

ALL-ARAMID COMPOSITES: THE MORPHOLOGY, MECHANICAL PROPERTIES AND CRYSTALLIZATION

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ABSTRACT

A new type of self-reinforced composite based on high-performance aramid fibers was developed to produce an 'all-aramid' composite by applying a surface-dissolution method to fuse poly(*p*-phenyleneterephthalamide) (PPTA) fibers together. After immersion in concentrated sulphuric acid for a selected period of time, partially dissolved fiber surfaces are converted into a PPTA matrix phase. Following extraction of sulphuric acid and drying, a consolidated composite structure is formed. By examining the microstructure and mechanical properties of all-aramid composites, it was found in our previous study that the optimal immersion time of aramid fibers in 95% sulphuric acid was 120sec. In this paper, other processing variables, including initial and final coagulation, coagulation time, consolidation pressure and time were regulated and their effects on the morphology, mechanical properties and crystallization of all-aramid composites were investigated and discussed. A series of optimal surface-dissolution processing conditions were achieved in order to obtain the best achievable microstructure and mechanical properties of all-aramid composites. All-aramid composites prepared with these optimum conditions possess excellent mechanical properties with tensile strength of 1.44GPa and tensile modulus of 76.8GPa. Since fiber, matrix and interphase in all-aramid composites are based on the same high-temperature resistant PPTA polymer, these materials have the prospective potential for high-temperature applications.

1 INTRODUCTION

In recent years, a new class of composite materials "self-reinforced composites" or "all-polymer composites", which are based on similar or identical materials for both matrix and reinforcement have generated considerable interest due to their advantages in terms of processing and recyclability. Also in terms of interfacial compatibility these materials have shown beneficial characteristics as both fiber and matrix are of the same chemical origin, unlike traditional fiber reinforced plastics. Numerous studies have been carried out on the preparation and characterization of these composites[1] based on a large range of polymers, including polyethylene (PE)[2-7], polypropylene (PP)[8-17], poly(ethylene terephthalate) (PET)[18-20], cellulose[21-23], liquid-crystalline copolyesters[24,25].

In our previous work[26], a new type of self-reinforced composite based on high-performance aramid fibers was developed to produce an 'all-aramid' composite by applying a surface-dissolution method to fuse poly(*p*-phenyleneterephthalamide) (PPTA) fibers together. These all-aramid composites featured unidirectional high reinforcement content (~75vol.%) and good interfacial bonding, resulting in a Young's modulus of ~65GPa at room temperature, and a tensile strength of 1.4GPa, which are comparable with or exceed corresponding values of conventional aramid/epoxy composites. Interestingly, a high modulus of ~50GPa was maintained up to 250°C, demonstrating the potential of these composites for high-temperature applications. This method yields unique high-temperature-resistant materials with excellent mechanical properties compared to traditional aramid/epoxy composites or other all-polymer composites, which are mainly based on thermoplastic fibers of

moderate performance and temperature resistance such as PP and PET. The surface-dissolution method helps to expand the research areas of all-polymer composites to high performance polymers.

However, the only processing variable of surface-dissolution method in our previous work[26] was the immersion time of aramid fibers in concentrated (95%) sulphuric acid solution. The optimum immersion time was found to be 120sec according to tensile test results and SEM morphological investigations. Other processing variables, including initial and final coagulation, coagulation time, consolidation pressure and time were not studied. To optimize the surface dissolution process in order to obtain the best achievable microstructure and mechanical properties of all-aramid composites, the above processing multivariables have to be examined. Therefore, the purpose of this paper is to study the effects of these processing multivariables on the morphology, mechanical properties and crystallization of all-aramid composites (while immersion time was kept constant at 120sec), and thus to obtain the optimized processing sequences and parameters. Meanwhile, this study is expected to reveal more fundamental insights for the preparation of all-aramid composites by fibre surface dissolution approach.

