산화 PAN 섬유, 몰딩컴파운드 및 복합재료의 향상된 열안정성에 대한 열중량분석 연구

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A Thermogravimetric Study on the Improved Thermal Stabilities of Oxidized PAN Fiber, the Molding Compound and the Composite

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요 약: 본 연구는 PAN계 탄소섬유 제조공정 동안 얻을 수 있는 중간재료인 산화 또는 안정화 폴리아크릴로니트릴 섬유 (OXI-PAN 섬유)와 관련 재료의 열적특성의 향상에 관한 것이다. 인산용액으로 표면이 코팅된 섬유로 이루어진 OXI-PAN 섬유, OXI-PAN 섬유/페놀수지 몰딩컴파운드 및 그 복합재료의 열안정성과 산화저항성을 동적과 정적 열중량분석 방법을 사용하여 코팅되지 않은 것과 폭 넓게 비교, 조사하였다. 결과적으로 섬유, 몰딩컴파운드 그리고 복합재료의 열안정성과 산화저항성은 코팅한 섬유를 사용하므로써 특히 600 ℃ 이상에서 효과적으로 향상되었다. 인산의 도입은 복합재료에서 매트릭스수지 부분보다는 오히려 OXI-PAN 섬유 부분의 열산화 반응을 지연시키는데 중요하게 기여하였다.

ABSTRACT: The present study is about the improvement of the thermal properties of oxidized or stabilized polyacrylonitrile fiber (here referred to as OXI-PAN fiber), which is an intermediate material available during PAN-based carbon fiber manufacturing processes and related materials. The thermal stabilities and oxidation resistances of OXI-PAN fiber, OXI-PAN fiber/phenolic molding compound and the composite made of the fiber coated with phosphoric acid solutions were extensively examined with the uncoated counterparts, using dynamic and static thermogravimetric analysis (TGA) methods. As a result, the thermal stabilities and oxidation resistances of the fiber, the molding compound and the composite were effectively improved, especially above 600 ℃, by use of the coated fiber in contrast to the uncoated materials. An introduction of phosphoric acid significantly contributes to the retardation of thermal oxidation of the OXI-PAN fiber part rather than the matrix resin part in the composite.

INTRODUCTION

Polyacrylonitrile (PAN) fiber converts into high performance carbon fiber or graphite fiber through a series of stabilization, carbonization and selective graphitization processes under the conditions of required temperature, atmosphere and tension.[1] During the stabilization step, oxidized or stabilized PAN fiber, which is hereafter referred to simply as OXI-PAN fiber, can be obtained after exposing PAN precursor to 200~300 °C in an oxidative atmosphere under tension. Here, acrylonitrile units cyclize forming ladder polymeric chains and then crosslink.[2,3] This fiber has many oxygen containing groups on the surface such as hydroxyl, carbonyl and carboxyl.[2] It also contains about 10 wt% oxygen and 20 wt% nitrogen.[4] Hence, it has been found that the composite made of this fiber with polymeric resin exhibits good wetting and dense microstructure at the fiber/matrix interface.[5]

Simpler processing steps are required to produce OXI-PAN fiber and consequently the cost is much less than carbon fiber. Formerly, asbestos, glass fiber, Kevlar and phenolic fiber have been mainly used as heat-resistant fibers. But, recently OXI-PAN fibers have been increasingly used as interior fibers, heat or fire protection clothing, brake lining, etc. due to their excellent heat and chemical resistances. More interestingly, some reports[6,7] have suggested that it is possible to use OXI-PAN fiber as a promising starting material for fabricating carbon-carbon composite which is widely known as a unique artifact for a brake disk of an aircraft in high temperature use. However, the fiber and matrix in the OXI-PAN fiber reinforced polymer composite material simultaneously co-carbonize during pyrolysis. This phenomenon can provide the main causes of some processing drawbacks like high thermal shrinkage, weak strength and catastrophic failure of the composite.[5,8,9]

