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Role of Viscosity on Optimum Polymer-Fibre Interaction during Rotational Moulding Sintering

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Abstract. The present work investigated the effect of polymer viscosity properties on the sintering of a fibre-reinforced rotationally moulded composite part. Previous researchers have concluded that polymer characterisation is fundamental to achieving optimum composite materials processing in rotational moulding. Nevertheless, the presence of a disperse phase during sintering directly impacts the current understanding of how sintering works during heating. Lack of pressurisation during rotational moulding implies an absence of driving forces to strongly bond two materials together as necessary in composite structures. It means that sintering and densification are the fundamental phases in which two or more materials can create an interface that can transmit stresses. A novel single-particle interaction test (FPIT) investigated the effect of polymer adhesion during sintering. The test was developed to identify the optimum parameters to achieve the best polymer adhesion to the fibre. The test focused on measuring the polymers' angle of contact (AoC) to the fibre to better understand how to achieve optimum fibre coverage. Combinations of glass fibre (G.F.) with polyethylene (P.E.) of various melt flow indexes (MFI) were tested to identify the role of viscosity on fibre-polymer adhesion. Attempts to automate the contact angle measurement proved challenging, so mnual measurement proved to be more effective. Sintering results showed that polymer viscosity has a critical effect on fibre wetting, and the use of Hi-MFI resins or plasticisers can improve adhesion. Finally, results showed that polymer-fibre characterisation plays a crucial role in sintering and densification, and work is ongoing to present conclusions about how sintering and densification affect the full-scale manufacturing process.

Introduction

Rotational moulding is a process for manufacturing hollow plastic products. Although there is competition from blow moulding, thermoforming and injection moulding to manufacture such products, rotational moulding has particular advantages in terms of relatively low levels of residual stresses and relatively low-cost moulds [1]. Among all the polymers used in rotational moulding, polyethylene (P.E.) is the primary material used due to its low cost, low melting point and excellent thermal stability. Although PE's tensile strength and stiffness are below other materials, it stands out in terms of impact strength. Around ~90% of the rotomoulded parts produced worldwide are made from PE [2,3].

Nevertheless, there are still some challenges in terms of strength improvements as some parts manufactured for the industry require to be reinforced to maintain or improve their mechanical properties [3]. The classical rotomoulding cycle starts with the loading of the polymer in powder form to a mould. The mould undergoes a heating process (heating temperatures of 150°C-350°C), in which it is rotated so that the polymer powder can fully cover the inner mould surface. After the material has fully formed a molten polymer film, the rotating mould is subsequently moved to a cooling

chamber, in which the temperature decreases to solidify the part. Once the part is fully solid, the product can be de-moulded.

Sintering in rotational moulding has been studied several times in the past [4–9]. However, there is a lack of literature covering polymer sintering when reinforcing fibres are present. The idea of studying how fibres can affect sintering is necessary since sintering is the fundamental mechanism by which parts are created in rotational moulding. It is necessary to know how the polymer adheres to the fibre and how its presence affects how it naturally bonds to itself. This mechanism is essential as it determines which materials can be combined in the process. In the same way, the optimal adherence of the polymer to the fibre directly determines the strength of these composite material structures.

The bonding conditions between two materials differ between manufacturing methods. Processes such as injection moulding use temperature and pressure to bring matrices into contact with fibres. Viscosity is also another fundamental parameter since it is related to how the resins can flow on the surfaces of the fibres. In other fields such as adhesive development, pressure measurements are used to optimise the effectiveness of the bond between the substrates and the adhesive [10]. In general, pressure is the fundamental variable to reinforce the bonding between materials, maximising the contact surface. However, since rotational moulding is a low-pressure process, there is a need to look at other driving forces such as surface tension or capillarity to maximise fibre-polymer adhesion. This work specifically focuses on measuring the effect of polymer viscosity on fibre polymer adhesion.

The work presents a new testing method to analyse resin adherence to reinforcing fibres under similar conditions to a rotational moulding cycle. The method has been called the 'Fibre-Particle Interaction Test' (FPIT) and is based on similar methods previously used to study the sintering of resins for rotational moulding [4–6]. The main difference of this method is the reinforcing fibre incorporation of the reinforcing fibre, which is sought to show how the resin adheres to it. The work begins by briefly presenting the materials used in the test as well as by describing the testing method in more detail. It continues with the presentation of the results and a discussion interpreting the data. Finally, the conclusions obtained from the data measured are outlined.

