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Tensile and fatigue properties of long glass fibre-reinforced polypropylene immersed in hot water

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Tensile tests and pulsating-tension fatigue tests have been carried out using smooth specimens of two materials of long glass fibre-reinforced polypropylene (LGF/PP), with and without acid modified polypropylene (APP). Specimens were immersed in distilled water at 80 °C up to 6666 h. In both materials, the weight increased rapidly and reached the maximum, then decreased gradually with immersion time. The material without APP showed initially larger weight increase, but after immersion for over 2500 h more remarkable decrease was seen, indicating that the addition of APP was effective in improving water absorption characteristics of LGF/PP. Water entered along the fibre/resin interface and the weight loss of LGF/PP was attributed to leaching of surface treatment agents and dissolution of glass fibres, because the weight gain of the resin itself was negligible. Tensile and fatigue strengths were considerably decreased after hot water immersion because of the degradation of glass fibres, i.e. the reduction of fibre strength. The material with APP still exhibited higher strengths than the material without APP, also showing a beneficial effect of the addition of APP. Fracture mechanisms are discussed on the basis of close examination of fractured specimens. © *1998 Kluwer Academic Publishers*

1. Introduction

Long glass fibre-reinforced polypropylenes (LGF/PP) are now expected as candidates for structural use because of further improvement in strength and stiffness by using long fibres. However, studies on strength properties and fracture mechanisms, which are critical for structural materials, are very limited [1–3]. In a previous report [4], the authors have investigated fatigue properties and fracture mechanisms of two materials of LGF/PP with and without acid modified polypropylene (APP) in laboratory air at ambient temperature. Consequently, it was found that the material with APP showed higher tensile and fatigue strengths than the material without APP and thus the addition of APP was effective to enhance strengths of LGF/PP through an improvement in interfacial qualities between the fibres and the resin.

When LGF/PP is considered for automobile, offshore and marine structures, it is also necessary to characterize the effects of environments on the mechanical properties. Particularly, water can penetrate FRP and then significantly attacks fibres, resin or their interface, leading to lower strength and stiffness. Therefore, many studies have been performed on the effect of water environment on the mechanical properties of FRP, but there are few studies on GF/PP [5–7].

In the present study, tensile tests and pulsating-tension fatigue tests were carried out using two materials of LGF/PP with and without APP immersed in hot water. Tensile and fatigue strengths were evaluated, and the effect of hot water immersion on those properties and fracture mechanisms are discussed on the basis of macroscopic and microscopic observations of fractured specimen and specimen surface.

2. Experimental details

2.1. Materials and specimens

The starting materials are long glass fibre-reinforced polypropylene glanules containing 30 wt % of glass

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fibres of the average length of 13 mm and the diameter of 13 μm, with and without a coupling agent. Sheets of $250 \times 250 \times 4$ mm were compression-moulded using the above starting materials. The tensile strengths of the glass fibre and the resin were 2450∼3430 MPa and 39 MPa, respectively [4].

Acid modified polypropylene (APP) with an acid value of 70 mgKOH/g and a density of 900 kg/m^{-3} was used as a coupling agent. By the addition (5 phr, parts per hundred resin) of APP, the interfacial strength between the fibres and the resin is improved, resulting in higher tensile and fatigue strengths in laboratory air at room temperature [4]. Hereafter, the materials with and without APP are designated PP + APP and PP, respectively. In preliminary tests, it was found that the present materials had slightly different strength from the materials used in a previous study [4], thus the data in laboratory air at room temperature were acquired again.

Smooth specimens with 25 mm gauge length, 10 mm width and 4 mm thickness were used for both tensile and fatigue tests, which were machined from the above sheets.

2.2. Procedures

Specimens were immersed in distilled water at 80 °C. Five specimens were periodically removed from the tank and weighed on an analytic balance, accurate within 1 mg. The weight gain, M_g (in percent), was defined as

$$M_g = (W_w - W_d)/W_d \tag{1}$$

where W_w and W_d are the weights after and before immersion, respectively. The average value of five specimens was employed as M_g for a given immersion time. Hereafter, immersed and not immersed specimens are designated wet and dry, respectively.