For the past two decades carbon fiber reinforced composite materials have become more significant and frequent in civilian, military and aerospace applications. It would be very exciting if OXI-PAN fiber could replace costly carbon fiber even in limited application. Phenol-formaldehyde resin, which is one of the popular thermosetting resins, is inexpensive, easy to handle and good to bond with carbon fibers or OXI-PAN fibers. It has been also well-known as a matrix resin for heat-resistant composite due to its high carbon yield.[10] Carbon containing materials are very sensitive to surrounding oxygen above 500 °C in practice. A key property of a material demanded under such a condition is thermal oxidation resistance. It has been reported that phosphorous compounds can contribute somewhat to improving flame-resistance and/or oxidation resistance of polymeric and carbon materials.[11-13] It would be, then, desirable on their performance at higher temperatures in air if the thermal properties of OXI-PAN fiber and related materials could be effectively increased by an introduction of phosphorous compound. Accordingly, this study focuses preliminarily on improving the thermal stability of OXI-PAN fiber by coating the fiber surface with a phosphoric acid solution and is then extended to OXI-PAN fiber/phenolic molding compound and composite, as examined using dynamic and static thermogravimetric analyses.

EXPERIMENTAL

Materials. OXI-PAN fibers without surface treatment supplied from Tae Kwang Ind. Co. were used throughout this work. They were obtained at the intermediate step of 200~300 °C during carbon fiber manufacturing processes. The

qiaverage fiber diameter was about 10.6 μm. Resol-type phenol-formaldehyde resin (KRD-HM2) with a solid content of 60% manufactured from Kolon Chemical Co. was used without any modification. The cured resin has a carbon yield of about 70% at 1100 ℃ under N_2, as shown in Fig. 1. Phosphoric acid (H_3PO_4) was used to coat the fiber surface for protecting or retarding the thermal oxidation of OXI-PAN fiber, OXI-PAN fiber/phenolic molding compound and the composite. Methanol was used with phosphoric acid for making the coating solutions with different concentrations.

Coated OXI-PAN Fiber. The surface of OXI-PAN fiber was homogeneously coated with phosphoric acid of 0.2~4.0 vol% concentrations. Each end of the fiber bundle of 20 cm long was fixed with the tape to prevent the pull-out of filaments. The fiber bundle was immersed in each phosphoric acid-methanol mixture for 5 min to allow sufficient infiltration and dried in an oven for 30 min at 70 ℃, for 4 hr at 150 ℃, and then overnight at 110 ℃. As-received OXI-PAN fiber was used as the uncoated counterpart for comparison.

OXI-PAN Fiber/Phenolic Molding Compound. The OXI-PAN fibers for the uncoated and coated molding compounds were prepared as mentioned above. The OXI-PAN fiber bundle was impregnated in the equivalent mixture of phenol-formaldehyde resin and methanol for several minutes. The impregnated bundle was ready for B-stage resin for 10 min at 100 ℃. After cutting into a proper size, the molding compound was kept in a freezer.

OXI-PAN Fiber/Phenolic Composite. The prepared molding compounds were cut in 5 mm size and randomly placed in a mold of 50 mm × 50 mm size. The uncoated and coated composites were prepared by a compression molding according to the cure profile described in Fig. 2. The ex-
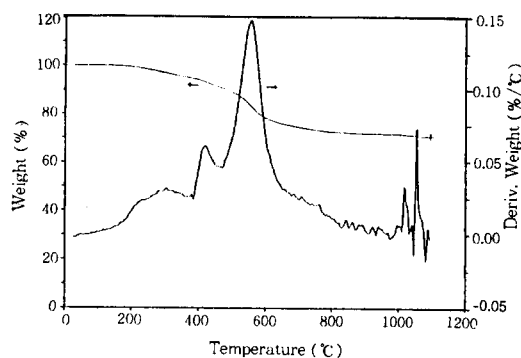

