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Rapid Multifunctional Composite Part Manufacturing using Controlled In-situ Polymerization of PA6 Nanocomposite

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Abstract

Currently, mass composite manufacturing is dominated by the fiber-reinforced thermosets due to the ease of its processing. However, the addition of multifunctionality to the thermoset composite requires an additional step of manufacturing. This work presents the single-step rapid manufacturing of bespoke designed multifunctional nanocomposite PA6 components. In this method, firstly, the liquid PA6 nanocomposite containing inorganic nano-inclusions was infused into a glass or carbon fibre matrix placed within the mould. Subsequently, the multifunctional composite component was formed via the anionic in-situ synthesis route. The flexibility of this method presented is akin to that of a polymer moulding process, which ensures a reduction in the manufacturing cycle times and increases the production efficiency of the bespoke component. The in-situ reaction is optimised by setting the specific volume of the activator, initiator and including polymer chain terminator, PEG. To prepare the polymer with at least 50% and above crystallinity, the most suitable activator-initiator combination was found to be 0.143 ml and 0.096 ml respectively, with 0.1 g of PEG-6000 for 5 g sample preparation. Such thermoplastic-based components can be easily recycled, present better impact resistance and can be easily formed or fused with heat; eliminating the cost and time associated with the assembly of composite part, unlike thermoset components.

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Keywords: Composite; Thermoplastic; PA6 Polymer; Rapid Manufacturing; Infusion.

1. Introduction

Multifunctional materials are becoming important part of composite industry as they have more than one primary function occurring at the same time. Many companies in aerospace industries are developing components with multifunction such as structural stability of composite winglet

combined with the communication enabler VHF antenna.

However, the development of multifunction components is fraught with many challenges. Conventionally, the polymeric material is mixed with nanoparticles to produce the bulk material, which, subsequently, is processed further to integrate with structural component such as winglet. The various possibilities of multi-functionalities that can be achieved by suitable nano-inclusions or involving reinforcements, that can be easily combined with the proposed part manufacturing technique for structural applications is summarised in Fig. 1. The proposed process ensures the uniform dispersion of nanoparticles in the polymeric matrix, which sometimes is a challenge at high nanoparticle concentration. Ensuring uniform dispersion and seamless integration with structural composite components is a key to deliver a component with multifunctional abilities. This new method uses magnetic nanoparticles containing polymer nanocomposite to coat the

Nomenclature

CL	ϵ -caprolactam
EtMgBr	ethylmagnesium bromide
NACL	N-acetylcaptoprolactam
PEG	polyethylene glycol
DSC	Differential Scanning Calorimetry
FTIR	Fourier-transform infrared spectroscopy
T_g	Glass transition temperature ($^{\circ}\text{C}$)
T_m	Melting temperature ($^{\circ}\text{C}$)

carbon fibre reinforced polymer (CFRP) component (dog bone shape). It can be useful in self-healing, reducing viscosity of oil in oil-water separator [1] where this material can ensure magnetic pulsing through extrinsic stimuli and ensure structural integrity requirements. The work here only proof of concept to manufacture such type of component and focus is not on measuring its functional properties. Our previous publication shows an example related to the magnetic nanocomposite multifunctionality [5].

Many components are now made using thermoplastics due to their resistance to environmental impacts and superior fatigue-crack response. Unlike thermosets, they also do not demand additional setting for crosslinking. Though melt-processing of thermoplastics-based nanocomposite is quite challenging, due to rheology of the melted polymer. As their high viscosity doesn't facilitate the state of rapid manufacturing.

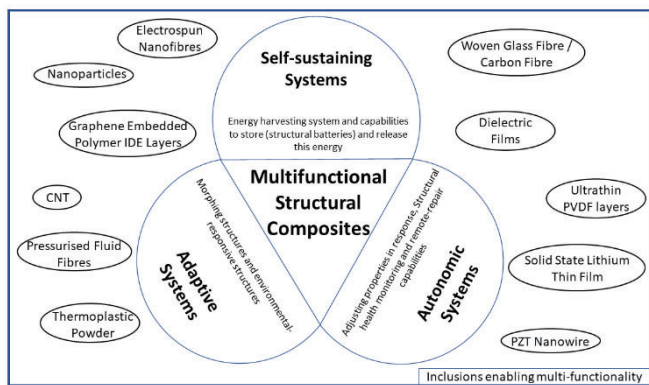


Fig. 1. Possibilities of multi-functionalities with the proposed part manufacturing technique for structural applications.