Fig. 1 – Poor (left) and optimum (right) fibre adherence and distribution of a rotationally moulded part.

Materials

This work is focused on testing Hi-MFI resins to find out the effect of viscosity on adherence to fibres. During previous investigations, it was observed that the way the resins flowed over the fibres during heating could be related to how they wet and covered the fibres. For this reason, it was decided to carry out a series of experiments that would test how the contact angle of low viscosity resins (Hi-MFI) varies in an FPIT experiment. The experimental plan consisted of combining three low-viscosity resins with chemically treated glass fibres. The glass fibre used was the OCV™ Reinforcements fibres coded 952-13C. These fibres were treated and identified as silane-treated (F1), untreated (F1-W), acid-treated (F1-AC) and alkali-treated (F1-AK). The fibres were combined with the RH1, RH2 and RH3 resins detailed below and were tested using the FPIT method. The resins

used were of low-density polyethylene (LDPE), which formulation included a plasticiser to increase its MFI. Tab. 1 summarises the 3 resins used, in which the resins RH1, RH2 and RH3 are identified with the MFI indices 7.5, 22 and 70, respectively. RH1 resin has an MFI of 7.5, which puts it close to the range of rotational moulding resins, and RH2 and RH3 resins have higher indices than those used in R.M.

Tab. 1 – Hi-MFI resins used during the trials.

Code	TBW Name	ρ [g/cm3]	MFI [g/10min]	MP [°C]	σ_y [MPa]	ε [%]	E [MPa]
RH1	LDPE 1070MN18C	0.918	7.5	108	9	450	170
RH2	LDPE 1200MN18C	0.918	22	106	8	250	160
RH3	LDPE 1700MN18C	0.918	70	105	8	120	150

Fibre Treatment Procedure

The fibre chemical treatment was based on the literature consulted [3,11,12]. Although more complex techniques can be used, combining washing and soaking to simplify the process makes treating large quantities of fibres time-efficient. The process comprises two stages: the first stage was washing using distillate water at ambient temperature (20 - 25°C) and atmospheric pressure for 20 minutes. This procedure produced what it is referred to as "washed" or "untreated" fibres (F1-W). The second stage was the submersion of the washed fibres into an aqueous 1 N solution of either H_2SO_4 (acid – F1-AC) or NaOH (alkali – F1-AK). Finally, the fourth treatment investigated was silane treated fibres, which consisted of fibres unwashed with its original silane treatment provided by the manufacturer (F1). Concentrations prepared were 1 N based on previous researchers work [3], and normality was used to assure the same number of equivalents. Finally, a Memmert U universal heating oven was set at 60° C, and the fibres were placed for 24h.

FPIT Method

Fig. 2 – Illustration of the setup used for FPIT. Microscope (left), fibre-particle contact (centre) and a 1X picture of the sample (right).

This new method, called 'Fibre-Particle Interaction Test', consists of a microscope with a heating stage, in which a sample made up of a resin particle and fibre to be tested is located. The fibre part of the sample comprises a group of about 4.5 to 6 mm long and 1 to 1.5 mm wide. The particle part is made up of a 1x1x1 mm approximately cubic resin particle that has been prefabricated with the help of the Platen Press. The fibre-particle group is placed horizontally in the microscope while the cubic particle is located in the upper part of the fibre, guaranteeing contact with tweezers. The hot stage is then used to warm up the group while taking pictures with a digital camera connected to the microscope. The images show how the heat softens Trends and melts the plastic and how this adheres to the fibres in a process similar to wetting. Finally, image processing software is used to manually measure the angle of contact (AoC) between the resin and the fibre to produce contact angle measurements concerning time. In this way, resins that adhere better to the fibre will describe a different angle than those that adhere worse. Experiments were performed once with no repetitions, and the images were measured three times per sample.