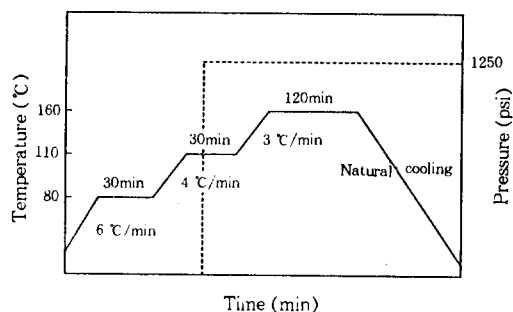**Figure 1.** Weight loss change of cured phenolic resin as a function of temperature in N_2.

Figure 2. A cure profile as functions of temperature, pressure and time for fabricating OXI-PAN fiber/phenolic composite.

cess resin was about 5% and the resin content was 46~48%. Both composites had a thickness of about 7~8 mm and a density of 1300 kgm^{-3}.

Thermal Stability Test. Thermal stability tests of the uncoated and coated OXI-PAN fibers, the molding compounds and the composites were performed up to 1100 ℃ in air using a thermogravimetric analyzer (DuPont 951 TGA). Heating rates were 10 ℃/min in a dynamic method and 20 ℃/min in a static method. The thermal stability of the molding compound was also measured under the conditions similar to temperature, time and heating rate for the molding.

Fiber Surface Observation. Scanning electron microscope (SEM, Hitachi S-2400) was used
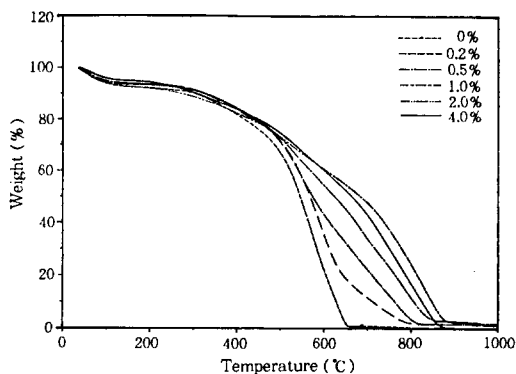
Figure 3. TGA thermograms in air of the OXI-PAN fibers coated with different concentrations of phosphoric acid solution.

to observe the surfaces before and after the coating of phosphoric acid on OXI-PAN fiber surface.

RESULTS AND DISCUSSION

Fig. 3 compares the thermal stability in air of the uncoated (as-received) OXI-PAN fiber with that of the fiber coated with phosphoric acid solutions of different concentrations. The coated fibers always showed better thermal stability than the uncoated one, with highly increased thermal oxidation resistance above 500 ℃. The thermal oxidation resistance was continuously improved up to 2.0% coating concentration but lowered above the concentration. This implies that at lower concentrations the oxidation resistance increases with the increase in quantity of phosphoric acid and so an optimal coating is necessary for better effect. A significant effect of phosphoric acid on the thermal stability of the fiber below 500 ℃ was hardly found. However, there was the weight loss caused by volatilization during a transformation of phosphoric acid which existed on the fiber surface, even after a complete drying, into pyro- and meta-phosphoric acids with increasing temperature. Above 500 ℃, OXI-PAN fiber begins to carbonize, becomes of its sensitivity to surrounding

oxygens and hence seriously loses its weight by oxidation. The extra quantity by the volatilization was removed in the 4.0% coating concentration than in the 2.0%. This caused an ineffective result on the overall thermal stability above 500 ℃. The difference of complete burn-off points between the uncoated and 2.0% coated OXI-PAN fibers was greater than 200 ℃. Considering the thermal oxidation resistance and the fiber condition after the coating, it was reasonable that the 2.0% coating was suitable for the purpose of this study. Accordingly, this concentration has been hereafter used for improving the thermal properties of OXI-PAN fiber/phenolic molding compound and composite. The initial weight loss below 120 ℃ in Fig. 3 may be caused by some interactions between functional groups on the fiber surface and oxygen atoms introduced during the measurement and probably by removal of a small quantity of moisture adsorbed on the fiber surface. The weight losses in the range of 300~500 ℃ can be explained by the volatilization of small non-carbon molecules such as CO_2, HCN, NH_3, and H_2O, which were formed during stabilization and carbonization processes.[1]