The in-situ technique of polymerisation can easily facilitate overcome that challenge, by aiding dispersion of nano-inclusions in the low-viscosity monomer CL at first and then accomplishing anionic polymerisation via infusion route to synthesize the PA6 nanocomposite part. If this reaction moulding technique is combined with the nanoparticle mixing, the multifunctional component can be made in a single step. According to proposed method, by injecting the low-viscosity mixture into the mould containing CFRP component, the multifunctional composite can be made in a single step. This is akin to overmoulding technique, in which the layer of polymer is injected over existing component to coat or form a layer on the CFRP component. By injecting two part monomers over the CFRP component, the layer having multi-functionality can be added to the structural component. This allows to control the temperature of the CFRP component and monomer mixtures within the mould, and hence the bonding between these layers can be ensured. The key challenge of this work is to control the polymerization time and crystallinity of the resulting PA6 polymer. Ensuring enough polymerisation time will ensure that the reaction would occur in the mould instead of the injection system. Secondly, tuning the polymerisation time also allows controlling the crystallinity and size of crystallites, ensuring good mechanical properties of the resulting PA6 nanocomposite [3,4]. The bonding capability between the used

CFRP tape and, the designed nanocomposite is well-established in previous study [5].

Interestingly, the rate of polymerisation of in-situ anionic technique can be controlled as demanded by the infusion manufacturing technique, by suitable selection and appropriate proportion of the activator & initiator combinations [2]. Hence, the choice of following the in-situ anionic polymerisation method in this study. The mechanical and thermal properties of the resulting PA6 composite has a close relationship with its crystallinity, hence, to achieve an application-suitable composite its very critical to select the right combination of the initiator and activator [3,4,5]. The effect of increased crystallinity on some of the properties is represented in the Table 1 below by either increase or decrease of the particular property [6].

Table 1. Effects on properties caused by increased crystallinity [5].

Increases	Decreases
Stiffness	Elongation
Density	Impact resistance
Tensile and yield stress	Thermal expansion
Chemical and abrasion resistance	Permeability

Herein to manufacture PA6 composite part, it was decided to apply anionic ring-opening polymerisation of caprolactam with a choice of EtMgBr as initiator and NACL as activator, considering the previous research [3-5]. The volumetric concentration tested earlier [3] was taken as basis and other four concentrations were established by varying the volume of activator and initiator. Two of the concentrations were established by varying EtMgBr concentration and another two by varying NACL concentration. The concentrations tested for polymerisation of five grams of monomer CL is listed in Table 2.

Table 2. Concentrations combination of initiator and activator tested.

Sample/Concentration	EtMgBr (ml)	NACL (ml)
C1	0.200	0.160
C2	0.286	0.160
C3	0.143	0.032
C4	0.143	0.096

Adding Fe₃O₄ nanoparticles as the nano-inclusions facilitates the magnetic sensing and stimuli-responsive healing multifunctionality for structural applications [5].

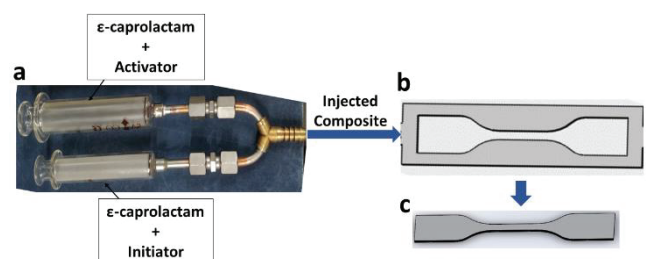


Fig. 2. (a) Syringe setup for infusion polymerisation; (b) Standard Dog-bone mould with prepeg for rapid manufacturing and (c) Prepared composite part.