The main FPIT components of the equipment used were a platen press for sample preparation, a compound microscope for image acquisition, and image processing software for image analysis. The platen press used was a COLLIN P200P machine. The Queen's University of Belfast kindly supplied a small, squared mould to use combined with the platen press. Likewise, a standard set of blades was used to section samples from the polymer plate to replicate a polymeric particle. Furthermore, a Nikon Eclipse ME600 microscope with diascopic/episcopic illumination was used. A Nikon Digital Sight DS-5M digital camera was used to acquire the images from the microscope. A PS1-Stage Mic 10mm/0.1mm standardised calibration scale by Graticules Pyser-SGI LTD was used to achieve a traceable pixel-to-length measurement. A programmable THMS 600 hot plate by Linkam Scientific Instruments was used to control the heating process accurately. Finally, Java-based image processing software named ImageJ developed at the National Institutes of Health and the Laboratory for Optical and Computational Instrumentation was used to manually measure the AoC three times in each set of images.
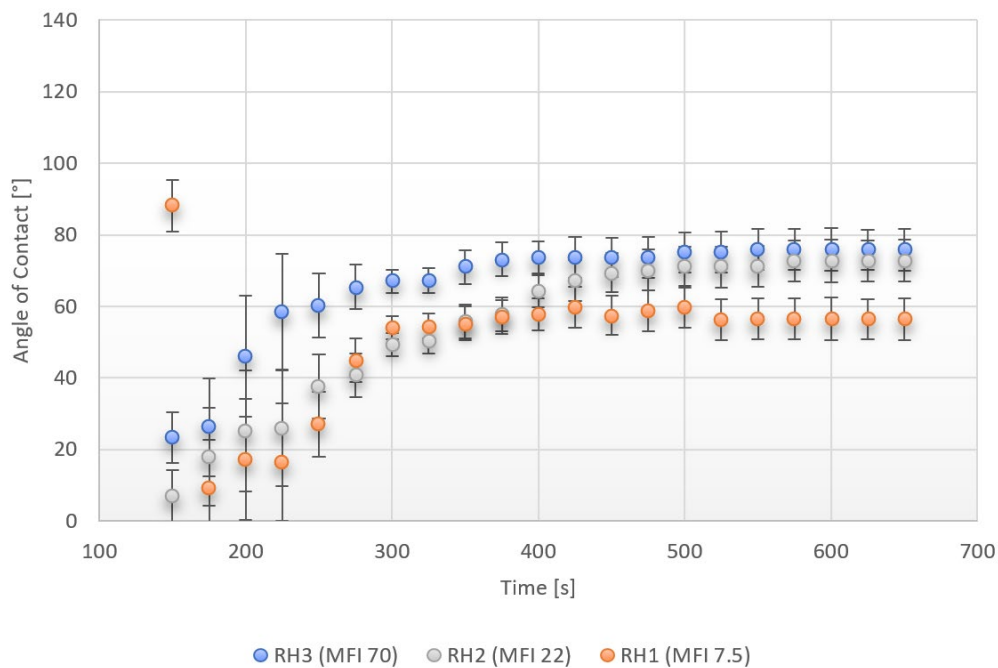
Results

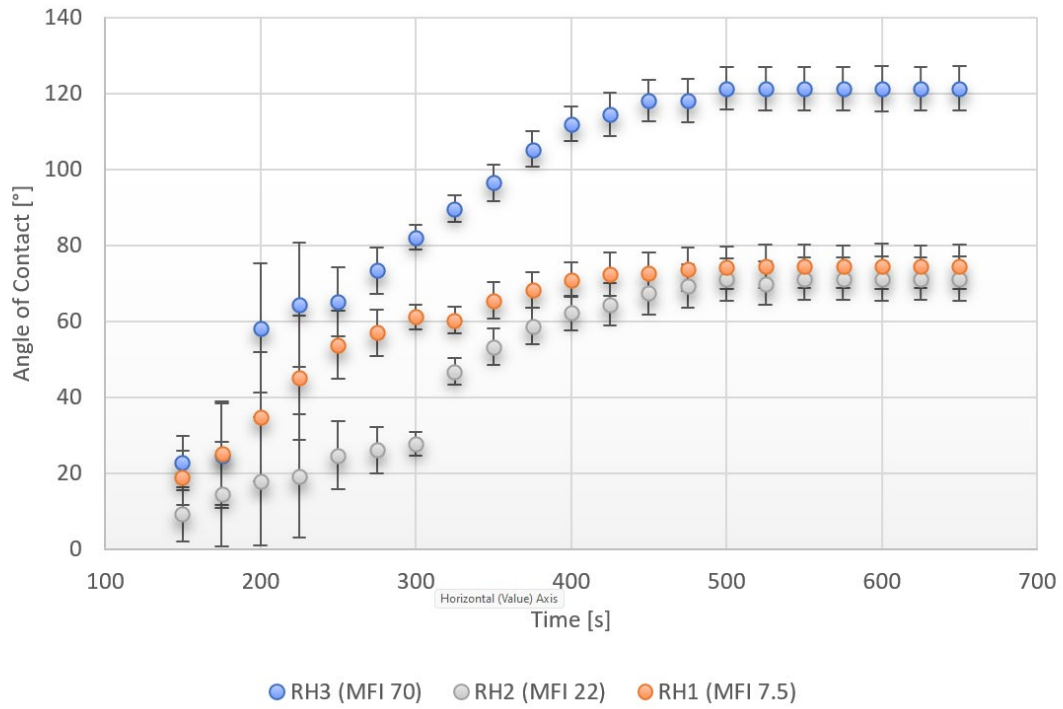Fig. 3 – FPIT of Untreated Glass Fibres (F1-W) with Hi-MFI LDPE resins.

