} and ε_f was the focus of the 2017 data set[20] as described in Table 1. This dataset is visually explored in scatter plots, where each data point for the mechanical properties is plotted as a function of clay weight loading for the different HDPE grades and clay types as shown in Figure 2. There is a lot of variation in the ε_f data and, as a result, it is difficult to draw any sensible conclusions from the plots.

Clay loading

A general observation from Figure 2 is that, as clay is added to the polymer system, there is a decrease in σ_{FPS} from the neat case for all polymer grades and clay types, which indicates a weak interaction between the polymer and clay.[2] Depending on the HDPE/clay system, either an increase or further decrease is observed at higher clay loadings (≥5 wt%). σ_{FPS} for HDPE B7750 is less variable than for HDPE C7260 and HDPE D7255. For example, referring to the HDPE B7750/DHT4-A composite system, the largest difference in σ_{FPS} between two consecutive clay loadings is 3.55 MPa, which was the initial decrease from neat to a loading of 2.5 wt%. There is at most a 0.55 MPa change in σ_{FPS} for clay loadings larger than 10 wt%. Similar observations are made for the other HDPE/clay composite systems. We can therefore conclude that the difference in σ_{FPS} due to clay loading is not meaningful enough to determine either an optimum clay loading or the point at which the material strength starts to degrade. There is a general decrease in ε_f with the addition of clay. This is to be expected for a semi-crystalline polymer. For the HDPE B7750/DHT4A composite system, it is clear from Figure 2B that there is a degradation in the material ductility as the ε_f mean decreases from 39.91% at 10 wt% to 9.50% and 8.24% for 15 and 20 wt%, respectively. This degradation in material properties is potentially due to an increase of particle agglomeration.[5] There is a lot of variability in ε_f for clay loadings below 10 wt%, even within individual clay types. This indicates that even though the manufacturing process is kept constant, the possibility for variability within the composite morphology exists, most likely due to the polymer-clay interaction.

Polymer grade

For the influence of the polymer grade, it is observed from the σ_{FPS} mean in Table 2 that neat HDPE B7750 has the highest mean with 22.26 MPa compared to HDPE C7260 (20.38 MPa) and HDPE D7260 (19.61 MPa). With the inclusion of clay, we note that, in general, HDPE C7260 has a higher σ_{FPS} mean irrespective of clay type. There appears to be no noticeable trend for ε_f between the different HDPE grades as the mean values are within 1% or less of one another.

Clay type

Alcamizer 1 provides a higher σ_{FPS} followed by DHT4-A and Uncoated Alcamizer. This is surprising, since Alcamizer 1 is designed for compatibility with PVC (a highly polar polymer). The surface treatment of Uncoated Alcamizer 1 does little to improve mechanical properties, as the means of σ_{FPS} for Alcamizer 1 and Uncoated Alcamizer 1 are very close. The variability in the results for Uncoated Alcamizer 1 is larger than Alcamizer 1 and DHT4-A, with DHT4-A providing the least variability. From Figure 2, we observe that Alcamizer 1 and DHT4-A tend to have higher values for ε_f compared to Uncoated Alcamizer 1. Alcamizer 1 and DHT4-A are treated with a surface coating, whereas the surface coating was removed for Uncoated Alcamizer 1. This clearly indicates that clay