Fig. 4 shows the result of thermal aging for the uncoated and coated OXI-PAN fibers at different isotherms in air. It is noticed that the coating on the fiber surface contributes to the retardation of the thermal oxidation, especially at higher temperatures where the weight loss or aging by oxidation predominantly takes place. This effect on the thermal oxidation resistance was better than the effect on the carbon fiber reported previously.[14] This means that phosphoric acid plays a more effective role in increasing the thermal properties of reactive OXI-PAN fiber than hardly reactive carbon fiber. As a result, the weight loss of OXI-PAN fiber could be somewhat inhibited during carbonization.
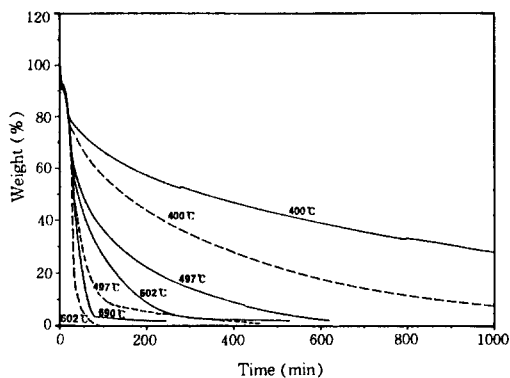
A comparison of the fiber surfaces before and

Figure 4. TGA thermograms showing the aging effect of the uncoated (dotted line) and coated (solid line) OXI-PAN fibers at different isotherms in air.

after the coating is shown in Fig. 5. An average diameter of a single OXI-PAN fiber was about 10.6 μm before the coating. It increased to about 12 μm after the coating. It was microscopically observed that the surface of OXI-PAN fiber had a sheath structure and roughness due to the introduction of oxygen during stabilization. The state of the fiber surface was not changed much by the coating. The wrinkles seen on the surface are resulted from a structural change of the PAN fiber to a ladder polymer structure along the direction of tension during stabilization. Ko et al.[15] has insisted that the formation of ladder structure begins in the amorphous phase and spreads to the crystalline phase with a complete breakdown of the crystalline order during heat treatment. There is also an increase in the crystallite size, crystal perfection and crystal orientation during heat treatment of the fiber. This may be ascribed to the transformation of acrylonitrile units from the amorphous phase to the ordered phase.

The thermal stability of the uncoated and coated OXI-PAN fiber/phenolic molding compounds measured in air is represented in Fig. 6. Here, the initial weight loss below 100 °C at which preheating was done for B-staging the resin did not take place, but the primary weight loss by remov-
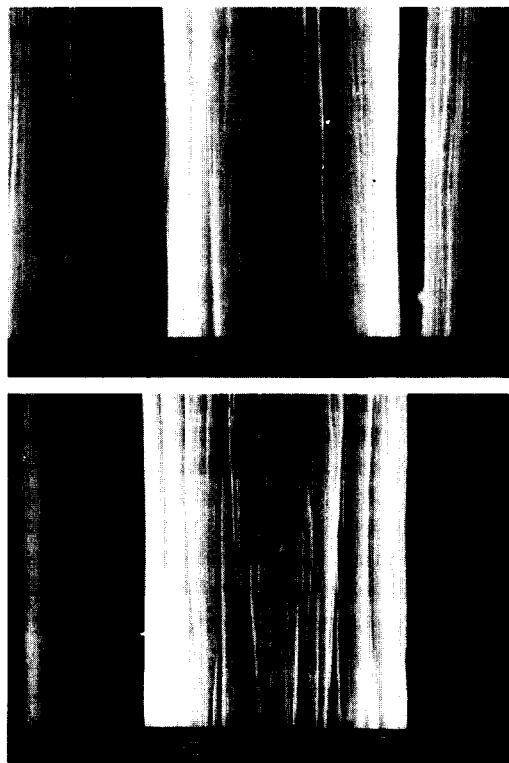