Tensile tests and fatigue tests were conducted on a 47 kN capacity electro servohydraulic fatigue testing machine. In tensile tests, loading rate was not controlled. Fatigue tests were performed at a frequency of 10 Hz and a stress ratio, R, of 0. The variation of rigidity with stress cycling was measured by an extensometer equipped between grips of the fatigue testing machine. Since the grips gradually cut into the specimens at the beginning of fatigue test, elastic modulus at 100 cycles was employed as an initial value, E_0. The elastic modulus decay ratio, E_n/E_0, was defined as the ratio of the elastic modulus at arbitrary cycles, E_n, to E_0.

Optical microscope and scanning electron microscope (SEM) were used for surface observation of tensile and fatigue specimens and fracture surface examination, respectively.

3. Results

3.1. Weight change in hot water immersion

The weight changes for LGF/PP are shown in Fig. 1 as a function of immersion time. In both materials, the weight increases rapidly and reaches the maximum values in a short time, then decreases gradually with immersion time. PP shows initially larger weight increase, but after immersion for over 2500 h more remarkable decrease can be seen, being less weight than PP + APP. At approximately 5000 h, PP has the same weight as before immersion.

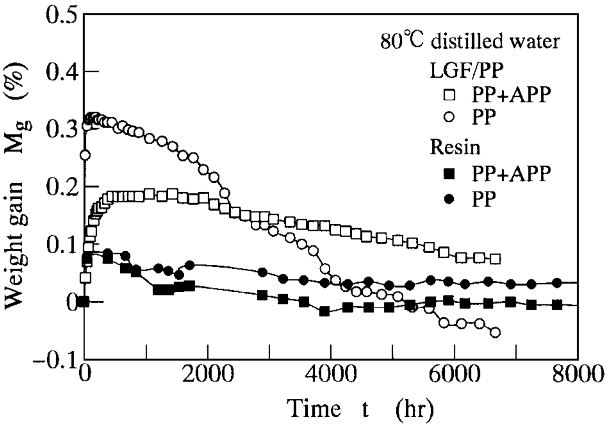

Figure 1 Weight changes with immersion time for LGF/PP and resin in distilled water at 80 °C.

Specimens immersed for 6666 h were dried at 80 °C for 3 h in an electric furnace and then the weight was measured. The obtained weight gains were −0.399% and −0.665% for PP + APP and PP, respectively. Because the weight of LGF/PP itself does not appear changed by drying, the differences between those values and the weight gains after immersion would be a real water absorption at the immersion time of 6666 h, which are 0.473% for PP + APP and 0.613% for PP, suggesting that water absorption continues after the weight loss has occurred.

The sites of water absorption are considered to be three components, i.e. resin, glass fibre and interface between both. The weight change of the resin was also measured and the data are included in Fig. 1, in which both materials show initially a slight increase and then gradual decrease. Such decrease may be due to leaching of the resin [8, 9]. After immersion for long time, crackings were found in the interior of specimens in both materials, indicating the degradation of the resin. The weight gain of the resin is small, thus the leaching of the resin is not the cause of the weight loss of LGF/PP in hot water immersion. It is generally accepted that glass fibres do not absorb water [5, 10]. Therefore, the weight loss of LGF/PP may be attributed to leaching of surface treatment agents and dissolution of glass fibres [11]. Fig. 2 shows the surface of the specimens immersed for 2800 h in coloured water. Black lines or regions on the specimen surface reveal water penetration, which can be seen around fibre bundles or cluster of fibres, particularly in PP, thus water is considered to travel preferentially along the interface.

3.2. Tensile strength

Tensile strengths, σ_B, for dry and wet specimens are listed in Table I, where three specimens in each condition were employed in tensile tests, and the individual results and the averages are given. In both materials, it can be seen that σ_B for wet specimens is lower than that for dry specimens. In dry condition, PP + APP

TABLE I Tensile test results

Material code	Tensile strength σ_B (MPa)			
	Dry		Wet (80 °C)	
	82.1		58.5	
PP + APP	97.3	96.9*	70.2	66.6*
	111.4		71.0	
	82.2		58.5	
PP	85.5	86.6*	60.4	61.7*
	92.2		66.3	

*Average value.