To ensure proper mixture and synthesis of the PA6 composite part, the setup of two glass syringes connected with manufactured 'Y' connector was used with the standard dog-bone mould already containing the CFRP part, as shown in Fig. 2.

The various concentrations were tested and then the final optimised concentrations suitable for resulting in the desired crystallinity was used to manufacture the dog-bone composite sample using this setup.

2. Materials and Methods

2.1. Materials

CL with a 99% purity and Molecular weight of 113.16 g/mol in solid, white granules form, NACL with 99% purity and Molecular weight of 155.19 g/mol, EtMgBr solution 3.0 M in diethyl ether, Iron (III) oxide (Fe_3O_4) with particle size of <50 nm (BET) and PEG – 6000 grade was used as received from Sigma-Aldrich Company Ltd. Gillingham, UK. Electronic weighing scales with $\pm 5\%$ uncertainty was used for all weight measurements.

2.2. Methodology

The first step was to test the effect of variable activator and initiator on the properties of the synthesised samples. So, we weigh 5 g of CL into to the glass vial, prepare required amount of a NACL as well as EtMgBr into the separate syringes, which later will be used for injection into the melted monomer. Then the CL in glass vial is placed on the electric heating plate and heated up to 69 °C, the melting temperature of CL. Further heating continued and temperature reaches around 130 °C EtMgBr is injected. After that, the mixture is slightly heated up to 150 °C at which point NACL is injected. PEG 6000 with 2 w/w % of CL i.e. 0.1 g was used with each sample to improve upon the plastic behavior of the samples. All measurements were subject to uncertainty of $\pm 5\%$, either due to the experimental limitations of the instruments involved or human factor. The time of polymerisation in each case was noted and the degree of crystallinity was calculated analyzing the DSC curve. And the resulting polymer backbones were analysed with FTIR analysis.

Once identifying the most suitable combination, we used the optimised proportion of initiator and CL in one syringe and activator with CL in another syringe; included with 2 w/w % of PEG and 1 w/w % of iron nanoparticles divided in the two syringes as per their volume proportion. The inclusion of nanoparticles was just to make possible the nanocomposite preparation, as a multifunctional material for suitable application [4]. The method was followed similar to that reported in earlier study [3]. The method was followed similar to that reported in earlier study [3]. Upon heating the monomer to 150 °C, the two parts monomers were injected simultaneously into the mould using Harvard PhD 4400 syringe pump setup at 100 ml/min rate. The syringe pump was fitted with an attachment which can drive both syringes simultaneously to inject the both materials into the mould.

DSC was performed on a TA Instruments DSC Q100 at a heating rate of 10°C/min under a nitrogen purge within the temperature range of 20°C to 250°C. and the T_g and T_m were determined. The polymer backbones of nanocomposite samples were characterized using a Perkin-Elmer ATR-FTIR (Attenuated Total Reflection - Fourier-Transform Infrared Spectroscopy) using a DGS-KBr sensor to identify functional groups and structural changes after addition of the iron oxide NPs. Nanocomposite films averaging 0.1 mm thickness were prepared and a total of 30 scans in range of 525-4000 cm^{-1} wavenumber were carried out at a resolution of 4 cm^{-1} .

3. Results and Discussions

The results of DSC for four samples made using the different concentrations are plotted in Fig. 3. The DSC plots of heat-cool-heat cycle provided information such as exothermic peak during cooling, which is re-crystallisation peak and we used the second endothermic melting peak for measurement of crystallinity. Since, the concentration of the Fe_3O_4 NPs nano-inclusion was only 1 w/w% and its effect on the resulting mixtures viscosity was negligible. Though, this will be a critical parameter for the CL viscosity and the resulting nanocomposites' crystallinity, if the concentration of NPs is 20 w/w% or higher [4].