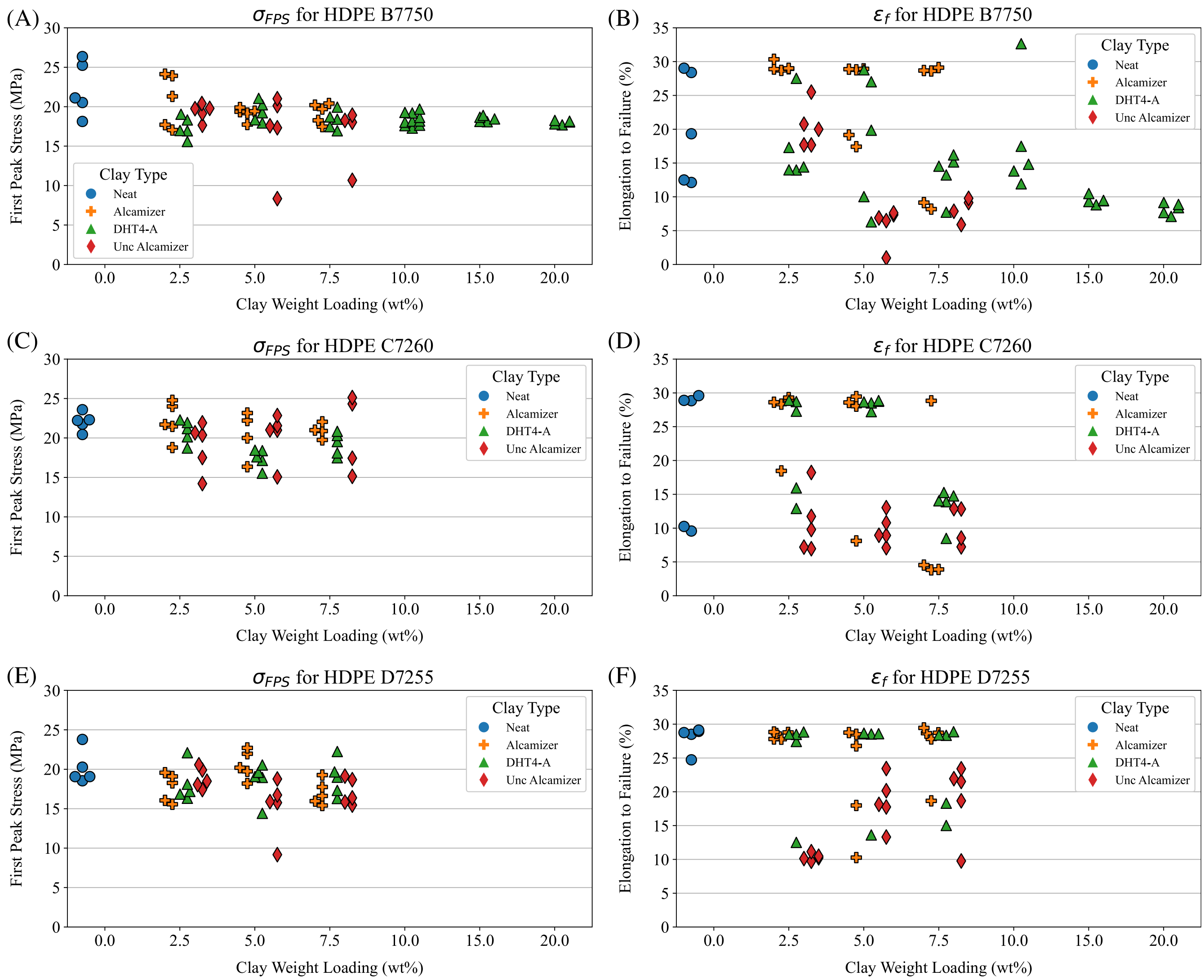

FIGURE 2 Influence of the material system variables on σ_{FPS} and ε_f. Each HDPE grade is in a new column of the figure and the clay types are represented by different markers where Unc Alcamizer refers to Uncoated Alacamizer.

surface coating has a noticeable influence on the material ductility.

The variability in both σ_{FPS} and ε_f highlights the inconsistent interaction between the polymer and clay, especially in the cases where there is no surface coating (e.g., Uncoated Alcamizer 1). This surface coating normally acts as a lubrication to improve polymer-clay interaction.

3.2.2 | Manufacturing and testing system influence

The influence of the manufacturing and testing system variables on the mechanical properties of interest (i.e., σ_{FPS} and ε_f) is shown in Figure 3.

Number of extrusions

From Figure 3A, there is a definite influence from 1 to 2 extrusions, where σ_{FPS} increases with an increase in the number of extrusions. This is expected due to better mixing of the clay in the polymer, but not too much to degrade the material. However, when increasing the number of extrusions to 3 there is no significant enhancement in σ_{FPS}. Generally, an increase in the number of extrusions causes a material to become more brittle, which will influence its processability.[5] This could lead to the sample experiencing failure before yielding occurs, consequently decreasing σ_{FPS}.

Press time

In Figure 3B, there is a decrease in σ_{FPS} as the clay weight loading increases, but σ_{FPS} appears to be constant from

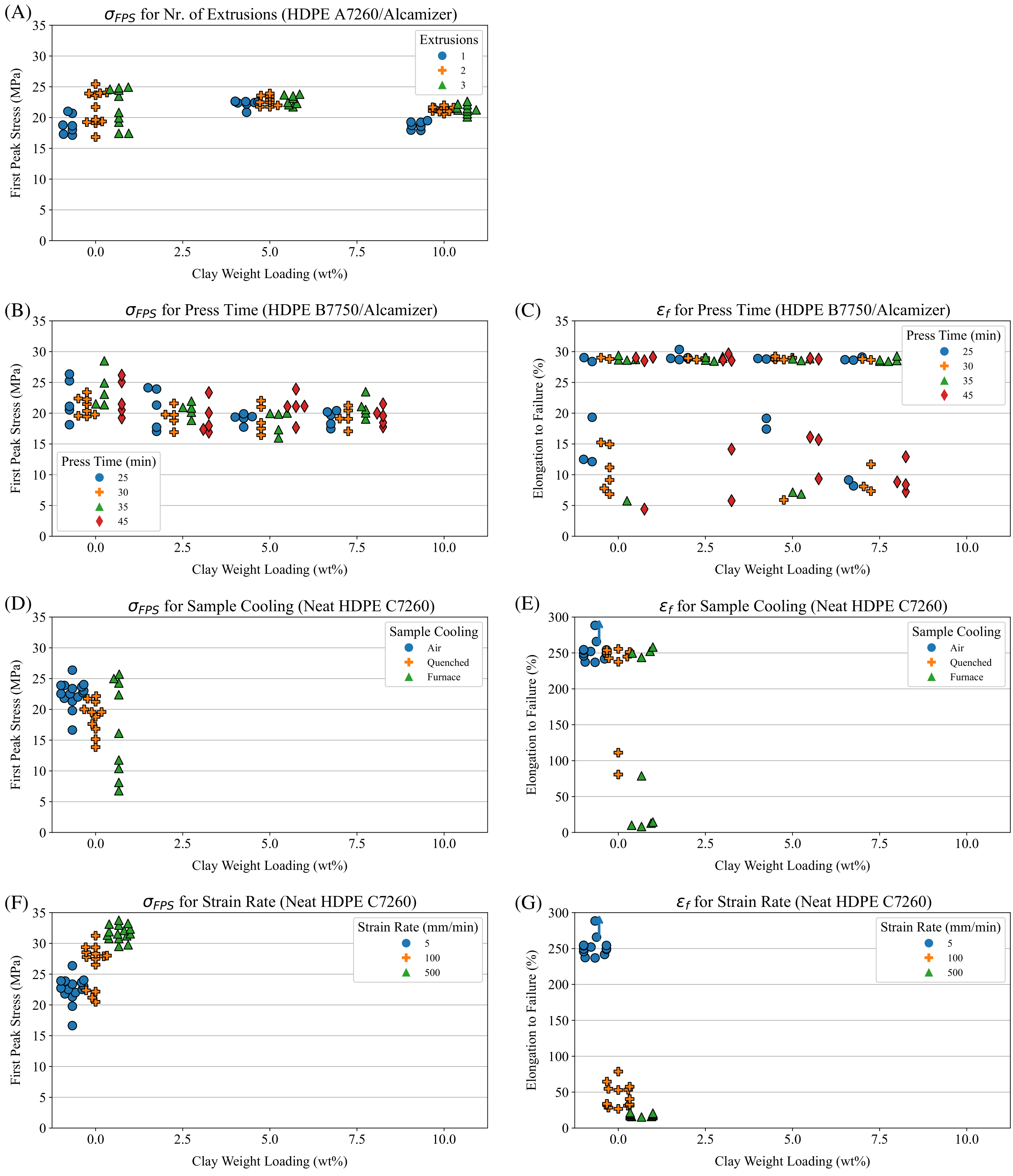

FIGURE 3 Influence of the material system variables on σ_{FPS} and ε_f. Each row in the figure represents a manufacturing condition. Markers denote each of the variations within a manufacturing condition and an up arrow denotes more data points outside the y-axis limit.