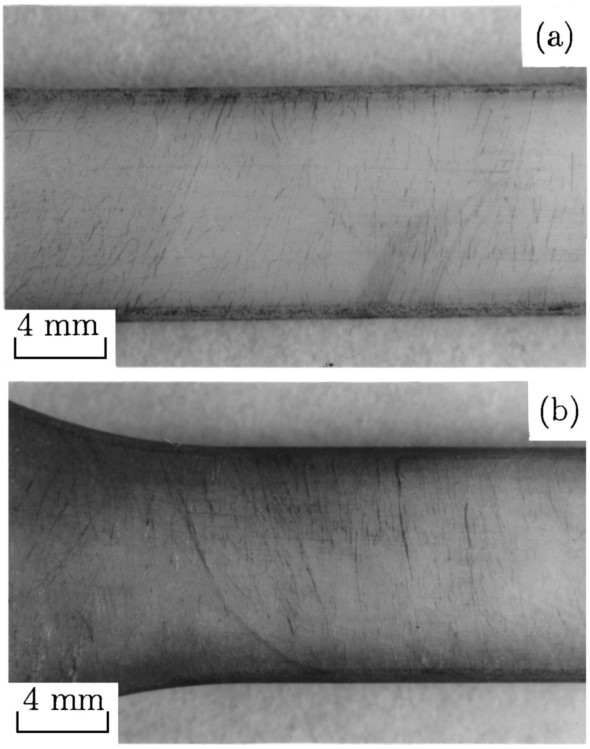

Figure 2 Optical micrographs of LGF/PP specimens immersed in coloured water for 2800 h: (a) PP + APP and (b) PP. Black lines or regions on the specimen surface indicate that water travels around fibre bundles or along interface between resin and fibres.

indicates higher σ_B than PP because of improved interfacial strength by the addition of APP [4]. In wet conditions, PP + APP also exhibits higher σ_B, thus the beneficial effect of the addition of APP is maintained after immersion.

Macroscopic appearance of fractured specimens is represented in Fig. 3. It should be noted that there is a significant difference between dry and wet specimens; fibres appeared on fracture surface are definitely shorter in the latter. In both conditions, fibres in PP + APP tend to be shorter than those in PP. Fig. 4 shows SEM micrographs of fibres. The adherence of the resin to the fibre surface can be seen for dry specimens in both materials, more remarkable in PP + APP, while the fibre surface for wet specimens are smooth in both materials.

3.3. Fatigue properties

3.3.1. Fatigue strength

The relationships between maximum stress and number of cycles to failure (*S–N* curves) for dry and wet specimens in both materials are shown in Fig. 5. Tests were conducted after immersion of 4000∼5500 h and terminated at 3 × 10^6 cycles. In dry condition, PP + APP exhibits higher fatigue strength than PP because of improved interfacial strength by the addition of APP [4]. It should be recognized that fatigue strength is decreased

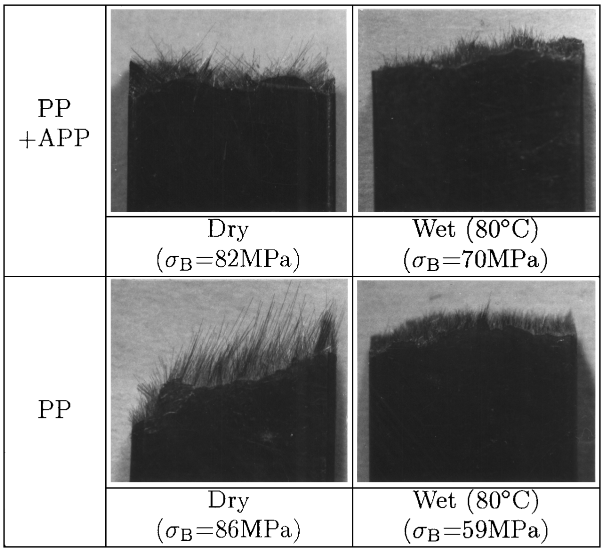

Figure 3 Macroscopic appearance of tensile fractured specimens.