The CL melting peak did not appear only on C2, hinting that all the CL was converted to PA6. It was also noticed that temperature of PA6 melting peak, T_m was highest and almost similar for C1 and C2 and lowest for C3; this can be due to the highest and lowest conversion ratio of CL in C1 & C2 and C3 respectively. Finally, crystallinity percentage was calculated with reference to that of a 100% crystalline PA6 sample (190 J/g) [5] and is summarised in Table 3. The samples C2 and C4 happened to show the highest degree of crystallinity. Also, the ca. time of polymerisation (T) in seconds was also observed and included along with the other analysis results.

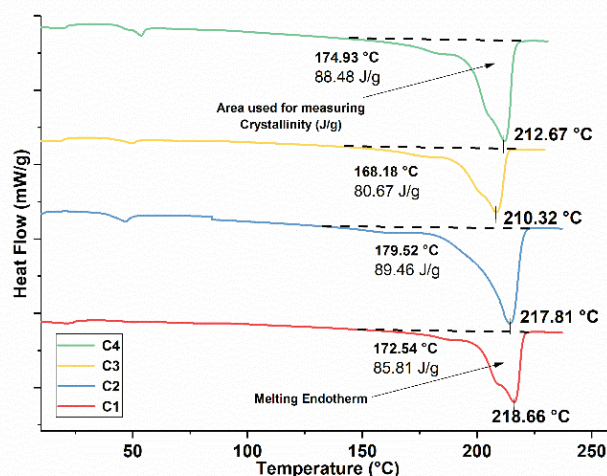


Fig. 3. DSC curves of the variable concentration samples.

Though the crystallinity of both C2 and C4 is highest, which is much desirable for superior thermal and mechanical

properties; but the T for C4 was highest, which is even desirable in this application, to ensure sufficient time for the mixing to happen in the Y-channel when used with the syringe setup. The higher T in case of sample C3 is due to the obvious reason that there's very less activator available for per unit of CL conversion.

Table 3. DSC results of all the samples.

Concentration	T _m (°C)	Enthalpy (J/g)	Degree of Crystallinity (%)	Time for Polymerisation (T) (sec)
C1	218.66±2	85.81±2	45.16±2	110±5
C2	217.81±1	89.46±2	47.08±2	120±5
C3	210.32±2	80.67±3	42.46±3	174±10
C4	212.67±2	88.48±2	46.57±2	145±5

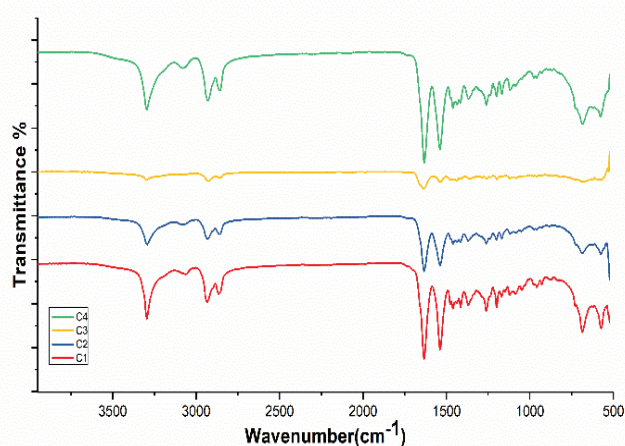


Fig. 4. FTIR plots of the variable concentration samples.

The peaks related with wavelength values of different bonds observed (Fig. 4) in different concentration samples were compared to that observed in commercial PA6 [6] and by taking the closest matching values and the strongest signal transmittance. The N-H symmetric stretching of secondary amine is observed in the wavelength range of 3350 to 3310 cm⁻¹, hence C3 and C4 were found closest with wavelength value of 3296 cm⁻¹, indicating small shift. The C-H stretching of alkene is in the range of 3100-3000 cm⁻¹ and was similar for all four concentrations. The methylene CH₂ asymmetric stretching vibrations range of 2930 to 2850 cm⁻¹ (Stuart 2000) was seen for all concentrations. The C=O bond stretching of 1680 cm⁻¹ and value of 1640 cm⁻¹ & 1630 cm⁻¹ for secondary and tertiary amide respectively, therefore all these peaks matched all four different concentrations spectra. The N-H bond bending of amine is 1650 to 1580 cm⁻¹, but the observed values for the different concentration polymers are little shifted as they are in the range of 1538 to 1540 cm⁻¹ and the sample C4 being closest to the desired value. The C-H bond bending of methylene group alkane has wavelength of 1465 cm⁻¹ and methyl group alkane of 1450 cm⁻¹, therefore the best matching values were of samples C1, C2 and C4. Moreover, the strongest signal transmittance occurred in sample C4 polymer which matched