2 EXPERIMENTAL

Six essential steps in a general preparation process of all-aramid composites are illustrated in Fig. 1. Unidirectional composites were prepared by first aligning the fibers through winding them on a glass frame (Fig. 1A). The aligned fibers were constrained to prevent shrinkage and distortion. The assembly of the glass frame comprising the fibers was then immersed in concentrated sulphuric acid in order to dissolve a certain amount of fiber surface (Fig. 1B). After a designated period of residence time in the acid (e.g. 120s) the specimens were immersed in distilled water (Fig. 1C) to partially coagulate the fibers and to prevent dissolved fiber surfaces from adhering to the glass plate, which was used for consolidation. Subsequently, mild pressure was applied onto the specimens (Fig. 1D). After consolidation, the specimen was immersed in distilled water for final coagulation (optional step). Residual H₂SO₄ was extracted in a 20 wt% sodium hydroxide (NaOH) solution (Fig. 1E), followed by solidification and neutralization in distilled water (Fig. 1F). The samples thus produced were kept overnight (~18h) in water (pH 7) for complete neutralization. Finally, the resulting specimens were dried in a vacuum oven at 80 °C for 24h while applying a low pressure (~1kPa) to prevent warping. To study the effect of processing multivariables on the morphology, mechanical properties and crystallization of all-aramid composites, different variables in processing steps were proposed in Table 1. For each investigation, one variable was changed while the others were kept constant.

3 RESULTS AND DISCUSSIONS

3.1 The effect of initial coagulation time

It has been noticed that immediate coagulation in water after immersion in acid can prevent excessive dissolution in the subsequent process and form a smooth and unified surface. The tensile test results in Fig. 2 indicate that coagulation in water for 60sec before applying the consolidation pressure results in better mechanical properties.

Initial coagulation in water for 1sec resulted in low tensile properties, as a result of inadequate coagulation. Inadequate coagulation before applying the consolidation pressure would lead to unconfined composite structure and possibly a weight loss in matrix phase during the following consolidation step. For longer coagulation times such as 10sec the sample exhibited improved mechanical properties while for 60sec coagulation time optimum coagulation properties were achieved and further coagulation to 300sec caused a reduction in mechanical properties as completely coagulated sample is unable to be adhered together by the consolidation pressure. According to the results above, initial coagulation in water for 60sec before consolidation seems to lead to optimum mechanical properties.

3.2 The effect of final coagulation

As can be seen the composites with a range of immersion times (from 5sec to 300sec) which were coagulated in distilled water for 5min before acid extraction exhibited a clear increase in tensile

strength and Young's modulus compared to composites prepared without coagulation before acid extraction. In fact, the tensile strength of composite prepared with an immersion time of 120sec in acid and coagulated for 5min (1.35GPa) is similar with that of composite prepared with an immersion time of 10sec in acid and without final coagulation (1.23GPa). The latter obviously contained more non-dissolved fibers and less matrix phase in the composite structure with such a short immersion time. The increase in mechanical properties with an additional coagulation step can be explained by the presence of higher amount of orientation in the samples prepared with coagulation before acid extraction. When the dissolved fibers are coagulated in water, X-ray diffraction revealed that water molecules are included in hydrogen-bonded planes to form a liquid crystal-like swollen structure[27]. After drying, PPTA polymer molecules are aligned to form the crystal structure of modification II. Therefore, we speculate that a slower coagulation process in distilled water compared with in NaOH solution gives the dissolved phases more time to reorient themselves into a liquid crystal-like swollen structure, resulting in better orientation and hence higher mechanical properties of the composites, an illustration of this speculation was shown in Fig. 3.