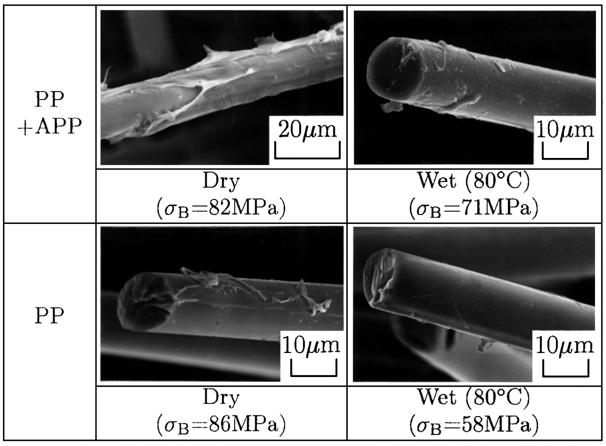

Figure 4 SEM micrographs of fibres appeared on fracture surface of tensile specimens. Note little or no adherence of resin to the fibre surface in wet specimens.

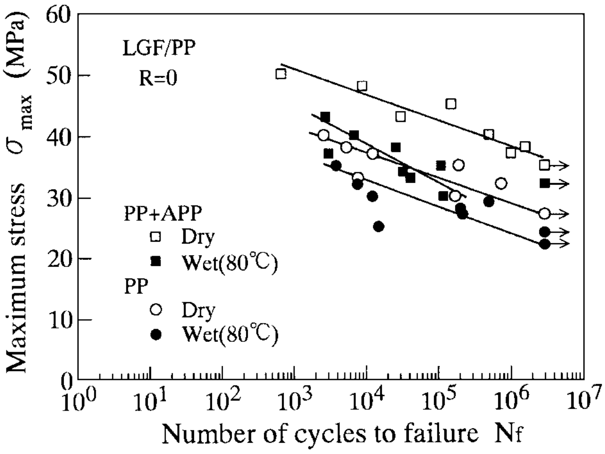

Figure 5 *S–N* diagram showing effect of immersion in distilled water at 80 °C.

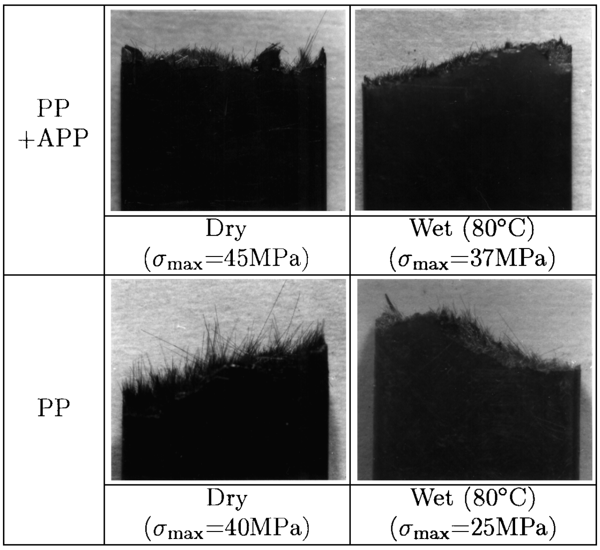

Figure 6 Macroscopic appearance of fatigue failured specimens.

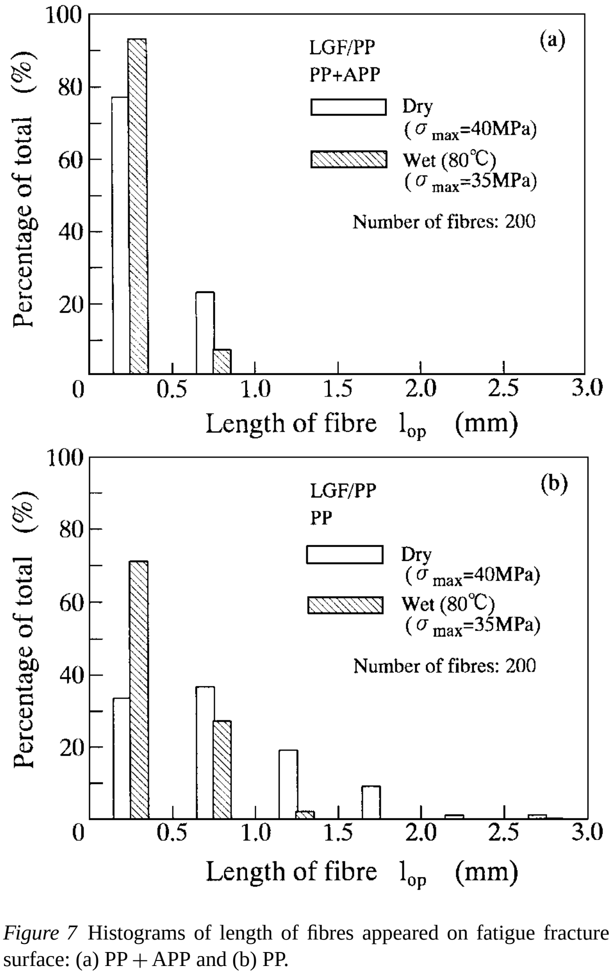

Figure 7 Histograms of length of fibres appeared on fatigue fracture surface: (a) PP + APP and (b) PP.

