

Novel high-performance all-aramid composites

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Self-reinforced polymer composites are prepared by applying an elaborately designed surface-dissolution method to fuse and consolidate poly(p-phenylene terephthalamide) fibers.

Advanced composite materials that are based on high-performance fibers (e.g., aramid or carbon fibers) exhibit excellent physical and mechanical properties. Such composites are therefore used in a wide range of applications, such as for transportation, sport, and shield materials. In most cases, composite materials are composed of three phases, i.e., the reinforcements, the matrix, and the interphase between the two. In recent years, however, a new class of ‘all-polymer’ or ‘self-reinforced polymer’ composites have emerged in which both the matrix and the reinforcements are made of similar or identical materials. These new composites have drawn much interest in both academia and industry because of their advantages—in terms of processing, interfacial properties, and recyclability—over traditional composites. Although many researchers are working on these all-polymer composites,^{1–13} they are mainly based on thermoplastic fibers that have moderate performance and temperature resistance, and their use in high-performance applications is therefore limited.

We have previously developed a new type of self-reinforced composite that is based on high-performance aramid fibers.¹⁴ To fabricate our ‘all-aramid’ composite, we applied a unique surface-dissolution method to fuse poly(p-phenyleneterephthalamide), PPTA, fibers together. Unfortunately, however, we have found that the dissolution behavior of the composite in highly concentrated sulfuric acid (H_2SO_4) was difficult to control (i.e., dissolution occurred in a matter of seconds). In addition, we observed undissolved PPTA fibers inside the composites, whereas the outer surface layer of the samples often exhibited heavily dissolved fibers. The resulting inhomogeneities in composite morphology thus gave rise to poor interface or matrix-dominated properties.

In this work,¹⁵ we have therefore proposed the use of milder acid solvents to achieve longer dissolution times and better process control. After we had conducted preliminary screening experiments, we selected a mixture of phosphoric acid (H_3PO_4) and H_2SO_4 (v_p and v_s , respectively) in 1:1 and 1:2 volume/volume (v/v) mixing ratios for further

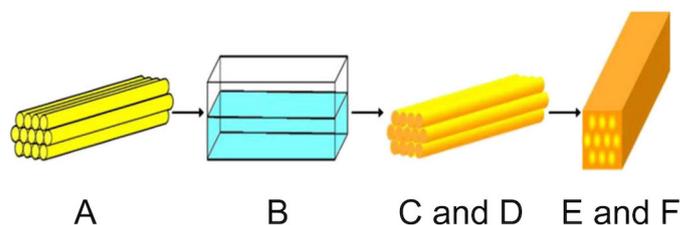


Figure 1. Schematic illustration of the aramid fiber surface-dissolution process for the preparation of the ‘all-aramid’ composites. The process involves (a) fiber alignment and constraint, (b) immersion in acid, (c) initial coagulation in water, (d) consolidation by pressure, (e) final coagulation, and (f) acid extraction.

investigation. With these milder solvents, we require longer immersion times to partially dissolve the PPTA fiber surfaces, and we can realize a more controllable consolidation process to create the all-aramid composites (with more homogeneous microstructures and adhesion levels). Specifically, in our study, we immersed the PPTA fibers in the mixed solvents for periods of 5, 30, 60, and 90 minutes to dissolve the fiber surfaces. After subsequent acid extraction and drying (see Figure 1), we formed the consolidated all-aramid composite samples.

In our study we also conducted tensile tests—in both the longitudinal and transverse directions—on our all-aramid composites. From these measurements we determined the optimum immersion time (i.e., interphase condition) as the point where we achieved a good balance between the longitudinal and transverse tensile strength (indicated by the gray bands in Figure 2). We also find (see Table 1) that the tensile properties of our all-aramid composites compare favorably with a conventional unidirectional aramid/epoxy composite.¹⁶ Furthermore, the results given in Table 1—for all-aramid composites prepared in 95wt% v_s for 120 seconds¹⁴ and in a mixed solvent (1:1 v_p/v_s) for 60 minutes—show that the samples prepared in a more controlled manner (i.e., with a longer dissolution time) have significantly better transverse properties, albeit at the expense of the longitudinal properties.