The additional coagulation step before extraction of excessive acid has an apparent positive effect on the mechanical properties of all-aramid composites. In addition, the effect of coagulation time on mechanical properties of the composites was also investigated. It is noticed that with increasing coagulation time in distilled water from 5min to 15min the mechanical properties of all-aramid composites slightly increase. Tensile strength of the composites increased from 1.2GPa at 5min to 1.4GPa at 15min(+17%) and tensile modulus increased from 67.7GPa at 5min to 73.4GPa at 15mins(+8%), respectively. This could be explained in the same way as the additional coagulation step. Longer coagulation times give more time for molecular reorientation, resulting in higher tensile strength and modulus. However, there is a decrease in mechanical properties for the composites with 30min coagulation time. As a result, 15min was chosen to be the optimum final coagulation time to prepare all-aramid composites with good mechanical properties. An additional coagulation step led to a composite with good adhesion and highly compacted morphology, resulting in a steep increase in tensile strength.

Scanning electron micrographs presented in Fig.4 illustrate the cross-sectional morphology of the composites prepared with and without a final coagulation step. It is obvious that composites prepared without an additional coagulation step exhibit more voids (indicated by red arrows) than composites prepared with this coagulation step.

The XRD results in Fig. 5 showed the similar diffraction profiles and crystal sizes for 5, 15 and 30min final coagulation times, indicating crystalline structure for composites prepared with different final coagulation time was alike, which is correlated with the similar mechanical properties. Meanwhile, for a final coagulation time of 5min, higher intensity for the peak ($2\theta = 17.5^\circ$) indicating crystal structure of modification II is shown, which is in accordance with the theory that more polymer molecules were oriented and formed the crystal structure of modification II during final coagulation.

4 FIGURES AND TABLES

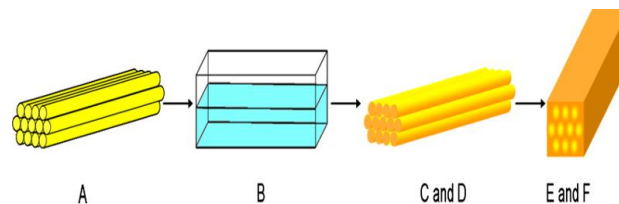


Figure 1. Schematics of the selective surface dissolution process of aramid fibers for preparation of "all-aramid" composite: (A) fiber alignment and constraining; (B) immersion in acid; (C) initial coagulation in water; (D) consolidation by pressure; (E) acid extraction; and (F) neutralization in water.

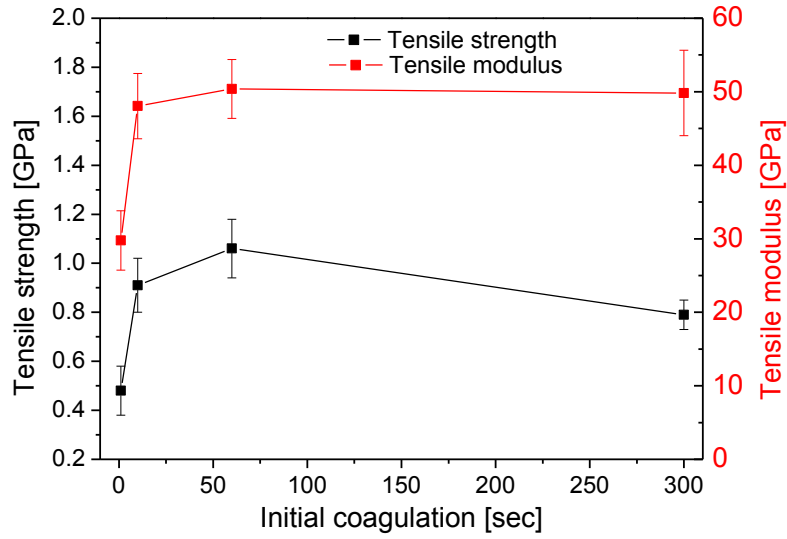


Figure 2. The mechanical properties of all-aramid composites which were prepared with initial coagulation time of 1, 10, 60 and 300sec, respectively.