by hot water immersion in both materials. PP + APP still has higher fatigue strength than PP in wet condition, thus the addition of APP is also effective for improving fatigue strength after immersion, as well as tensile strength.

Fig. 6 reveals macroscopic appearance of fatigue failured specimens which is quite similar to tensile fracture shown in Fig. 3. In PP + APP, the lengths of fibres appeared on fracture surface are shorter for both specimens, but longer fibres can be seen for dry specimens. In PP, the fibre length is long for dry specimens, but short for wet specimens. The length of 200 fibres arbitrarily chosen was measured using SEM and the obtained histograms are shown in Fig. 7. In PP + APP, the frequency of shorter fibres tends to increase and the lengths of most fibres are shorter than 1.0 mm in both conditions. In PP, longer fibres, which are seen for dry specimens, are not observed for wet specimens and the frequency of shorter fibres than 0.5 mm largely increases. SEM micrographs of fibres appeared on fracture surface are represented in Fig. 8. In PP + APP, the adherence of the resin to the fibre surface can be seen in dry specimens, but not observed in wet specimens. On the contrary, in PP, the fibre surfaces are very smooth in both conditions.

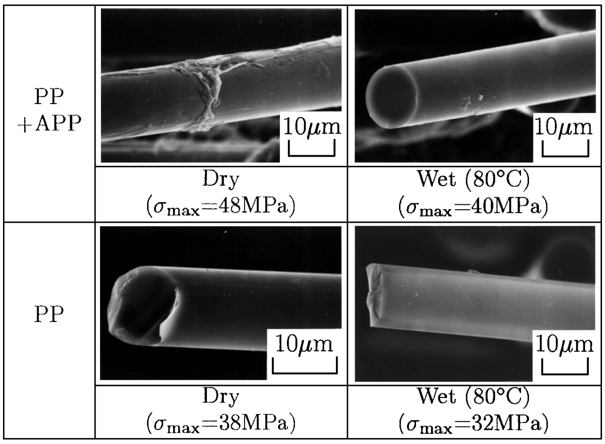

Figure 8 SEM micrographs of fibres appeared on fatigue fracture surface. Note no adherence of resin to the fibre surface in wet specimens.

3.3.2. Variation of rigidity and damage development

The relationship between E_n/E_0 and cycle ratio, n/N_f, is shown in Fig. 9. In both materials, E_n/E_0 for dry specimens decreases gradually with stress cycling except for the early and final stages of fatigue life, N_f, while wet specimens represent almost constant E_n/E_0. The authors have indicated that such variation of rigidity reflected damage development during stress cycling [4]. In order to examine fatigue damage, additional fatigue tests were performed and interrupted at 10, 50 and

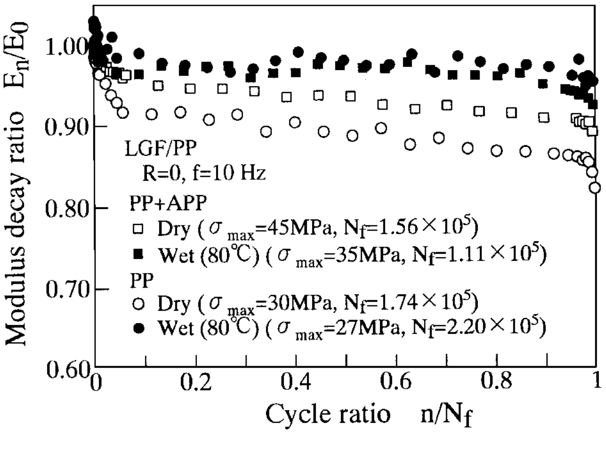

Figure 9 Variation of rigidity with stress cycling.