with the commercial PA6 spectra very closely. The summary observation of all the samples is put up in Table 4.

Thus, both the DSC and FTIR hinted towards the suitability of using sample C4's concentration for the composite part manufacturing using the designed setup.

Table 4. Summary results of the observed FTIR spectra of all the samples.

Identification	C1	C2	C3	C4
N-H stretching amine	3295	3294	3296	3296
C-H stretching alkene	3064	3082	3060	3080
CH ₂ stretching alkane	2934/2865	2932/2860	2926/2855	2930/2858
C=O stretching tertiary amide	1635	1634	1636	1634
N-H bending amine	1539	1539	1538	1540
C-H bending alkane	1462	1461	1438	1461

4. Composite part manufacturing

For manufacturing the nanocomposite component, it was decided to use 30 g of monomer and because syringes volumes ratio was 2:1, thus the monomer was split into 20 g and 10 g parts. Amounts of initiator and activator were calculated for polymerisation of 30 g of monomer, therefore 0.858 ml of EtMgBr were injected into the vial containing 20 g of melted monomer (since it was the bigger volume, hence used with the bigger syringe) and 0.576 ml of NACL were injected into the vial containing 10 g of melted monomer. The mixture was transferred to the respective syringes, which were preheated. This was quite challenging, as the monomer demands uniform heating to maintain its melt state; which can be overcome by designing a uniform heating jacket setup for the syringes, but this would be an advanced stage.

Furthermore, there was challenge in pumping the mixtures together and hence led to uneven mixing. The resulting mixture was directly poured into the designed dog-bone mould and the mixture polymerized or rather solidified quickly. The sample formed is as shown in Fig. 5.



Fig. 5. The formed nanocomposite sample using the infusion method syringe setup.

The sample was not complete polymer nanocomposite, though most of the component contained polymerized sections. The testing of the sample revealed that almost 30% was still monomer and the reason being uneven mixing caused during

the infusion process of the syringes. Though the regions that were polymerized, show the quality to be as good as that of the commercial grade PA6 composite. The result of two such regions are summarised in Table 5 below.

Table 5. DSC result of the final polymer nanocomposite sample formed.

Region	T _m (°C)	Enthalpy (J/g)	Degree of Crystallinity (%)
1	215±2	83.25±2	43.81±2
2	214±2	80.59±4	42.41±4

5. Conclusions

Here, in this study we employed the anionic in-situ polymerisation technique of PA6 synthesis for composite part manufacturing. This is a novel method for facilitating rapid manufacturing of thermoplastic composite part manufacturing. The one-step manufacturing method was designed, optimised and implemented. The optimisation of the polymerisation method presented 0.858 ml of EtMgBr and 0.576 ml of NACL was the most suitable proportion to be used as activator and initiator for obtaining superior degree of crystallinity of almost 46%, as desired for improved mechanical and thermal properties. The slow rate of polymerisation attained with this combination for sample C4 presented the possibility of enough mixing time of the two mixtures. Though the final component produced was not an actual polymer nanocomposite, but there were enough traces of formed polymers that proves the possibility of this method as applicable for rapid composite part manufacturing. If the methodology of the syringe setup; considering the syringe sizes, heating rate, syringe pumping

rate, the mixing channel, etc. is studied and tuned for proper mixing while injecting the mixtures. The method can be developed to ensure quality for rapid composite manufacturing with multifunctional capabilities.

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