about 5 wt%. The maximum mean σ_{FPS} enhancement is found to be 6.67% for neat HDPE and 4.9% for 2.5 wt% at a 35 min press time; and 12.06% for 5 wt% and 1.85% for 7.5 wt% at a press time of 45 min. This enhancement in mean σ_{FPS} is not considered enough of an improvement to warrant the additional time and effort required to press the tensile samples during manufacturing. The variability in press time across the different clay types is rather large. This is likely due to the compression molding process itself, which is known to have a non-uniform heating distribution. This inconsistent heating process affects the composite morphology, consequently affecting the mechanical response which could explain the observed variations.[28,29] ε_f in Figure 3E does not provide additional insight into the influence of press time as there is no observable trend in the data. Most of the samples reached the prescribed elongation of 30%, with several samples failing before then. This could be attributed to the changes in composite morphology (i.e., an increase in clay agglomerates and therefore material brittleness) due to the inconsistent heating process in compression molding.

Sample cooling method

As noted in Figure 3C, the lowest mean σ_{FPS} is equal to 16.73 MPa, whereas the air cooled samples yielded the highest σ_{FPS} (22.51 MPa), and the quenched sample mean σ_{FPS} is equal to 19.33 MPa. The air-cooled samples were highly ductile with ε_f higher than 200%, as observed in Figure 3F. The level of ductility decreased for the quenched and furnaced samples. This is to be expected as the method of cooling the tensile samples influences the material crystallinity, which consequently influences its ductility.

Strain rate

In Figure 3D, a linear increase in σ_{FPS} is observed with an increase in strain rate, where the mean σ_{FPS} is 20.38 MPa for 5 mm/min, 26.41 MPa for 100 mm/min and 31.73 MPa for 500 mm/min. The material ductility decreases as ε_f decreases with an increase in strain rate, as shown in Figure 3G. Therefore, the strain rate has an influence on the mechanical properties. During tensile testing, as the sample is pulled in tension, the polymer chains extend. For a low strain rate, the polymer chains have ample time to extend, and therefore tend to exhibit more ductile behavior. On the other hand, at higher strain rates, the polymer chains do not have enough time to extend and tend to break quickly, resulting in more brittle behavior.

3.3 | Statistical analysis

From the summary statistics shown in Table 2, the number of observations per group is large, and the standard error of the mean is quite small compared to the mean for each response. This provides an indication that it should be possible to quantify statistically significant effects of the experimental variables, and significant differences between the levels of the variables of interest.

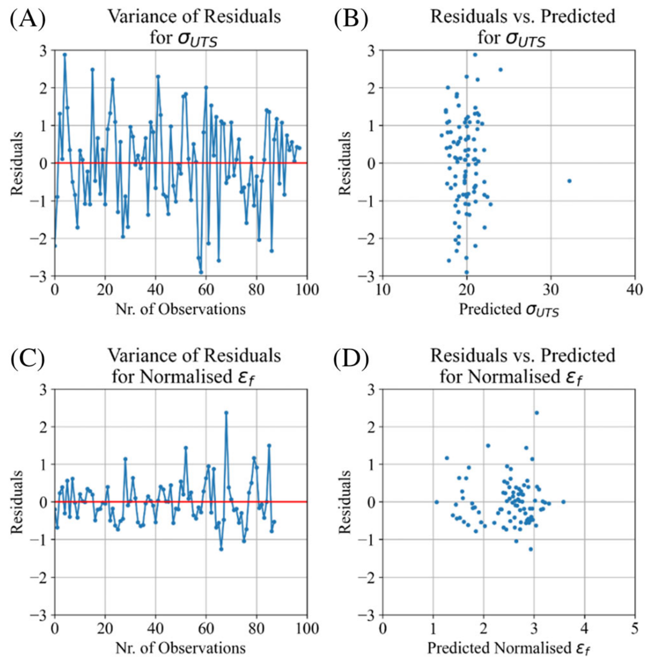

FIGURE 4 ANOVA assumptions for (A) variance of the residuals for σ_{FPS}, (B) residuals versus predicted values for σ_{FPS}, (C) variance of the residuals for normalized ε_f, and (D) residuals versus predicted values for normalized ε_f.

Specifically, the effects of polymer grade, clay type, clay loading, number of extrusions, press time and strain rate on the responses, σ_{FPS} and ε_f, were of interest.

3.3.1 | Analysis of variance (ANOVA)

In this section, the effects of the variables on σ_{FPS} and normalized ε_f are quantified through the analysis of variance (ANOVA).[27] The validity of the ANOVA *F*-test is based on the assumptions of constant variance between the populations compared, and whether the data originated from simple random sampling, that is, residuals are normally distributed, approximately. Therefore, for the ANOVA analysis it is good practice to first determine if the assumptions of constant variance and random distribution of the errors hold. The results for the ANOVA analysis of σ_{FPS} and normalized ε_f are shown in Figure 4. From Figure 4A,C the variability of the residuals is within an acceptable range varying at most 3 units from the mean for σ_{FPS}, and 1 unit from the mean except for a few outliers for normalized ε_f. The residuals versus predicted results in Figure 4B,D indicate randomness, which confirms simple random sampling. It can therefore be concluded that the ANOVA assumptions are upheld.