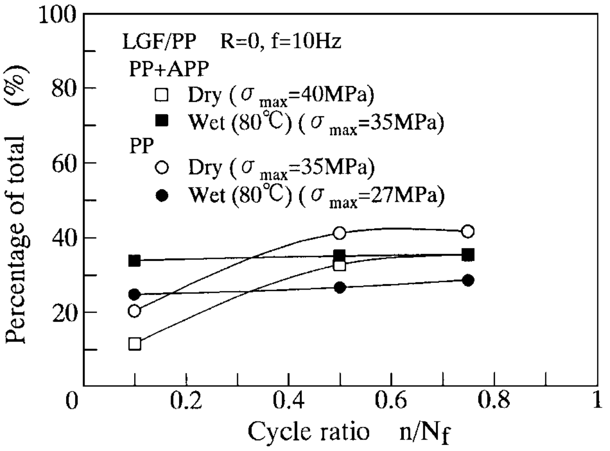

Figure 10 Fraction of damaged fibres as a function of cycle ratio. For wet specimens, fibre breakage was observed in both materials, while for dry specimens, fibre pull-out and fibre breakage were seen in PP and PP + APP, respectively.

75% of N_f, and then the specimen surface was observed carefully. Consequently, in dry conditions, fibre breakage and fibre pull-out were seen in PP + APP and PP respectively, and in wet conditions, fibre breakage was observed in both materials. Fig. 10 represents quantitative damage accumulation, where the fraction of broken fibres and pulled-out fibres was measured in an area of 10 mm^2 on the specimen surface. In dry conditions, fibre damage increases gradually and tends to be saturated at the middle or final stage of N_f, while in wet conditions, the fraction of broken fibres is nearly constant or slightly increases. Since the degradation of fibres takes place during hot water immersion, most fibres are broken immediately after cyclic stress is applied. It can be seen that the above damage development well corresponds to the variation of rigidity shown in Fig. 9.

4. Discussion

4.1. Water absorption and fibre degradation

As shown in Fig. 1, the weight loss of LGF/PP occurred by hot water immersion in both materials. Bunsell [9] has studied water absorption of glass fibre reinforced epoxy at a temperature range of 22∼100 °C and reported weight loss above 50 °C. Morii *et al.* [6] have also indicated weight loss in hot water immersion at 60 and 80 °C for glass mat reinforced polypropylene. These results suggest that weight loss is closely related to water temperature. Thus, immersion tests were conducted in distilled water at ambient temperature. The obtained results are shown in Fig. 11, which are quite different from the results in hot water immersion (see Fig. 1): in both materials, the weight increases gradually with time after a rapid increase and no weight loss is seen up to approximately 9500 h of immersion. PP represents larger weight gain than PP + APP. Based on this results, it is realized that hot water is an aggressive or accelerated environment, and the results shown in Fig. 11 seem to correspond to the weight changes for short time scale before weight reaches the maximum in hot water immersion.

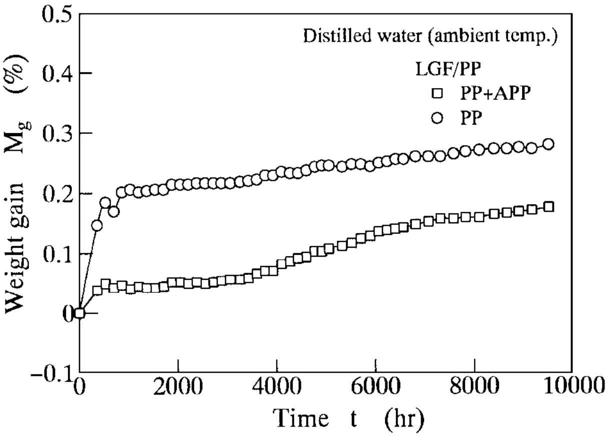

Figure 11 Weight changes with immersion time for LGF/PP in distilled water at ambient temperature.

Since glass fibres do not absorb water and the weight gain of the resin was negligible, the weight loss of LGF/PP may be due to leaching of surface treatment agents and dissolution of glass fibres [11]. It is not possible to determine which factor is dominant, but the former would be a main cause of the weight loss, because many treatments including coupling agents were performed on the fibre surface. In water immersion at ambient temperature, small amounts of water can enter along the interface, so the extent of the leaching of surface treatment agents and the dissolution of glass fibres is much smaller, thus the weight gain directly means water absorption. In hot water immersion, on the other hand, a lot of water are supplied around glass fibres and elevated temperature assists the leaching of surface treatment agents and the dissolution of glass fibres, leading to the degradation of fibres, then resulting in the reduction in fibre strength.