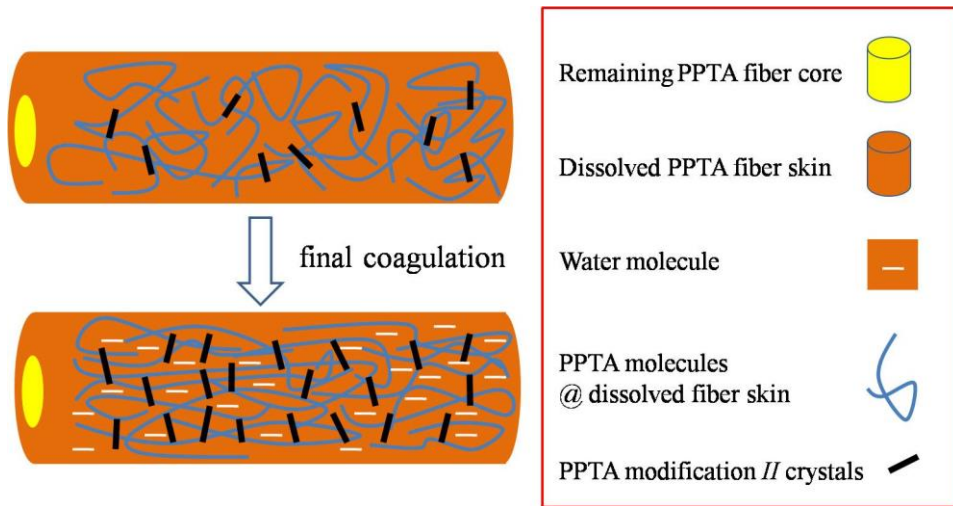


Figure 3. An illustration of how final coagulation affects orientation and crystallization of PPTA molecules at dissolved fiber skin.

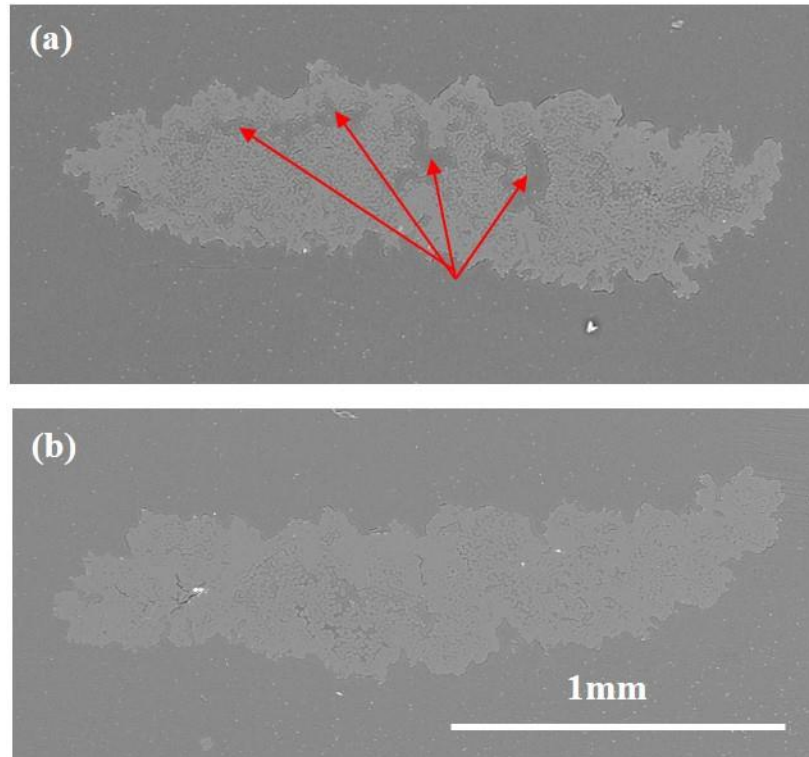


Figure 4. Scanning electron micrographs of samples prepared with 120sec immersion time in acid: (a)without final coagulation; (b)with 5mincoagulation before acid extraction