The ANOVA results are given in Table 3 for σ_{FPS}. Polymer grade, clay type and strain rate have a statistically significant effect on σ_{FPS}. All these variables have a p-value of less than 0.05, which indicates a statistically significant effect at the 5% significance level. On the other hand, number of extrusions, clay loading, and press time have p-values larger than 0.05, which indicate that they have no statistically significant effect on σ_{FPS}.

The ANOVA results for the normalized ε_f are shown in Table 4. Note that all variables have a statistically significant effect (p-value <0.05) on the normalized ε_f, except for press time (p-value >0.05). The most surprising result here is that clay loading is concluded to have no statistically significant effect on σ_{FPS}. It is a known from literature that clay loading does influence the properties of a polymer-clay composite system. The EDA corroborated this influence where we observed a decrease in both σ_{FPS} and ε_f with an increase in clay loading.

TABLE 4 Analysis of variance for normalized ε_f.

	Df	Sum Sq	F-value	Pr (>F)
Intercept	1.0	18.64	66.36	4.90e^{-12}***
Polymer grade	2.0	2.30	4.10	2.02e^{-02}*
Clay type	3.0	20.55	24.39	3.11e^{-11}***
Extrusions	1.0	4.88	17.37	7.88e^{-05}***
Clay loading	1.0	2.69	9.58	2.74e^{-03}**
Strain rate	1.0	2.32	8.27	5.21e^{-03}**
Press time	1.0	0.34	1.20	0.28
Residual	78.0	21.90		

Note: A significant effect is when Pr (>F) (p-value) <0.05. Significance codes: "***": 0–0.001, "**": 0.001–0.01, "*": 0.01–0.05, ".": 0.05–0.1, " ": 0.1–1.0.

3.3.2 | Linear (or regression) model

Now that we know which experimental variables have a statistically significant effect, the next step is to determine whether there are any statistically significant differences between the different levels of each experimental variable. To achieve this, a linear (or regression) model is developed as a function of the experimental variables using the least squares method.

It is required to first determine if the assumption of normal distribution of residuals hold. This is visually observed by means of a probability plot where the percentiles of the residuals would approximate the percentiles of the standard normal distribution and the points will fall on a straight line, approximately.[27] The probability plots for the linear regression models for both σ_{FPS} and normalized ε_f are shown in Figure 5. The residuals follow a standard normal distribution approximately. Both the R^2 and adjusted R^2 values are close to one another, which indicates that the model can provide good predictability. This observation is valid for both response variables.

The linear regression model results are shown in Table 5 for σ_{FPS}. Note that the first level of the variable is used for comparison which is why Polymer Grade (T. A7260), Clay Type (T.Alcamizer) and Extrusions (T.1) do not appear in Table 5. Similarly, Polymer Grade (T. B7750) and Clay Type (T.Alcamizer) do not appear in Table 6. Note for the linear model the statistical significance is quantified by comparing the ratio of the estimate to its standard error for the variable to a t-distribution with specified degrees of freedom.[27]

From Table 5 we note that the adjusted $R^2 = 0.664$, that is, relatively close to 0.7, which is the minimum threshold specified, and it is concluded that the model

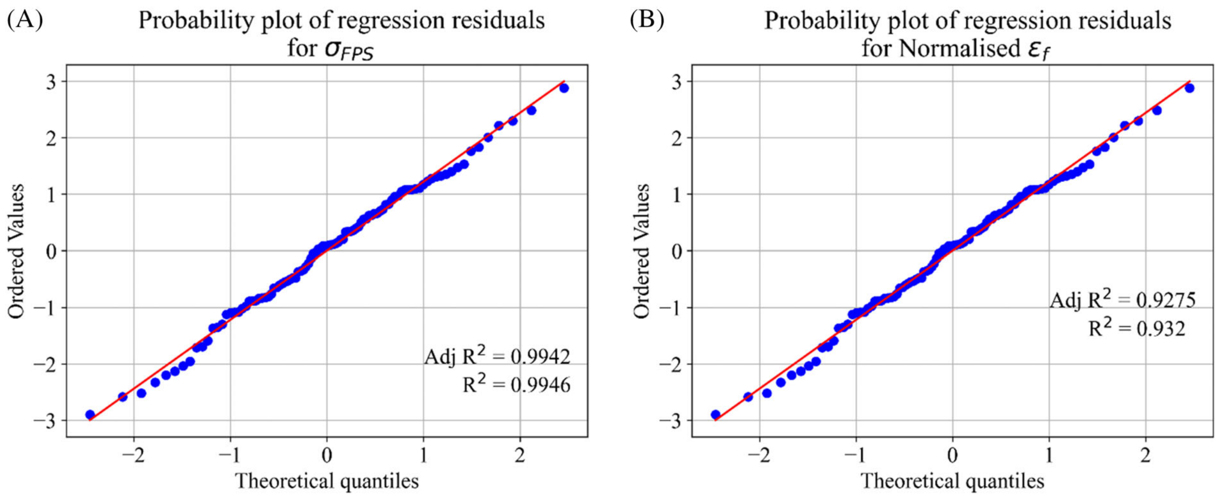

FIGURE 5 Probability plot of the residuals for (A) σ_{FPS} and (B) normalized ε_f.

TABLE 5 Linear model for σ_{FPS}, where a significant effect is when Pr (>|*t*|) (*p*-value) <0.05.