Figure 5. Scanning electron micrographs for the surfaces of the uncoated (top) and H$_3$PO$_4$-coated (bottom) OXI-PAN monofilaments.
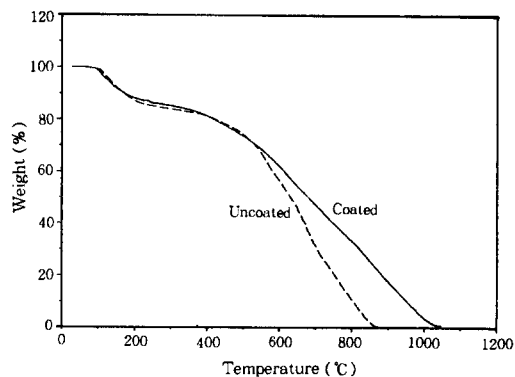

Figure 6. A comparison of the thermal stability in air between the uncoated and coated OXI-PAN fiber/phenolic molding compounds.

al of the uncured portions was found to be over 10% up to 200 °C. Above 200 °C, non-carbon

compounds of low molecular weight in the fiber are separated. Simultaneously, some unreacted components remaining in the cured resin can be post-cured and then decomposed, resulting in the secondary weight loss. For both composites the weight losses above 600 ℃ are predominantly influenced by carbonized OXI-PAN fibers. The rate of loss becomes accelerated by oxygen introduced in an aerial surrounding. Similarly to the result of OXI-PAN fiber, the molding compound with the coated fibers shows better thermal stability than the uncoated counterpart. It may be expected from this result that the coating method would give a positive effect on improving the thermal oxidation resistance of OXI-PAN fiber/phenolic composite.

The experiment seen in Fig. 7 was carried out, based upon the practical temperature, dwell time and heating rate described in Fig. 2, to examine the thermal stability of the molding compounds used in the present work. The pressure condition was excluded due to an experimental difficulty and no importance was put on the weight change. It can be estimated that the weight loss of both molding compounds would be about 10% after a completion of cure cycle. The uncoated one showed less weight loss than the coated. This can be mainly resulted from volatilization of phosphoric acid on the fiber surface. The weight loss was accelerated during the dwell times given at 80, 110 and 160 ℃. Based upon the largest difference in the weight loss after 110 ℃ where the cure is most active, phosphoric acid is believed to somewhat promote the cure reaction of phenolic resin adjacent to the fiber. An effect of heating rate on the compound was studied in Fig. 8. An inspection of the weight loss between the range of 100～160 ℃ where most of the cure has taken place indicates that the coated molding compound exhibits greater weight loss than the uncoated one, at the given heating rates of 3, 5 and 10 ℃/min. At the
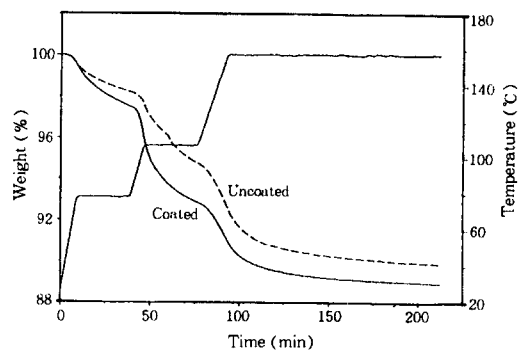