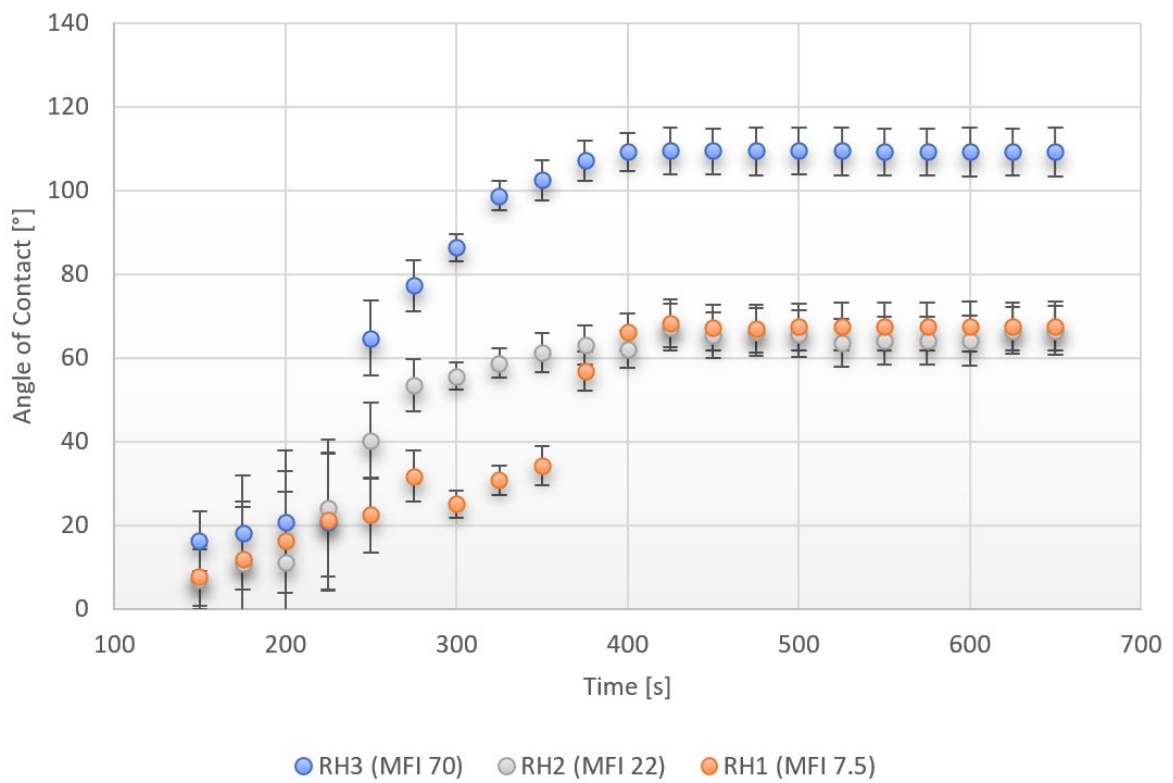Fig. 4 – Silane Treated Glass Fibres (F1) with Hi-MFI LDPE resins.