4.2. Fracture mechanisms of immersed specimens

In PP + APP, predominant fracture mode in dry and wet conditions was fibre breakage, while in PP, transforms from fibre pull-out to fibre breakage by hot water immersion. Close examination of fibre surface by SEM revealed that the interfacial adhesion was degraded by hot water supplied around the interface (see Figs. 4 and 8). If the interfacial strength are largely decreased, then the predominant fracture mode would be fibre pull-out in wet condition. In reality, however, fibre lengths became short (fibre breakage) in both materials. Therefore, it is considered that the degradation of fibres, i.e. the reduction in fibre strength [11, 12], rather than the decrease in interfacial strength by hot water immersion, may be primarily attributed to the decrease in tensile and fatigue strengths.

4.3. Effect of water immersion on fatigue strength

Since elevated temperature significantly affected the weight change of LGF/PP, the effect of temperature on fatigue strength should be considered. Additional

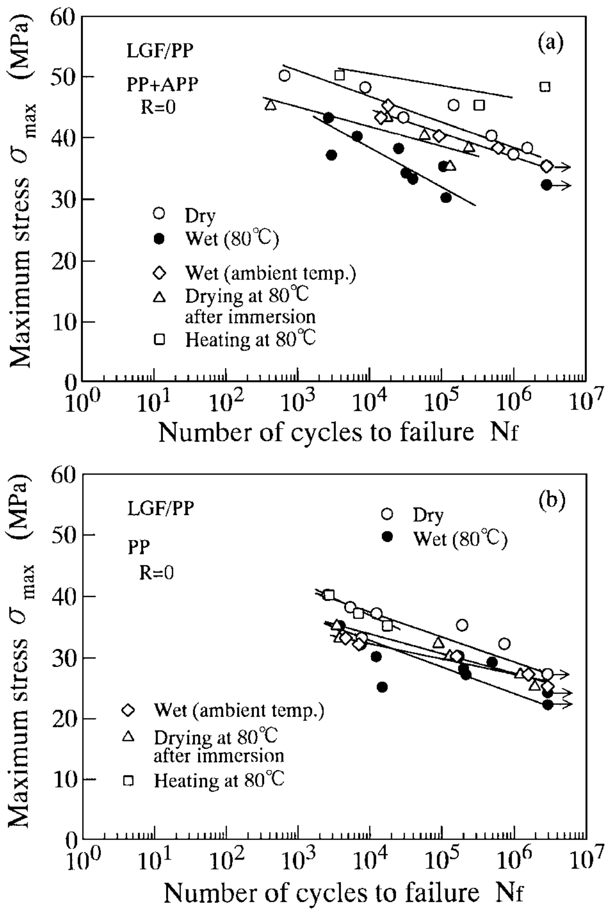

Figure 12 *S–N* diagrams showing effects of water temperature and heating: (a) PP + APP and (b) PP.

fatigue tests were carried out using specimens which were subjected to three different treatments: dry specimens heated at 80 °C for 3 h (hereafter, heated dry specimens), specimens immersed in distilled water at ambient temperature (water immersed specimens), and wet specimens dried at 80 °C for 3 h (dried wet specimens). The results are represented in Fig. 12.

The fatigue strength of heated dry specimens is slightly higher than (Fig. 12a), or almost similar to (Fig. 12b), that of dry specimens. At least heating at 80 °C does not reduce the fatigue strength of LGF/PP. In water immersed specimens, the difference in the interfacial quality is clearly emerged: PP + APP exhibits slightly lower fatigue strength compared with dry specimens, indicating a little effect of water immersion at ambient temperature, while in PP the fatigue strength is considerably lower than dry specimens. This is because the fatigue strength of LGF/PP is controlled by fibre strength degradation. Regardless of interfacial quality, elevated temperature should accelerate water absorption and, thus, hot water significantly attacks the surface of glass fibres, leading to leaching of surface treatment agents, which resulting in the reduction of fibre strength. On the contrary, in water immersion at ambient temperature, significant degradation of glass fibres does not seem to occur because weight loss was not observed. However, more decrease of fibre strength in PP having lower interfacial strength would take place, because of larger amounts of water compared with PP + APP.