In the next part of our work we investigated the failure modes and morphology of our all-aramid composites. Although Figure 2 shows

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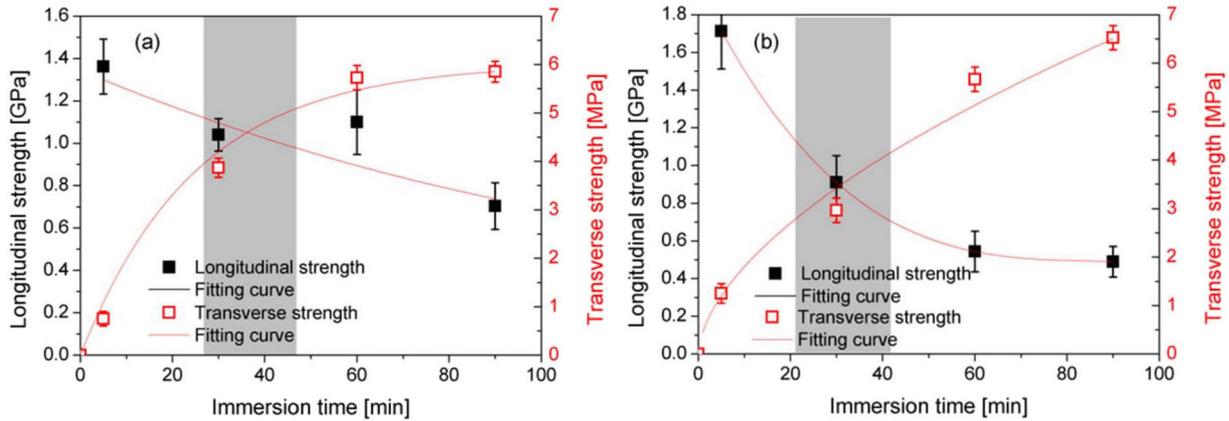


Figure 2. Longitudinal and transverse tensile strength of the all-aramid composites, as a function of immersion time. Results are shown for the samples prepared with solvents of phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) in (a) 1:1 volume/volume (v/v) and (b) 1:2v/v mixing ratio. The gray band in each diagram indicates the range of optimum immersion times, i.e., ten minutes either side of the immersion time at the crossing point of the two fitting curves.

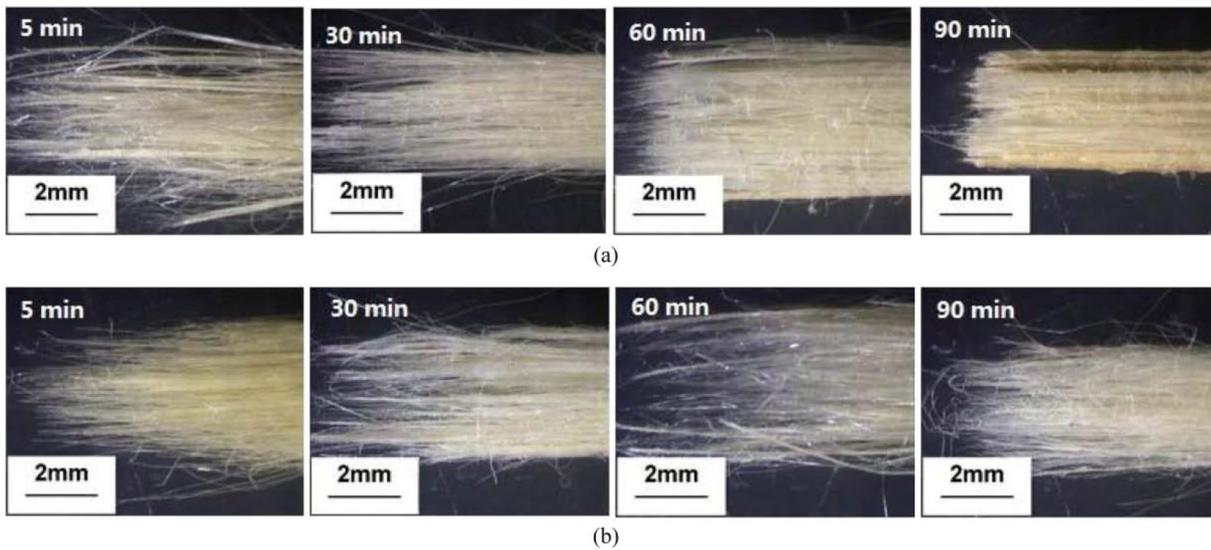


Figure 3. Images of the all-aramid composites showing the failure mode of the samples prepared with the (a) 1:1v/v H_3PO_4/H_2SO_4 (v_p/v_s) and (b) 1:2v/v (v_p/v_s) solvents for immersion times of 5, 30, 60, and 90 minutes.

that an immersion time of 30 minutes is close to the theoretical optimal dissolving time for the 1:1 v_p/v_s solvent, our morphological measurements (see Figures 3 and 4) indicate that an immersion time of 60 minutes resulted in a better interphase structure. Indeed, the immersion time of 60 minutes was sufficient to fuse the remaining fiber cores together. This provides a good level of adhesion between the fibers, but leaves a suitable fraction of the fiber core as the reinforcing phase.