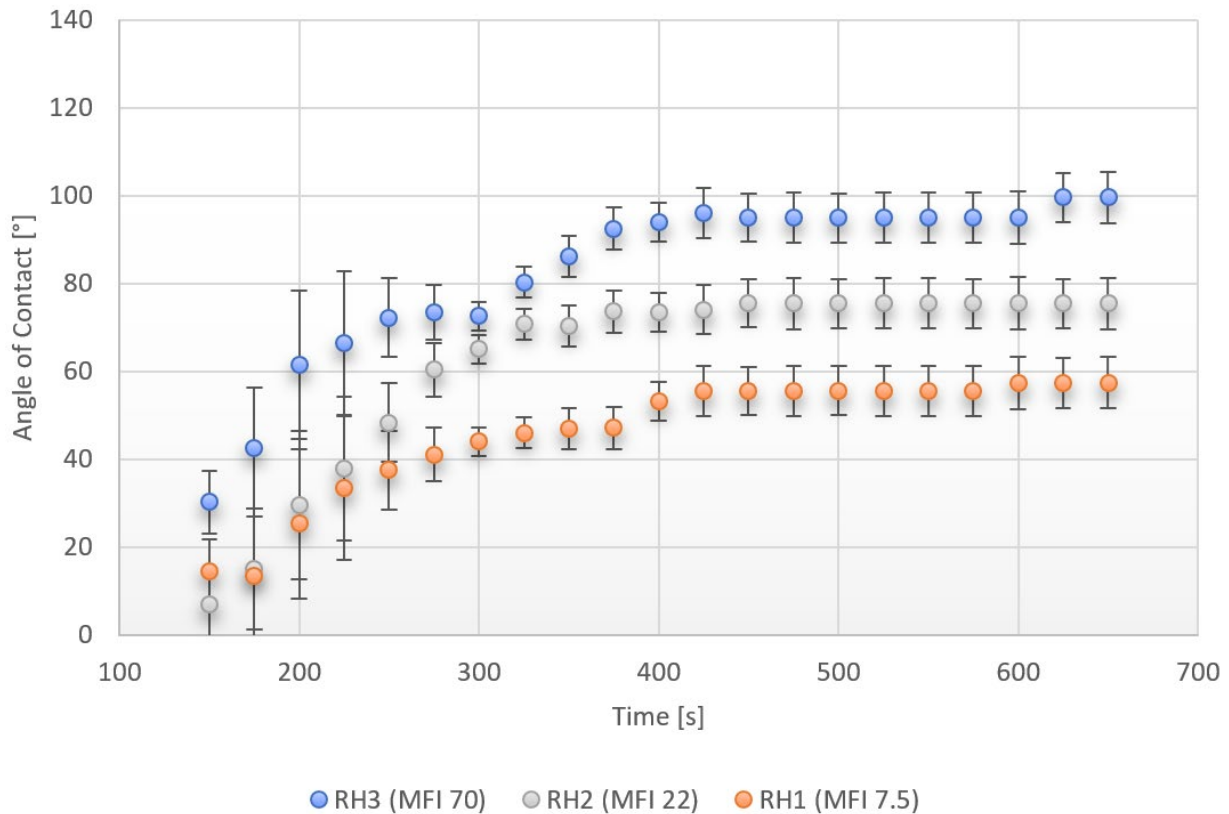Fig. 5 – Acid Treated Glass Fibres (F1-AC) with Hi-MFI LDPE resins.

Fig. 6 – Alkali Treated Glass Fibre (F1-AK) with Hi-MFI LDPE resins.
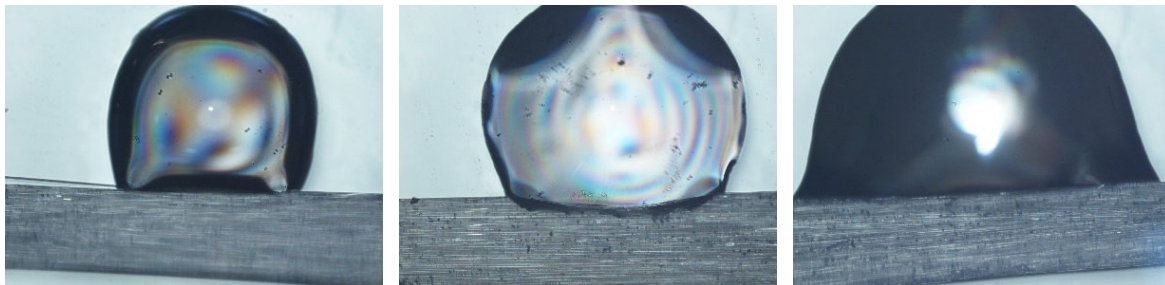
Discussion

Fig. 7 – FPIT images of RH1 (MFI 7.5), RH2 (MFI 22) and RH3 (MFI 70), respectively.

