Braking Performance of an Organic Brake Pad Based on a Chemically Modified Phenolic Resin Binder

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Braking Performance of an Organic Brake Pad Based on a Chemically Modified Phenolic Resin Binder

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An organic brake pad for railroad passenger-coach braking was prepared using a chemically modified phenolic resin (PF), that was designed and manufactured in our laboratory. The braking performance of the pad was investigated on a full-scale test bench. For comparison, a brake pad based on straight PF was also prepared and investigated. The results showed that the modified PF pad possessed much higher impact strength, and better braking stability and wear resistance than the straight PF pad. It is thought that the better overall properties of the modified PF pad resulted from the changes in chemical structure of the resin during the frictional process and the strong interreaction of the modified resin binder with the hybrid fibers.

Keywords: Organic brake pad, friction materials, phenolic resin modification, hybrid fibers, braking performance, sliding friction

1 Introduction

Organic friction materials, such as brake pads for railroad passenger-coach braking, generally contain multiple ingredients to achieve the desired performances. These ingredients mainly include organic binder, reinforcing fibers, friction modifiers and fillers. The organic binder is important for the friction materials, because it secures all the other ingredients together firmly, so that the composites can exhibit the desired performance adequately and reliably. Conventional brake pads for passenger-coach braking are generally composed of straight phenolic resin (PF) and a large amount of metal particles and fibers, known as semi-metallic friction materials. The main chain of the straight PF is easily broken during braking, resulting in heat fade, heat expansion and heat cracks. The cracks and voids in the pads are detrimental safety problems for the braking process.

In order to overcome the shortcomings of the straight PF, various modified PFs have been developed. A modified resin, manufactured by condensing phenol and alkylether, was reported by Kim and Jang (1). Compared with conventional straight PF, the modified resin possessed higher thermal stability and also improved the friction stability and reduced the friction fluctuations even at high temperature. Bijwe and his group (2, 3) investigated five friction materials prepared by 10 wt% of straight PF, alkyl benzene modified PF, cashew nut shell liquid modified PF, nitrile butadiene rubber (NBR) modified PF and linseed oil modified PF, respectively, each containing similar other additives, they were reinforcements (total 26 wt%) consisting of glass fibers, steel wool, polyacrylonitrile (PAN) and rock wools, friction modifiers (total 24 wt%), and space fillers (40 wt%). The results showed that none of the composite based on these modified resins proved best in all the selected performances, especially under severe braking conditions. The correlations between the tribological properties of the composites and the thermal stability of the resins or the mechanical properties of the composites were not clear. They also developed a series of thermosetting resins based on oxazine rings (4, 5), which are capable of heat induced ring opening polymerization. The composites based on these resins showed superior performances even under severe operating conditions.

It is well-known that polycondensation of straight PF catalyzed by hexamethylenetetramine (C12H4N4) unavoidably releases volatile products resulting in the formation of micro-cracks and cavities in cured products during
Braking Performance of a New Organic Brake Pad

Hot press processing, whereas the polyaddition reaction is volatile-free. The polyaddition cured PF resin possesses more adhesive structural units, and hence the interaction between the resin binder and the other ingredients in a composite should be strong. On the other hand, it is believed that different functional units in a binder are excited independently under various braking conditions, and hence can maintain stable friction coefficient and avoid sudden synchronous-breakage of the backbone chains.

In this study, from the point of view of changing the curing reaction of the PF resin from polycondensation to a polyaddition reaction, a modified PF with special structure was designed and synthesized in our laboratory as a binder for friction materials. Carboxylate rubber was selected as a modification component, which underwent an open-ring addition with the epoxy group of the pre-polymer generated from a base catalyzed substitution reaction between straight PF and epoxy chloropropane. A brake pad for passenger coach braking was prepared using the modified PF binder and reinforced with hybrid-fibers. The braking performance of the pad was investigated via a full-scale test bench. For comparison, a brake pad based on a conventional straight PF binder containing the same ingredients as the modified PF pad was also prepared and studied. The chemical structure changes of both resins with increasing temperature were studied systematically. Influences of the chemical structure of the resin binder on the braking performance of the brake pad are discussed.