We also used a dynamical mechanical analysis to examine the thermomechanical properties of our all-aramid composites. Our results indicate, for instance, that the composites still retain a reasonably high modulus (35GPa) for the 1:1 v_p/v_s solvent, 60 minute immersion time sample. These high modulus characteristics at elevated temperatures arise because the fibers and matrix of the composites are made from

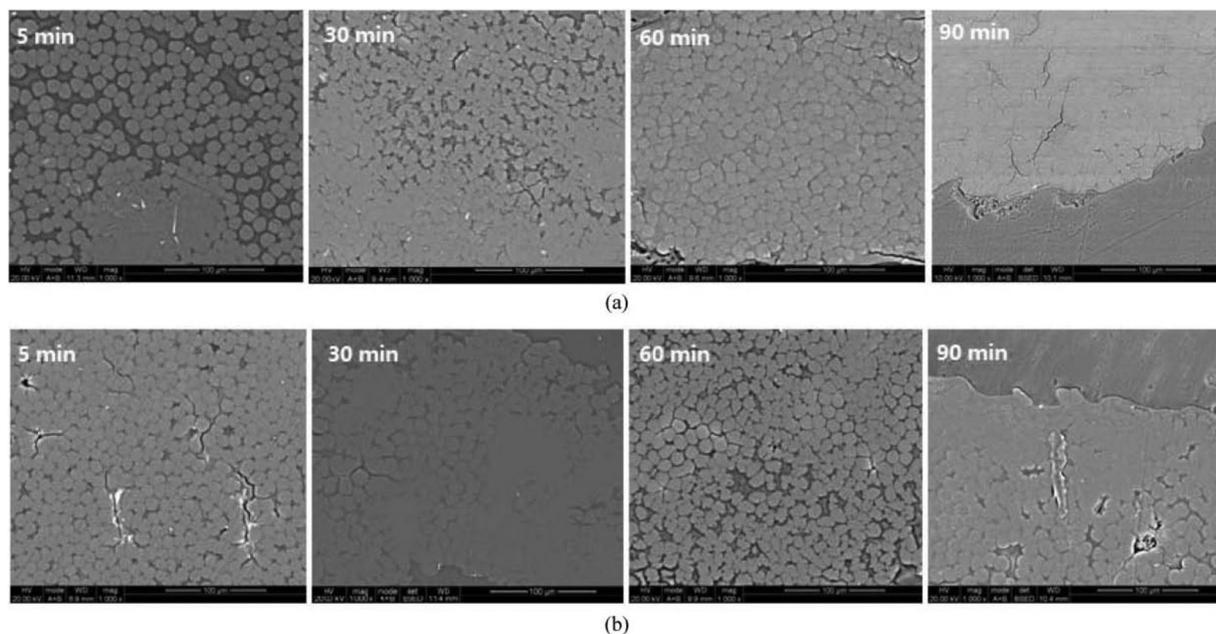


Figure 4. Scanning electron microscope images of cross sections through the all-aramid composites that were prepared in the (a) 1:1v/v (v_p/v_s) and (b) 1:2v/v (v_p/v_s) solvents for immersion times of 5, 30, 60, and 90 minutes.

Table 1. Mechanical properties of the all-aramid composites prepared in 95wt% H_2SO_4 for 120 seconds¹⁴ and in the 1:1v/v mixed H_3PO_4/H_2SO_4 solvent for 60 minutes, and of a conventional unidirectional aramid/epoxy composite (Twaron1000).¹⁶

	All-aramid 95% H_2SO_4 , 120s	All-aramid H_3PO_4/H_2SO_4 1:1, 60min	Twaron1000/ epoxy
Tensile strength [GPa]	1.40	1.10	0.94
Tensile modulus [GPa]	65	48.3	15.6
Strain at failure [%]	4.04	2.15	–
Transverse strength [MPa]	2.6	6.0	–

the same high-temperature-resistant PPTA material, which makes them particularly suitable for high-temperature applications. In addition, x-ray diffraction profiles that we obtained show the crystal size and apparent crystallinity of our samples decrease with increasing solvent immersion time. This is a result of the increasing dissolution of the highly crystalline fiber skins and the formation of the non-crystalline, or partially crystalline, matrix phase. We note, however, that the decrease in crystal size is not as dramatic as in our previous work,¹⁴ which

suggests there was an increase in the remaining crystal modification as a result of the weaker dissolution effect of the mixed solvent.

In summary, we have successfully prepared all-aramid composites by using a process of selective dissolution and fusion of aramid fiber surfaces in a mixed solvent of H_3PO_4 and H_2SO_4 . Our resulting all-aramid composites have oriented aramid fiber cores that are fused together by an aramid interphase or matrix. Our tensile test results and morphological observations indicate that the composites prepared with a 1:1 v_p/v_s solvent and an immersion time of 60 minutes exhibited good overall mechanical properties. We also find that our all-aramid composites have much higher mechanical and thermomechanical properties than other all-polymer composites, which means they are good candidates for high-performance (especially high-temperature) applications. In our future work, we hope to ultimately optimize the v_p/v_s mixing ratio and to further refine the immersion time in our process. Meanwhile, we are continuing to look for new ways to prepare high-performance all-polymer composites.

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