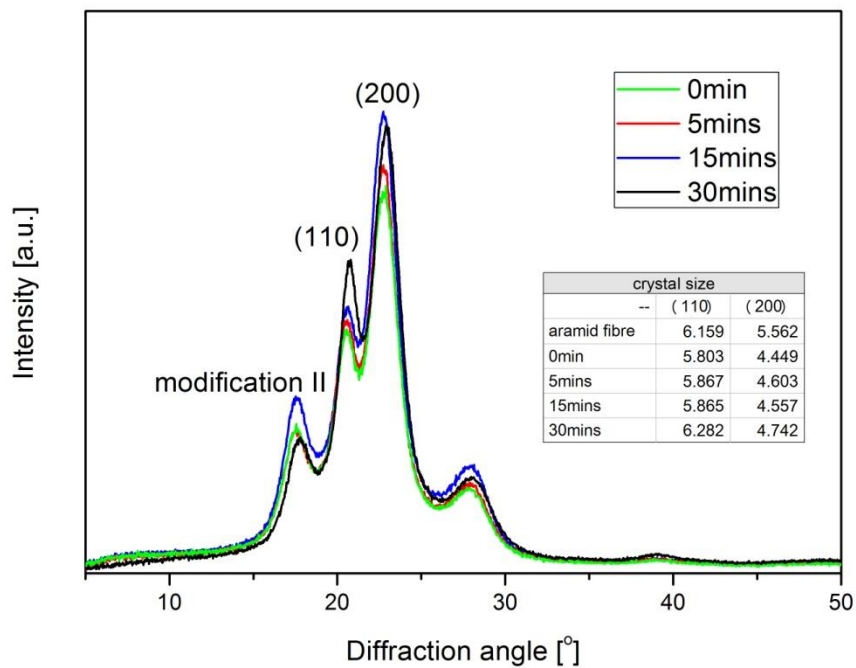


Figure 5. Equatorial X-ray diffraction profile of all-aramid composites prepared with 0, 5, 15, 30min final coagulation time, respectively; lateral crystal size normal to the (110) plane and (200) plane was calculated by means of Scherrer's equation and shown in the inserted table.

Step code	Step description
A	Fiber alignment and constraining
B	Immersion in acid for 120sec
C	Initial coagulation in water for 1, 10, 60, 300sec
D	Consolidation at 1kPa for 0, 1, 5, 10min; Consolidation for 1min at 0, 1, 6, 10kPa
C'	Final coagulation in water for 0, 5, 15, 30min
E	Acid extraction in NaOH for 30min
F	Neutralization in pH=7 water for 18hrs
G	Drying in vacuum oven at 80°C for 24hrs

Table 1. Variables in a proposed sequence of processing steps for all-aramid composites

5 CONCLUSIONS

All-aramid composites were prepared by partially surface-dissolution of aramid fibers. According to mechanical test results and morphological studies of the composites in a previous study, the optimum dissolution condition chosen was 120sec immersion in acid. The effects of other processing variables, such as initial coagulation time before consolidation, final coagulation before acid extraction and consolidation time and pressure, on mechanical properties, morphology and crystallization of the prepared composites were investigated in this paper. This study revealed more fundamental insights for the preparation of all-aramid composites by surface-dissolution approach and found the optimum processing sequence and parameters for all-aramid composites.

The optimum initial coagulation time was found to be 60sec, and consolidation for 5min at 6kPa was found as the optimum parameters for consolidation. Optimum final coagulation duration was found to be 15mins. Applying all these optimized processing parameters at the same time to prepare the all-aramid composite is expected to result in the composite with optimal microstructure and mechanical properties if the interaction between multivariables does not make any interference. All-aramid composites prepared with these optimum conditions possess excellent mechanical properties with tensile strength of 1.44GPa, tensile modulus of 76.8GPa and maximum strain of 3.41%. Since fiber, matrix and interphase in all-aramid composites are based on the same high-temperature resistant PPTA polymer, these materials have the prospective potential for high-temperature applications.

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