2 Experimental

2.1 Structure of the Matrix Binders

Two different binders were used in this study. One was the modified PF designed and synthesized in our laboratory. In this newly modified resin, latex rubber particles were chemically connected to the resin (Fig. 1(a)). The synthesis route of the resin is described in detail in our previous report (6). The soft latex particles were grafted onto the rigid main chains of the macromolecule. The resin can form crosslinked structures during the curing process.

The other matrix binder was straight PF (Fig. 1(b)), a commercial product (Trademark 2123) containing 6–7% curing agent of hexamethylenetetramine (C₆H₁₂N₄) from Henan Bangde Ltd. Co., China; it is universally used as a binder in various friction materials.

2.2 Fabrication and Characterization of the Brake Pads

Table 1 lists the composition of the brake pad based on the modified PF binder. Hybrid-fibers, composed of a mixture of carbon fibers, wollastonite whiskers and sepiolite fibers, were used as reinforcement. For the straight PF brake pad, the composition and content of the ingredients were the same as for the modified PF brake pad, except the matrix binder type. Acrylonitrile rubber particles at a mass fraction of 5% were added to improve the toughness and the impact strength of the straight PF pad.

The fabrication method for both brake pads was the same. All the ingredients were completely blended in a Z-type kneading machine to form molding powder. The molding powder was hot-pressed at 155 ± 2°C under 30 MPa for 50 min, and subsequently was post-cured at 155 ± 2°C.

![Chemical structure of the latex particle modified PF (a) and the straight PF (b) resins.](image)
Table 2. The physical and mechanical properties of the brake pads and the required values regulated by TB/T 3118-2005

<table>
<thead>
<tr>
<th>Properties</th>
<th>Modified PF pad</th>
<th>Straight PF pad</th>
<th>Required value</th>
<th>Test standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
<td>2.13</td>
<td>2.17</td>
<td>—</td>
<td>GB/T 1033-1986</td>
</tr>
<tr>
<td>Impact strength, kJ/m²</td>
<td>6.9</td>
<td>3.3</td>
<td>≥3.0</td>
<td>GB/T 1043-1993</td>
</tr>
<tr>
<td>Compress strength, MPa</td>
<td>24.9</td>
<td>25.8</td>
<td>≥20</td>
<td>GB/T 1041-1992</td>
</tr>
<tr>
<td>Compress modulus, MPa</td>
<td>549</td>
<td>895</td>
<td>≤1000</td>
<td></td>
</tr>
<tr>
<td>Rockwell hardness (HRR)</td>
<td>69</td>
<td>85</td>
<td>50–90</td>
<td>GB/T 9342-1988</td>
</tr>
</tbody>
</table>

for 50 min. The area and thickness of the brake pads were 175 cm² and 28.0±0.1 mm, respectively. The brake surface of the pads was polished with a grinding machine to remove the cured skin in order to diminish the mold releasing agent.

The density, impact strength, compressive strength, compressive modulus and Rockwell hardness were measured as per the corresponding China standards; all the testing samples were cut from the pads. Table 2 lists the measured results of the brake pads and the required values regulated by TB/T 3118-2005 (Standard of China Railway Ministry “The brake lining made of composite materials for rolling stock”).

2.3 Braking Test Procedure

The braking tests were conducted on a full-scale test bench as per TB/T 3118-2005 at the Vehicle Inspection Station of Product Quality Monitoring Center of the Railway Ministry, People’s Republic of China. The details of the test program can be obtained from our previous report (6). The matched material was a pearlitic gray cast iron disc with a diameter of 640 mm, the diameter of the matching wheel was 915 mm. The pads were placed against opposite sides of the brake disc, and the friction radius of the pad on the disc was 250 mm (the sliding speed of 27.3 m/s at the outer radius of the pad corresponds to a coach speed of 180 km/h). The load on the pads was adjusted to keep the required values; the shaft weight was 17.6 t. A thermoelectric couple 1 mm under the brake disc surface was used to estimate the nominal temperature of the frictional interface. If the measured temperature exceeded 400°C, the test would be stopped automatically. The braking tests were carried out at room temperature after establishing 70% conformal contact between the matching pad and disc. The instantaneous friction coefficient was recorded by an attached computer. The average friction coefficient can be automatically calculated and given by the computer based on the following equation:

\[ \mu_m = \frac{1}{s_2} \times \int_0^{s_2} \mu_a \times ds \]

where \( \mu_a \) is instantaneous friction coefficient, and \( s_2 \) is braking distance.

2.4 Analysis

The curing character of the resins was evaluated by differential scanning calorimetry (DSC, Perkin-Elmer Pyris 1, USA). The thermal properties were evaluated by thermogravimetric analysis (TGA, Perkin-Elmer Pyris 1, USA) under a flowing air atmosphere of 40 mL/min and at a heating rate of 20°C/min (Table 3).

The resins were heat treated at various temperatures under air atmosphere for about 1 min for analyzing the changes in the chemical structure caused by heat. Fourier transform infrared spectroscopy (FTIR, Nicolet NEXUS 470, USA) and solid state \(^{13}\)C-NMR spectroscopy (Infinity Plus model 300 WB, Varian, USA) were used to obtain the changes during heating. KBr pellets with a diameter of 13 mm were prepared for FTIR analysis. The high resolution \(^{13}\)C-NMR measurements were conducted with a frequency of 75 MHz and a 4 mm MAS probe head. The \(^{13}\)C NMR spectra were obtained by cross-polarization (CP) and magic angle sample spinning (MAS) under the following conditions: 90° pulse length 4 µs, contact time 1.5 ms, recycle delay 3 s and MAS rate 12 kHz. The \(^{13}\)C

Table 3. The characteristic infrared bands with the assignments for the resins (11–14)

<table>
<thead>
<tr>
<th>Band position, cm⁻¹</th>
<th>Character</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3425</td>
<td>broad</td>
<td>-OH</td>
</tr>
<tr>
<td>3013</td>
<td>weak</td>
<td>Aromatic CH stretching</td>
</tr>
<tr>
<td>2925</td>
<td>medium</td>
<td>Aliphatic CH₂ asymmetric stretching, CH₃</td>
</tr>
<tr>
<td>2852</td>
<td>weak</td>
<td>Aliphatic CH₂ symmetric stretching</td>
</tr>
<tr>
<td>2239</td>
<td>weak</td>
<td>C = N</td>
</tr>
<tr>
<td>1736</td>
<td>weak</td>
<td>Ester group</td>
</tr>
<tr>
<td>1642</td>
<td>strong</td>
<td>benzophenone</td>
</tr>
<tr>
<td>1604</td>
<td>strong</td>
<td>Benzene ring stretching</td>
</tr>
<tr>
<td>1507</td>
<td>strong</td>
<td>Semicircle ring stretching</td>
</tr>
<tr>
<td>1445</td>
<td>strong</td>
<td>Aliphatic CH₂ scissor bending</td>
</tr>
<tr>
<td>1356</td>
<td>weak</td>
<td>OH, stretching CH₃</td>
</tr>
<tr>
<td>1233</td>
<td>strong</td>
<td>phenol –OH</td>
</tr>
<tr>
<td>1101</td>
<td>medium</td>
<td>In plane ring deformation</td>
</tr>
<tr>
<td>1009</td>
<td>medium</td>
<td>CH₃ attached to the aromatic ring</td>
</tr>
<tr>
<td>918</td>
<td>weak</td>
<td>Aliphatic CH₂ wagging</td>
</tr>
<tr>
<td>820</td>
<td>medium</td>
<td>Out of plane ring deformation</td>
</tr>
<tr>
<td>758</td>
<td>medium</td>
<td>Out of plane ring deformation</td>
</tr>
</tbody>
</table>
Table 4. The chemical shift assignment of the modified and straight PF resins (15, 16)