No. observations	98	*R*-squared		0.702
Df residuals	86	Adjusted *R*-squared		0.664
Df model	11	*F*-statistic		18.46
		Residual standard error		1.28
	Estimate	**Std. error**	***t*-value**	**Pr (>|*t*|)**
Intercept	20.2450	0.894	22.639	0.000***
Polymer grade (T.B7750)	−1.4766	0.755	−1.955	0.054.
Polymer grade (T.C7260)	−0.3909	0.772	−0.506	0.614
Polymer grade (T.D7255)	−2.6314	0.775	−3.396	0.001***
Clay type (T.DHT4-A)	−1.0894	0.364	−2.990	0.004**
Clay type (T.Neat)	0.5988	0.470	1.275	0.206
Clay type (T.Uncoated Alcamizer 1)	−0.9418	0.384	−2.451	0.016*
Extrusions (T.2)	1.4276	0.822	1.737	0.086.
Extrusions (T.3)	1.8135	0.994	1.825	0.071.
Clay loading	−0.0836	0.051	−1.647	0.103
Strain rate	0.0205	0.003	7.533	0.000***
Press time	0.0028	0.021	0.129	0.898

Note: Significance codes: "***": 0–0.001, "**": 0.001–0.01, "*": 0.01–0.05, ".": 0.05–0.1, " ": 0.1–1.0.

TABLE 6 Linear model for normalized ε_f, where a significant effect is when Pr (>|*t*|) (p-value) <0.05.

No. observations	88	*R*-squared		0.600
Df residuals	78	Adjusted *R*-squared		0.554
Df model	9	*F*-statistic		13.03
		Residual standard error		0.530
	Estimate	**Std. error**	***t*-value**	**Pr (>|*t*|)**
Intercept	4.2949	0.527	8.146	0.000***
Polymer grade (T.C7260)	0.3972	0.142	2.796	0.007**
Polymer grade (T.D7255)	0.2737	0.142	1.933	0.057.
Clay type (T.DHT4-A)	−0.2546	0.155	−1.648	0.103
Clay type (T.Neat)	−0.5108	0.210	−2.430	0.017*
Clay type (T.Uncoated Alcamizer 1)	−1.3475	0.160	−8.406	0.000***
Extrusions (T.2)	−1.6989	0.408	−4.168	0.000***
Clay loading	−0.0684	0.022	−3.094	0.003**
Strain rate	−0.0033	0.001	−2.875	0.005**
Press time	0.0098	0.009	1.094	0.277

Note: Significance codes: "***": 0–0.001, "**": 0.001–0.01, "*": 0.01–0.05, ".": 0.05–0.1, " ": 0.1–1.0.

will be able to predict σ_{FPS} with acceptable accuracy. The residual standard error of the model is 1.28, which is very small compared to the overall mean of 20.245 (estimate value for intercept in Table 5), and indicates that statistically significant effects of the variables on σ_{FPS} can be quantified.

The values in the Estimate column are the average change in σ_{FPS} for the specific level of the variable compared to its first level given in alphabetical order. Note that a variable is always compared to its first entry which is not shown in the table (i.e., Polymer Grade [T.A7260], Clay Type [T.Alcamizer], and Extrusions [T.1]). For

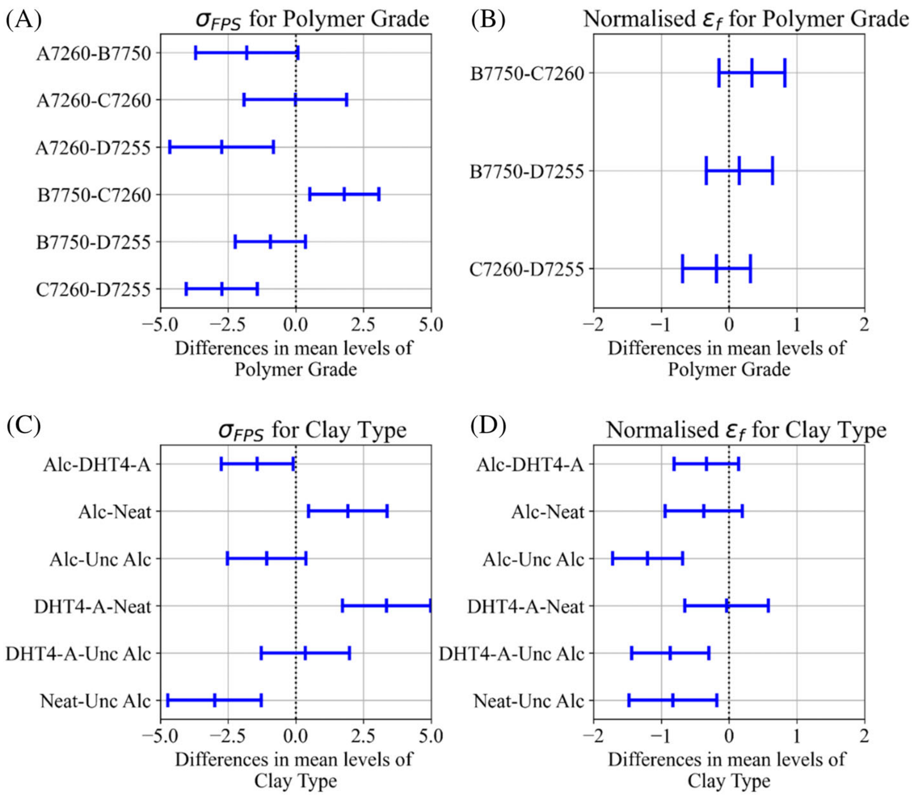

FIGURE 6 Tukey HSD test to determine the statistical significance of polymer grade and clay type for σ_{FPS} and normalized ε_f.

example, the σ_{FPS} of HDPE B7750 is on average 1.4766 MPa lower than the σ_{FPS} of HDPE A7260. Again, the p-value (Pr (>|t|)), indicates the probability that the effect is only by chance, and a statistically significant effect is when the p-value is less than 0.05.

