A thermoplastic resin matrix and its physical properties suitable for deformable mandrel

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Abstract. The mandrel is able to shape the part cavity, therefore is of great significance for composite parts in the manufacturing of carbon fiber reinforced polymer (CFRP) composite part. However, in the manufacturing of composite parts with complex cavities, traditional rigid mandrel cannot be removed out of the cavity in any direction after the outer prepreg is cured. To solve the problem of difficult demolding, a kind of deformable mandrel emerged. The deformable mandrel is rigid at room temperature to support composite part curing. While at relatively high temperatures, the mandrel is softened so that the mandrel can be easily removed from the composite part despite the complex part cavity shape, therefore resolving complications regarding the demolding process. In this paper, a thermoplastic resin material matrix suitable for the preparation of deformable mandrel is proposed. Ingredient and manufacturing flow of the thermoplastic resin matrix are introduced, and the applicability of the proposed matrix with regard to the deformable mandrel is validated through dynamic mechanical analysis.

Keywords: Thermoplastic, resin matrix, deformable mandrel, softening ability.

1. Introduction
Composite is a kind of advanced material made by the combination of two or more materials through certain manufacturing methods. Among various composites, the most widely used is carbon fiber reinforced polymer (CFRP) composite materials. Compared with traditional materials, CFRP composite has the advantages of designable performances, high specific strength and high specific modulus, so they are immensely applied in aviation and other industrial fields [1]. With the rapid expansion of applications, CFRP composite materials are gradually being used to manufacture parts with complex shapes, such as aircraft spars, S-shaped air ducts with variable cross-sections [2], etc.

Normally, the mandrel is involved to shape the complex cavities in the manufacturing of parts with complex shapes. Nevertheless, a problem may arise when using traditional rigid mandrels for manufacturing these CFRP parts: the mandrel cannot be removed out of the cavity in any direction after the outer part is cured.
To solve the problem of difficult demolding, developments of mandrel materials that enable easy demolding gradually become a noteworthy research topic. Water-soluble mandrel [3] and rubber mandrel [4] appeared successively with unique demolding methods of dissolving the mandrel and extracting the air inside the mandrel respectively, but their defects are also apparent. The water-soluble mandrel is a kind of one-off mandrel, and it is necessary to prepare mandrels for each part, so it lacks reusability. And the soft characteristics of the rubber mandrel cause uncontrollable deformation of the external prepreg during the curing process, which may affect the manufacturing accuracy of CFRP parts. Under the background that existing mandrel materials have shortcomings, carbon fiber reinforced thermoplastic polymer (CFRTP) composite gradually emerged as mandrel materials. CFRTP composite mandrel has sufficient strength to support the curing of outer prepreg that forms the part, while the lower glass transition temperature of this mandrel makes it easy to achieve heating-to-soften characteristic to enable mandrel reusability and simple demolding. Therefore, CFRTP is a relatively ideal mandrel material. The heating-to-soften characteristic means that the CFRTP mandrel can be deformed after being heated to its glass transition temperature so that the mandrel can be removed out of the part easily, so this kind of mandrel is also named the deformable mandrel.

This paper focuses on the thermoplastic resin matrix of CFRTP deformable mandrel that acquires heating-to-soften characteristics. In this paper, some existing materials that can be used to prepare deformable mandrel are studied, and a kind of thermoplastic resin matrix based on polymethyl methacrylate (PMMA) for the resin matrix of the thermoplastic deformable mandrel is proposed. After the proposed resin matrix is produced, its applicability is verified by dynamic mechanical analysis.

2. Existing thermoplastic materials suitable for deformable mandrel

The advantage of CFRTP as mandrel material is that the mandrel has sufficient strength at room temperature, and the mandrel can be softened when heated to a temperature above the glass transition temperature. This softening characteristic is controllable, so the mandrel can be softened when needed, and the problem of difficult demolding can be resolved.

To realize the softening characteristic of the deformable mandrel, experts and scholars have done a lot of research on materials suitable for thermoplastic deformable mandrel. Du et al. [5-6] prepared shape memory polymer mandrels with styrene-based shape memory polymer, winded prepreg on the mandrel, and cured the prepreg to produce an S-shaped air duct and dumbbell-shaped parts. Eventually, Du successfully removed the mandrel after heating and softening the mandrel. Later, Du et al. [7] carried out a two-step curing method to produce a deformable mandrel composed of two polystyrene shape memory polymer (SMP) materials. The glass transition temperatures of the two SMPs are different, so the mandrel acquires different shapes at different temperatures. This unique characteristic helps the mandrel to form different parts and demold. Li et al. [8] used the cross-linked polymer self-developed in the laboratory to prepare thermoplastic composite materials, which showed softening characteristics at around 80°C and had temporary shape setting and shape recovery capabilities.

Everhart et al. [9] proposed a shape memory polymer mandrel based on the shape memory polymer (Veriflex) developed by CRG company for the winding of prepreg and prepared honeycomb-shaped part and air duct part respectively assisted by proposed mandrels. Ahmad et al. [10] applied a commercial thermoplastic composite resin based on polystyrene to produce tensile test specimens, and their shape recovery ratio reached 90% at the temperature of 90°C. Wang et al. [11] prepared a Boron Nitride Nanosheet reinforced Ethylene Vinyl Acetate (BNNS/EVA) composite material, tested its bending resistance and shape memory ability through multiple bending tests, and discovered that this composite material has good thermal conductivity.