The results are shown in Fig. 3 to Fig. 6. Each figure represents an AoC curve for the high MFI resins in contact with the fibres of the four treatments. Error bars show the standard deviation of the three measurements taken. All samples were subjected to the same heating conditions, and the data generated curves consistent with results obtained in preliminary work. However, the tests carried out with these resins generated much higher contact angles. Standard deviation varied significantly at the beginning of the tests due to the higher adhesion speed at the beginning of test. The fastest the adhesion occurs, the harder it is to pinpoint the data point, and the more variation is observed. Adhesion speeds are calculated by linear regression of the angle data points until reaching 90% of the final angle described. The apparent "breaks" in the graphs are due to the relatively high adhesion speed, which give the impression of discontinuity. However, the images captured clearly show the continuity of the process.

First, Fig. 3 shows the results of Hi-MFI resins in contact with untreated fibres (F1-W). The data shows that the RH3 resin produced the most significant contact angle (75°), followed by the RH2 resin (70°) and finally by the RH1 resin (55°). However, the data suggests that the RH2 resin is slightly slower than the RH1 resin, as it shows an adhesion speed of 0.281°/s versus 0.359°/s. The fastest resin in contact with untreated fibre is RH3 resin, with a speed of 0.389°/s. An atypical

datapoint observed in Fig. 3 corresponds to the angle measurement of a squared sample shape at the beginning of the process, prior to sample melting. Hi-MFI resin's adhesion angles are considerably greater than those of the RM-type resin tested, which indicates flowability benefits the adhesion process.

Fig. 4 shows the results of the F1 fibres tested in contact with Hi-MFI resins. These data show a significant increase in the contact angle for the RH3 resin, which produced the highest contact angle tested to date (120°). The RH1 and RH2 resins showed lower angles, of 75° and 70°, respectively, but they are still much higher angles than most RM-resin measurements. The RH3 resin also proved to be the fastest, with a speed of 0.357°/s, followed by the resins RH1 and RH2 with speeds of 0.282°/s and 0.220°/s, respectively. Regarding the behaviour of Hi-MFI resins in contact with fibres treated with acid (F1-AC), the results are observed in Fig. 5. Again, the RH3 resin shows a high wetting capacity producing a significantly high angle (110°). In the same way that occurred with the F1 fibre, the RH1 and RH2 resins showed very similar angles, 68° and 64°, respectively. However, the angle of these resins was slightly lower than those shown in contact with the F1 fibre. The RH3 resin showed the highest speed recorded in this series, 0.472°/s, followed by the RH2 resin (0.365°/s) and the RH1 resin (0.218°/s).

Finally, Hi-MFI resins with alkali-treated fibres (F1-AK) showed similarities with previous data. The results are observed in Fig. 6, and it again shows how the RH3 resin produces the highest contact angle (93°), followed by the RH2 resin (75°) and RH1 (60°). In this case, the results are more distributed to cover the range of observed angles from 60° to 100°. However, the speed of the RH2 resin is the highest (0.365°/s), followed closely by the RH3 resin with a speed of 0.346°/s, finally by the RH1 resin with a speed of 0.155°/s.

The tests detected a dramatic impact on the adhesion angle when combining hi-MFI resins with reinforcing fibres. The effect is particularly noticeable in those chemically treated fibres. Increasing the resin's MFI from 7.5 to 70 showed an increase in contact angle of up to almost 120% between best and worst cases. This dramatic increase indicates that the use of high MFI resins can improve resin flowability, wetting and material distribution on the fibre surface due to its low viscosity. However, high MFI resins tend to cause the resin to lose mechanical properties, which is counterproductive to reinforcing rotomoulded parts. In the same way, temperature is a critical parameter that affects material properties, including viscosity. Consequently, heating parameters must be investigated to modify resin flowability by a change in resin temperature.

Conclusions

Given the data obtained in the results (summarised in Tab. 2 and Tab. 3), it can be concluded that the use of high MFI resins can assist in flowing, wetting, and distributing the material on the fibre surface due to their low viscosity. However, the use of high MFI resins tends to result in the loss of the resin's mechanical properties, which can be counterproductive to the objective of reinforcing rotomoulded parts. Therefore, it is recommended to explore varying heating parameters by increasing the fibres' temperature and decreasing viscosity. In this way, similar adhesion effects could be achieved without sacrificing the mechanical properties of the resin.

Tab. 2 – Summary of the AoC results.

[°]	RH1	RH2	RH3
F1-W	55	70	75
F1	75	70	120
F1-AC	68	64	110
F1-AK	60	75	93

Tab. 3 – Summary of the initial slope results.

[°/s]	RH1	RH2	RH3
F1-W	0.359	0.281	0.389
F1	0.282	0.220	0.357
F1-AC	0.218	0.365	0.472
F1-AK	0.155	0.365	0.346

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