We note that polymer grade has on average a negative effect on σ_{FPS}. Only HDPE D7255 has a statistically significant effect when compared to HDPE A7260 with a p-value lower than 0.05. The effect on σ_{FPS} due to clay type is more varied, with a negative effect for DHT4-A and Uncoated Alcamizer, and a positive effect for neat HDPE when compared to Alcamizer 1. Both DHT4-A and Uncoated Alcamizer have a statistically significant effect when compared to Alcamizer 1 with p-values less than 0.05. Strain rate has a positive effect on σ_{FPS} and increases on average by 0.0205 units for a 1 mm/min increase in strain rate. Strain rate is statistically significant with a p-value less than 0.05.

The linear regression model results for normalized ε_f are shown in Table 6. From Table 6 we note that the adjusted R^2 value is 0.554, that is, the model will therefore struggle to predict the normalized ε_f. The residual standard error is 0.530, which is smaller than the overall mean of 4.2949, indicating that statistically significant effects of the variables on the normalized ε_f can be quantified.

Polymer grade has on average a positive effect on the normalized ε_f. We note that only HDPE C7260 is statistically significant different (p-value <0.05) when compared to HDPE A7260. Neat HDPE and Uncoated Alcamizer both have a statistically significant effect (p-value <0.05), and have on average a negative effect on normalized ε_f. The number of extrusions, clay loading, and strain rate have on average a negative effect on the normalized ε_f, and are statistically significant.

3.3.3 | Tukey Honest Significant Difference (HSD)

The Tukey HSD test results are shown in Figure 6 for both σ_{FPS} and normalized ε_f. These are for all experimental variables which consist of more than one level, namely the polymer grade and clay type; and were found to have statistical significance from the ANOVA results. The intervals on the graph represent 95% confidence intervals (CI) for the mean difference in the response variable between the two levels of interest. If the confidence interval does not contain zero, the two levels of interest are statistically significantly different with 95% confidence. Note these are family wise 95% confidence intervals adjusted for the number of levels being compared.

From Figure 6A, we note that three levels of polymer grade are statistically significantly different from each other for σ_{FPS}, namely HDPE A7260-D7255, HDPE B7550-C7260 and HDPE C7260-D7255. HDPE A7260-

B7750, HDPE A7260-C7260. HDPE B7550-D7255 are not statistically significant different (zero on the *x*-axis is within the 95% CI). For normalized ε_f in Figure 6B, we note that none of the polymer grades are statistically significantly different from one another.

For clay type all levels are statistically significantly different for σ_{FPS}, except for Uncoated Alcamizer (UAlc in Figure 6C), which is not statistically significantly different from Alcamizer 1 or DHT4-A (zero on the *x*-axis is within the 95% CI). For normalized ε_f (cf. Figure 6D) Alcamizer 1 is not statistically significant different from DHT4-A or Neat HDPE, and Neat HDPE is not statistically significant different from DHT4-A. This is unexpected since Alcamizer 1 is less compatible with HDPE, while DHT4-A is.

4 | DISCUSSION

The most surprising results that emanated from the EDA and statistical analysis is the lack of any statistically significant effect of the clay loading, especially since these effects have been widely reported in the literature. It is well established in literature that there are enhancements in the mechanical properties with clay loadings as low as 5 wt%.[2,5,7,8,12,30] The lack of mechanical property enhancement for the HDPE/LDH system studied here could be attributable to a lack of good dispersion or clay-polymer interaction,[2,4] both of which are required for enhancements in mechanical properties.[2,7,11,12,30] The level of dispersion of the filler in the polymer matrix cannot be directly controlled, thus an ideal level of exfoliation cannot be guaranteed even when the compounding conditions are optimized.[30] Scanning electron microscopy (SEM) would need to be performed to confirm this hypothesis.

There have been several studies[31–36] which compared different types of Cloisite which, like DHT4-A, is designed to be compatible with thermoplastics such as polyethylene. Kelnar et al.,[37] on the other hand, considered three different clay types: Cloisite 30B (designed for compatibility with polyethylene), halloysite (designed for compatibility with PVC), and nanosilica (designed for compatibility with cement). Their results indicated, as expected, that Cloisite 30B, which is compatible with polyethylene enhanced the mechanical properties. This is contradictory to what was observed in the EDA where Alcamizer 1, unexpectedly, provided better overall mechanical properties than DHT4-A. This could again be attributed to the level of clay dispersion within the polymer matrix, as Kelnar et al.[37] has shown that the shape and type of clay can have an influence on the redistribution of the mechanical stress within the polymer-clay composite, which consequently affects the mechanical properties.

By modifying the clay surface, it ultimately allows for the expansion of the interlayer space, the area between the clay and polymer matrix. Surface modification thus improves diffusion of the polymer into the interlayer space, leading to improved dispersion.[5,38,39] In this study, the effect of modifying the clay surface was investigated by comparing Alcamizer 1, which already has a surface treatment, with an Uncoated Alcamizer 1, where the surface treatment is removed through a chemical process. The results indicated that there is no statistically significant difference between Alcamizer 1 and Uncoated Alcamizer 1. This additional chemical modification therefore played no role in the clay-polymer interaction. This strengthens our hypothesis that there is a poor interaction between the polymer matrix and the clay.

Polymer grade does have a statistically significant effect on the mechanical properties. This corresponds to literature where Chu et al.[28] observed that a higher molecular weight HDPE provided an improvement in the overall mechanical properties, compared to the middle and low molecular weight HDPE's.