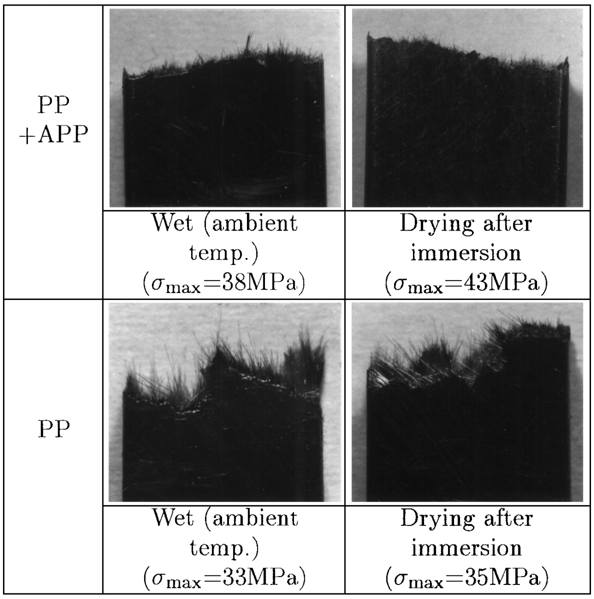

Figure 13 Macroscopic appearance of fatigue failured specimens which were immersed in distilled water at ambient temperature and dried at 80 °C after immersion in distilled water at 80 °C.

When wet specimens were dried, water within LGF/PP can vaporise and the degradation of the fibres and the resin is remained unchanged. Therefore, the fatigue strength of dried wet specimens was expected to be identical to that of wet specimens. However, the fatigue strength of dried wet specimens is slightly higher in PP + APP than, and similar in PP to, that of wet specimens. In PP + APP, the interfacial strength degraded by immersion may be recovered by drying, because heated dry specimens showed higher fatigue strength than dry specimens.

Fig. 13 reveals macroscopic appearance of water immersed specimens and dried wet specimens in both materials, showing longer fibres in the former than in the latter. When compared with Fig. 6, it can be seen that in PP + APP fibre length is longest for dry specimens, water immersed specimens follow this, and wet specimens and dried wet specimens are shortest, while in PP dry specimens, water immersed specimens, dried wet specimens and wet specimens are in the order of decreasing fibre length, suggesting that even in dried wet specimens and water immersed specimens, the degradation of glass fibres has occurred. Therefore, it is concluded that the reduction of fibre strength is primarily responsible for the decrease of fatigue strength in LGF/PP by water immersion.

5. Conclusions

1. When immersed in hot water at 80 °C, the weight increased rapidly and reached the maximum in a short time, and then decreased gradually with time in both materials, with (PP + APP) and without (PP) acid modified polypropylene (APP). The rate of weight increase and weight gain were larger in PP than in PP + APP. The rate of weight decrease was also larger in PP and thus the weight became less than PP + APP for over approximately 2500 h.

2. Because the weight gain of the resin itself was negligible, the site of water absorption was the interface,

and the leaching of surface treatment agents and the dissolution of glass fibres assisted with elevated temperature were responsible for the weight loss of LGF/PP.

3. Weight change was strongly dependent on water temperature. In water immersion at ambient temperature, both materials showed gradually increased weight (absorption) with time. Weight gain was larger in PP than in PP + APP, indicating that the addition of APP was effective for improving water absorption characteristics of LGF/PP regardless of water temperature.

4. In both materials, tensile and fatigue strengths were significantly decreased by hot water immersion, and PP + APP indicated higher strengths than PP. In PP + APP, fatigue strength of the specimens immersed in water at ambient temperature was almost the same as that of dry specimens, while in PP, decreased compared with dry specimens, but higher than that of the specimens immersed in hot water. The decrease of fatigue strength by water and hot water immersion was primarily attributed to the reduction of fibre strength.

5. The rigidity of dry specimens decreased gradually with stress cycling except for the early and final stages, while specimens immersed in hot water showed nearly constant rigidity. Fatigue damage developed gradually with stress cycling in dry specimens and saturated at the middle or final stages of fatigue life, but specimens immersed in hot water indicated nearly constant or a slight increase in fibre damage. The variation of rigidity corresponded to the damage development of glass fibres.

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