Figure 7. A comparison of the weight loss of the uncoated and coated OXI-PAN fiber/phenolic molding compounds under the condition similar to the molding in the present study.
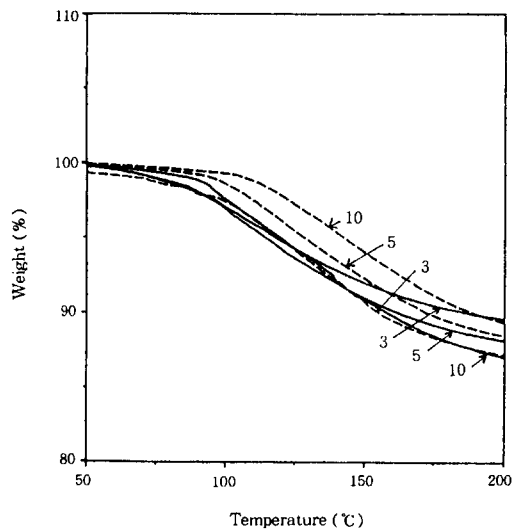

Figure 8. An effect of heating rate on the weight loss of the uncoated (dotted line) and coated (solid line) molding compounds in the range of molding temperature.

lowest heating rate, the uncoated molding compound has the largest weight loss at 200 ℃ due to a slow cure. It may be possible that with increasing heating rate the remaining unreacted quantity relatively increases, resulting in lower weight loss. On the other hand, in the case of the coated one, the resin cure with 3 ℃/min occurs at the earlier stage than that with 5 ℃/min and 10 ℃/min due
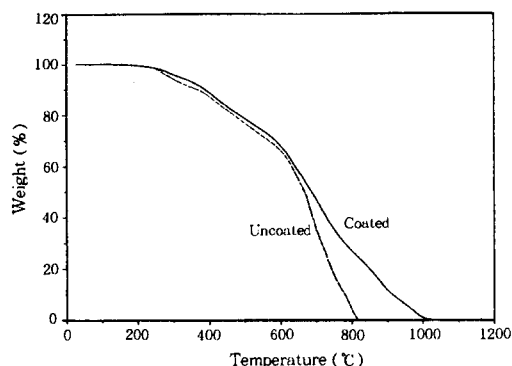
Figure 9. A comparison of the thermal stability in air between the uncoated and coated OXI-PAN fiber/phenolic composites.

Figure 10. Variations of derivative weight as a function of temperature for the uncoated (dotted line) and coated (solid line) composites after post-cure.

to a catalytic effect by phosphoric acid. A small amount of phosphoric acid slightly increases a quantity of the resin participating in the reaction. Hence, the weight loss at 200 ℃ is the smallest at 3 ℃/min.

Fig. 9 compares the TGA result measured in air for the uncoated OXI-PAN fiber/phenolic composite with that of the coated composite. There was no weight loss near 250 ℃, owing to the thermal experience during molding. After that, the cured resin and OXI-PAN fiber became decomposed and carbonized gradually. Above 600 ℃, the oxidation in the fiber part predominated. Use of the fiber coated with phosphoric acid increased the thermal oxidation resistance of OXI-PAN fiber/phenolic composite above 600 ℃, as explained in the earlier fiber study. A complete burn-off of the coated composite was also occurred at the temperature 200 ℃ higher than that of the uncoated one. The post-cure was performed for 24 h at 190 ℃ to know how it influences the high temperature resistance. Fig. 10 shows the result calculated for the variations of derivative weights as a function of temperature. As expected, the oxidation rate for the uncoated composite above 600 ℃ was faster than that of the coated one. It indicated that the coating effect on the thermal oxidation resistance was also useful
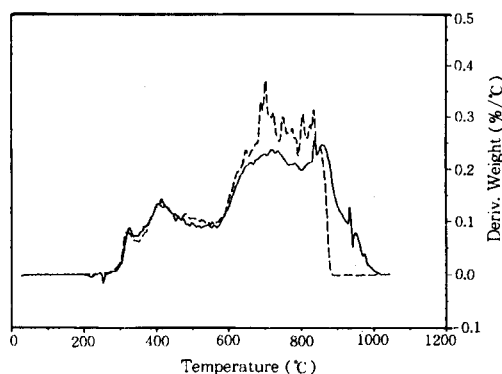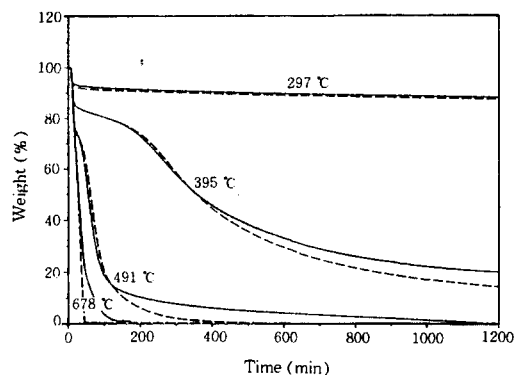