Literature has no consensus on the effect due to the number of extrusions where La Mantia et al.[40] observed a decrease in the mechanical performance with an increase in the number of extrusions, Scaffaro et al.[41] observed an increase and Mistretta et al.[42] found no significant effect. These differences in observations could be due to the level of clay dispersion and the clay-polymer interaction as Scaffaro et al.[41] considered a compatibilizer. In the current study the number of extrusions were found not to have a statistically significant effect, and observations in the EDA showed that there was an initial increase from 1 to 2 extrusions and thereafter no further effect. The variability in the performance of the reported results indicates the dependence of the reprocessing behavior on the compounding conditions and material system.[42]

Jo and Naguib[43–45] performed the same analysis considering two different compression molding press times, 10 and 15 min, in each study. Comparing these results showed that there is no observable effect of the press time on the Young's modulus. The results from this study, in both the EDA and statistical analysis, also indicated that there is no statistically significant effect on the mechanical properties with a change in press time. This indicates that the time under which a compression mold is under pressure does not have a direct influence on the composite morphology.

Similar to this study, Jo and Nagui[46] investigated the influence of hot-plate cooling, air cooling and water quenching. They found that the method of sample cooling affects the crystallinity of the composite morphology consequently affecting the mechanical properties. Based on their results air cooling provided the best overall improvements in mechanical properties. The results from the current study mirror those of Jo and Naguib[46] where air cooled samples also provided the best overall improvements in mechanical properties.

The same observations were made regarding the strain rate. Jo and Naguib[46] investigated three strain rates, increasing logarithmically (1, 5, and 50 mm/min), and found that the tensile strength increases with an increase in strain rate. There is a clear influence based on strain rate as observed in the current study in both the EDA and statistical analysis. This is expected as the polymer chains extend during tensile testing and, by applying a quicker strain rate, these tensile samples break earlier, but they exhibit higher stiffness compared to a lower strain rate.

Overall, there was significant variability in the data, in fact, this variability far exceeded the effect due to an increase in clay weight loading. The statistical variability observed in the historical experimental data could be attributed to human error, to manufacturing, or could be inherent in the material system.

5 | CONCLUSION

An exploratory data analysis (EDA) and statistical analysis were performed to explore the historical data to gain potential insight and understanding into the effects of material, manufacturing, and testing system parameters.

The results indicated that, contrary to literature, an increase in clay loading had no statistically significant effect on the mechanical properties. Another unexpected observation was the clay type where Alcamizer 1, compatible with PVC, performed better than DHT4-A which is compatible with HDPE. Both these observations will require further investigation. The manufacturing parameters have slight influences, but the small improvements in mechanical properties do not outweigh the substantial investment in time and resources required to achieve the improved properties. The strain rate had a statistically significant effect on the mechanical properties.

Generally, there were difficulties in obtaining consistent and significant results, with large variations observed in both mechanical responses. Based on the historical data alone, it is not possible to determine the origin of these variations and further investigations are therefore needed.

This study demonstrated very clearly how important and invaluable the application of statistical analysis is to gain insight from a high volume of experimental data.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in University of Pretoria Research Data Repository (Figshare) at https://doi.org/10.25403/UPresearchdata.22126433.v1.

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REFERENCES

1. Gao F. Clay/polymer composites: the story. *Mater Today*. 2004;7:50-55.
2. Jordan J, Jacob KI, Tannenbaum R, Sharaf MA, Jasiuk I. Experimental trends in polymer nanocomposites – a review. *Mater Sci Eng A*. 2005;393:1-11.
3. Crosby AJ, Lee J-Y. Polymer nanocomposites: the "nano" effect on mechanical properties. *Polym Rev*. 2007;47:217-229.
4. Fu S-Y, Feng X-Q, Lauke B, Mai Y-W. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites. *Compos Part B Eng*. 2008;39:933-961.
5. Azeez AA, Rhee KY, Park SJ, Hui D. Epoxy clay nanocomposites – processing, properties and applications: a review. *Compos Part B Eng*. 2013;45:308-320.
6. El-Sheikhy R, Al-Shamrani M. On the processing and properties of clay/polymer nanocomposites CPNC. *Latin Am J Solids Struct*. 2015;12:385-419.
7. Khanam PN, AlMaadeed MAA. Processing and characterization of polyethylene-based composites. *Adv Manuf: Polym Compos Sci*. 2015;1(2):63-79.
8. Quaresimin M, Schulte K, Zappalorto M, Chandrasekaran S. Toughening mechanisms in polymer nanocomposites: from experiments to modelling. *Compos Sci Technol*. 2016;123:187-204.
9. Romo-Uribe A. Polymers in 2D confinement: a nanoscale mechanism for thermo-mechanical reinforcement. *Polym Adv Technol*. 2017;29:507-516.
10. Mittal G, Rhee KY, Mišković-Stanković V, Hui D. Reinforcements in multi-scale polymer composites: processing, properties, and applications. *Compos Part B Eng*. 2018;138:122-139.
11. Pandey JC, Singh M. Dielectric polymer nanocomposites: past advances and future prospects in electrical insulation perspective. *SPE Polym*. 2021;2(2):236-256.
12. Albdiry MT, Yousif BF, Ku H, Lau KT. A critical review on the manufacturing processes in relation to the properties of nanoclay/polymer composites. *J Compos Mater*. 2012;47:1093-1115.
13. Zabihi O, Ahmadi M, Nikafshar S, Preyeswary KC, Naebe M. A technical review on epoxy-clay nanocomposites: structure, properties, and their applications in fiber reinforced composites. *Compos Part B Eng*. 2018;135:1-24.
14. Rueda MM, Auscher MC, Fulchiron R, et al. Rheology and applications of highly filled polymers: a review of current understanding. *Prog Polym Sci*. 2017;66:22-53.
15. Botha N, Inglis HM, Labuschagne FJWJ. Analysis of mechanical property degradation in polymer nanoclay composites. Third International Conference on Composites, Biocomposites and Nanocomposites, Port Elizabeth, South Africa, 7-9 November 2018, 2018.