The aforementioned existing research exhibits a variety of thermoplastic resin materials that are qualified to be used as the deformable mandrel matrix. In addition to these existing resin formulations, this paper will also propose a kind of thermoplastic resin material suitable for the preparation of deformable mandrel, and then conduct related tests after preparing the thermoplastic resin.
3. Experiments

3.1. Materials
The proposed thermoplastic resin matrix is composed of thermoplastic resin polymethyl methacrylate (PMMA) and epoxy resin NPEF-170, with PMMA as the main ingredient. Some material parameters of PMMA are shown in Table 1. These material parameters indicate that the deformable mandrel based on this PMMA resin has sufficient strength to support the paving and curing of CFRP prepreg. The PMMA (Elium 150, ARKEMA) resin is liquid at room temperature and cures at 20-60°C within approximately 30 minutes after mixing its curing agent. Therefore this kind of PMMA resin is suitable for forming deformable mandrel by resin transfer molding process.

Table 1. Material parameters of Elium 150 PMMA resin.

| Item                  | Value   |
|-----------------------|---------|
| Tensile strength (MPa)| 66      |
| Tensile modulus (GPa) | 3.17    |
| Flexural strength (MPa)| 111     |
| Flexural modulus (GPa)| 123     |
| Coefficient of thermal expansion (mm/m/°C) | 0.065 |

The glass transition temperature of PMMA is around 110°C, which is relatively high. To adjust the glass transition temperature of the whole resin matrix, epoxy resin NPEF 170, with the glass transition temperature of 90°C, is added to the PMMA resin to obtain the appropriate glass transition temperature of the matrix. In addition, the toughener liquid nitrile rubber can be added selectively to adjust the extent of softening of the matrix so that deformable mandrels with different softening characteristics can be obtained.

The proposed resin matrix is prepared with a 4:1 mass ratio of PMMA and NPEF-170. Both resins were dried in a vacuum drying oven for eight hours before use. In preparation of the matrix, first of all the corresponding curing agent and toughening agent are added to the PMMA. After stirring for 15 minutes, NPEF-170 resin and its D230 curing agent are then added. After stirring for 15 minutes, the resin mixture is degassed with a centrifuge. After 10 minutes of degassing, the resin matrix can be used for the RTM process to prepare the deformable mandrel - the overall manufacture flow of the mandrel is illustrated in figure 1.

3.2. Dynamic mechanical analysis of the matrix
The glass transition temperature of the thermoplastic resin matrix is directly related to its heating and softening function, and thus, is the most critical performance indicator of the mandrel. After preparing specimens following the manufacture flow of the matrix, DMA Q800 (TA Instruments, USA) is adopted to perform the dynamic mechanical analysis and obtain the glass transition temperature of the mandrel material. The tensile mode of the device is set, and the movement mode is set to displacement control. The working frequency is set to 1Hz, while the specimen size is 10mm*3.5mm*2.5mm, and the
temperature range of the test process is 25°C -120°C. The DMA test is performed at three heating rates of 1°C /min, 2.5°C /min, and 5°C /min.

The test results of the dynamic mechanical analysis are shown in figure 2. It is shown that when the mandrel material is heated from 25°C to 120°C, the storage modulus decreases more than a thousand times. At low temperatures, the mandrel is at glass state. After the temperature rises above glass transition temperature, the mandrel enters rubber state with high elasticity. Besides, as the heating rate increases, the molecular motion of the mandrel material needs to overcome larger internal friction and get more thermal energy, and the storage modulus curve will move to the higher temperature side.

![Figure 2. Results of dynamic mechanical analysis of resin matrix.](image)

The glass transition temperature of mandrel material can be determined by the peak value of the loss modulus and the peak value of the derivative of storage modulus [12]. According to the measured storage modulus and loss modulus, the corresponding $T_g$ can be calculated, and the results are shown in Table 2 below. The results in the table show that the glass transition temperature of the mandrel material is between 90°C and 100°C. This temperature value means that the mandrel demolding temperature is around 100°C in which the cured CFRP part will not be affected. Therefore the resin matrix meets the requirements of the application of deformable mandrel.
Table 2. Glass transition temperature of the resin matrix.

| Heating rate | The peak value of the loss modulus | The peak value of derivative of storage modulus |
|--------------|-----------------------------------|-----------------------------------------------|
| 1°C/min      | 91                                | 91.5                                          |
| 2.5°C/min    | 96                                | 96.5                                          |
| 5°C/min      | 101                               | 100                                           |

4. Conclusions
In this paper, a thermoplastic resin matrix suitable for the application of deformable mandrel is proposed. Polymethyl methacrylate (PMMA) is used as the main ingredient of the matrix, and epoxy resin NPEF-170 is also added to adjust the glass transition temperature of the whole matrix. Based on the need for the softening extent of the deformable mandrel, the addition of toughener liquid nitrile rubber is optional. The manufacturing process flow of the thermoplastic matrix is proposed, and the process is performed to prepare specimens for dynamic mechanical analysis. Results of the dynamic mechanical analysis reveal that the glass transition temperature of the proposed thermoplastic resin matrix lies between 90°C and 100°C, which is suited to the application of deformable mandrel. Based on the proposed thermoplastic matrix, CFRTP deformable mandrel can be manufactured. And this deformable mandrel can be adopted to manufacture CFRP parts with complex cavities with the assistance of heating-to-soften characteristics to resolve complications regarding difficult mandrel demolding.

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