Figure 11. TGA thermograms showing the aging effect of the uncoated (dotted line) and coated (solid line) OXI-PAN fiber/phenolic composites at different isotherms in air.

even after the post-cure of the composite. Fig. 11 represents the result of thermal aging for the two composites at different isotherms in air. The coated composite exhibits higher thermal stability than the uncoated eventhough the effect is less than in the case of OXI-PAN fiber only, as noted in Fig. 4. Therefore, it can be assured that the phosphoric acid coating for the protection of the thermal oxidation and for the improvement of the thermal stability of the OXI-PAN fiber material is only more effective in the OXI-PAN fiber than in the composite composed of 50% resin approximately.

Consequently it is obvious that an introduction of phosphoric acid contributes more to the protection of oxidation of the fiber part rather than the matrix resin part. A reasonable explanation for the improved thermal stabilities of OXI-PAN fiber, the molding compound and the composite studied here can be extracted from the following microscopic results. In the previous study[16] the protective mechanism which occurred during thermal oxidation in OXI-PAN fibers coated with phosphoric acid was microstructurally elucidated. There were microstructural changes in the longitudinal surface and transverse cross-section of the fiber demonstrating the protection of thermal oxidation of OXI-PAN fiber by a phosphoric acid coating. It was also identified from an elemental analysis that phosphorus residues from phosphoric acid exist after heating on the longitudinal and transverse regions of the coated OXI-PAN fibers. During pyrolysis, the phosphorous compound uniformly distributed on the surface diffuses or migrates into the interior of a filament through microstructural defects in the fiber. Apparently the diffused or migrated phosphorous somewhat contributes to the retardation of possible reactions with surrounding oxygen by blocking many active sites. Accordingly, the coated OXI-PAN fibers in the molding compound and composite are mainly responsible for their improved thermal stabilities. It was also observed in Fig. 11 that the weight losses of both composites after an exposure to 297 ℃ for a long duration of 20 h were only 10%. This implies that an apparent improvement by the coating is not seen around 300 ℃ because the thermal stability in the temperature range is still importantly governed by the matrix phenolic resin.

CONCLUSIONS

As the surface of OXI-PAN fiber is coated with phosphoric acid solutions, the thermal stability above 500 ℃ in air is obviously increased with an increase of the coating concentration in comparison with the uncoated fiber. Especially, at 2.0% concentration a complete burn-off point of the coated fiber is about 200 ℃ higher than that of the uncoated counterpart. An introduction of phosphoric acid significantly contributes more to the retardation of the thermal oxidation of the OXI-PAN fiber part than that of the matrix resin part in the composite. It has been concluded that the use of the coated fibers improves the thermal stabilities and oxidation resistances of OXI-PAN fiber/phenolic molding compound and composite at temperatures above 600 ℃. It has also been found that some weight losses occurring during the composite molding depend upon heating rate, and phosphoric acid may somewhat catalyze the cure reaction of phenolic resin adjacent to the OXI-PAN fiber.

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