16. Kotal M, Bhowmick AK. Polymer nanocomposites from modified clays: recent advances and challenges. *Prog Polym Sci*. 2015;51:127-187.
17. Chen RS, Ahmad S, Gan S. Characterization of recycled thermoplastics-based nanocomposites: polymer-clay compatibility, blending procedure, processing condition, and clay content effects. *Compos Part B Eng*. 2017;131:91-99.
18. Botha N, Coetzer R, Inglis H, Labuschagne F. Understanding the Influence of manufacturing and material parameters on the mechanical properties of polymer-clay composites: an exploratory statistical analysis. In: *AIP Conference Proceedings*; 2019.
19. Parschau CG. *Influence of Manufacturing Parameters on the Tensile Properties of Clay-Polymer Nanocomposites*; 2016.
20. Ellis B. *Statistical Study of the Mechanical Properties of Polymer-Clay Nanocomposites: A Python Based Analysis of Experiments*; 2017.
21. Heymans DP. *Modelling of Particulate Composites with Finite Element Analysis in CalculiX*; 2018.
22. Braun KT. *A Statistical Investigation into the Effects that Additives have on the Tensile Properties of Polymer-Clay Nanocomposites Using a Taguchi's Design of Experiments*; 2018.
23. ASTM D638-14. *Standard Test Method for Tensile Properties of Plastics*. ASTM; 2014.
24. Osman MA, Atallah A. High-density polyethylene micro- and nanocomposites: effect of particle shape, size and surface treatment on polymer crystallinity and gas permeability. *Macromol Rapid Commun*. 2004;25:1540-1544.
25. Perktold S, Perktold S, Perktold J. Statsmodels: econometric and statistical modeling with python. In: *Proceedings of the 9th Python in Science Conference*; 2010.
26. Montgomery DC, Runger GC. *Applied Statistics and Probability for Engineers*. 4th ed. John Wiley & Sons, Inc; 2007.
27. Montgomery DC. *Design and Analysis of Experiments*. 8th ed. John Wiley & Sons, Inc; 2013.
28. Chu D, Nguyen Q, Baird DG. Effect of matrix molecular weight on the dispersion of nanoclay in unmodified high density polyethylene. *Polym Compos*. 2007;28:499-511.
29. Mistretta MC, Botta MML, Rifici S, Ceraulo M, Mantia FPL. Injection molding and mechanical properties of bio-based polymer nanocomposites. *Materials*. 2018;11:613.
30. Paul D, Robeson L. Polymer nanotechnology: nanocomposites. *Polymer*. 2008;49:3187-3204.
31. Brandeburg RF, Lofi A, Lepienski C, Coelho L, Becker D. Influence of mixing in mechanical properties of clay and carbon nanotube and high density polyethylene. In: *AIP Conference Proceedings*; 2014.
32. Silva BL, Nack FC, Lepienski CM, Coelho LAF, Becker D. Influence of intercalation methods in properties of clay and carbon nanotube and high density polyethylene nanocomposites. *Mater Res*. 2014;17(6):1628-1636.
33. Denchev Z, Dencheva N, Funari SS, Motovilin M, Schubert T, Stribeck N. Nanostructure and mechanical properties studied during dynamical straining of microfibrillar reinforced HDPE/PA blends. *J Polym Sci B*. 2010;48:237-250.
34. Esteki B, Garmabi H, Saeb MR, Hoffmann T. The crystallinity behavior of polyethylene/clay nanocomposites under the influence of water-assisted melt blending. *Polym-Plast Technol Eng*. 2013;52(15):1626-1636.
35. Mehrabzadeh M, Kamal MR. Melt processing of PA-66/clay, HDPE/clay and HDPE/PA-66/clay nanocomposites. *Polym Eng Sci*. 2004;44(6):1152-1161.
36. Merinska D, Kubisova H, Kalendova A, Svoboda P. Processing and properties of polyethylene/montmorillonite nanocomposites. *J Thermoplast Compos Mater*. 2012;25:115-131.
37. Kelnar I, Kratochvil J, Padovec Z. Nanofiller-modified microfibrillar composites: origin of complex effect of nanoparticles with different geometry. In: *Advanced Materials: TechConnect Briefs 2016*, Washington, USA; 2016.
38. Fu S, Sun Z, Huang P, Li Y, Hu N. Some basic aspects of polymer nanocomposites: a critical review. *Nano Materials Sci*. 2019;1:2-30.
39. Rong M, Zhang M, Ruan W. Surface modification of nanoscale fillers for improving properties of polymer nanocomposites: a review. *Mater Sci Technol*. 2006;22:787-796.
40. La Mantia FP, Mistretta MC, Morreale M. Recycling and thermomechanical degradation of LDPE/modified clay nanocomposites. *Macromol Mater Eng*. 2014;299:96-103.
41. Scaffaro R, Botta L, Mistretta C, La Mantia FP. Processing – morphology – property relationships of polyamide 6/polyethylene blend–clay nanocomposites. *eXPRESS Polym Lett*. 2013;7(10):873-884.
42. Mistretta MC, Morreale M, La Mantia FP. Thermomechanical degradation of polyethylene/polyamide 6 blend-clay nanocomposites. *Polym Degrad Stab*. 2014;99:61-67.
43. Jo C, Naguib HE. Effect of nanoclay and foaming conditions on the mechanical properties of HDPE/clay nanocomposite foams. In: *5th International Conference on Thermoplastic Foam*, Chicago, Illinois, USA; 2006.
44. Jo C, Naguib HE. Effect of nanoclay and foaming conditions on the mechanical properties of HDPE-clay nanocomposite foams. *J Cell Plast*. 2007;43:111-121.
45. Jo C, Naguib HE. Processing, characterization, and modeling of polymer/clay nanocomposite foams. *J Phys: Conf Ser*. 2007;61:861-868.
46. Jo C, Naguib HE. Modeling the effect of strain rate on the mechanical properties of HDPE/clay nanocomposite foams. *Polym Polym Compos*. 2008;16(8):561-575.

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