<table>
<thead>
<tr>
<th>δ (PPM)</th>
<th>Assignment</th>
<th>PF resin type</th>
</tr>
</thead>
<tbody>
<tr>
<td>151</td>
<td>Phenoxy carbons</td>
<td>both</td>
</tr>
<tr>
<td>129</td>
<td>Aromatic carbons</td>
<td>both</td>
</tr>
<tr>
<td>116</td>
<td>Non-substituted ortho carbons</td>
<td>both</td>
</tr>
<tr>
<td>74</td>
<td>Dimethylene ether bridges</td>
<td>straight PF</td>
</tr>
<tr>
<td>36</td>
<td>Para/ortho methylene bridges</td>
<td>both</td>
</tr>
<tr>
<td>16</td>
<td>Methyl carbons</td>
<td>straight PF</td>
</tr>
</tbody>
</table>

chemical shifts were reported relative to the external reference of adamantane (38.5 ppm) (Table 4).

The viscoelasticity of the brake pads was characterized by dynamic mechanical analysis (DMA 242, Netzsch Co., Germany) in oscillating dual cantilever mode in air at a frequency of 5 Hz. The specimens (50.0 × 5.0 × 2.5 mm) were cut from the pads. The temperature ranged from -50 to 450°C, and the heating rate was 3°C/min.

The morphology of the pad surface after the whole brake tests was observed by means of a digital camera (Sony W-1, Japan) and scanning electron microscopy (SEM, 5136MM, Tescan s.r.o. Co., Czech). The samples for SEM observation were coated with a thin gold film for rendering conductivity.

3 Results and Discussion

3.1 Thermal Analysis Results

Figure 2 shows DSC curves of the modified and straight PF resins. For the modified resin, the heat flow showed a broad exothermal peak with a maximum around 155°C as a result of curing reactions. In the case of the straight PF, a large and sharp peak at 156°C and a small and broad peak at 110°C were observed. The height of the curing reaction peak for the modified PF was much lower than that of the straight PF; this result may be due to the low thermal effect of ring-opening addition reactions of the modified PF. Figure 2 indicates that the curing temperature range of the modified resin was wider than that of the straight PF resin, implying that the heat molding processing of the modified PF pad would be easier than that of the straight PF pad.

Figure 3 shows the TGA and their differential curves (DTGA) for the modified and straight PF resins under air flow. The weight loss of the modified resin appeared in two steps. The first step, visible in the DTGA curve, was at 155°C with a weight loss of 2.1%; it corresponds to the polycondensation reaction. From this temperature to 360°C, the curve was almost linear, that is to say, after this initial weight loss, the sample remained relatively stable. This stabilization can be explained by the new structures being stable until the temperature was high enough to cause the collapse of the polymer structure. The second weight loss, starting at 360°C, was caused by resin degradation and the maximum weight loss rate was at 470°C. The total weight loss up to 800°C was 78%.

In the case of the straight PF (Fig. 3(b)), the weight loss appeared in four steps. The first step occurred at 80–140°C
(the maximum weight loss rate was at 110°C) and corresponds to the release of volatile products of 1.9%. The second step at 140–350°C (the maximum weight loss rate was at 156°C) corresponds to the curing reaction. The third step at 340–450°C (the maximum weight loss rate was at 410°C), was not obvious. After these initial weight losses of about 12%, the straight PF showed a sharp and large weight loss with the maximum weight loss rate of greater than 80% at 628°C. The weight loss up to 800°C was 96.5%.

Generally, the thickness of brake pads for railroad passenger-coaches is thicker than 25 cm. Consequently, volatile products seriously affect the quality of the finished pads. Figure 3 indicates that the conventional straight PF released much more volatile products than the modified PF, and this will result in micro-cracks and cavities in the cured pad during hot press processing. The micro-cracks may extend to form macroscopic cracks during severe braking conditions. On the contrary, the modified resin was almost volatile-free, and also showed a higher char residual weight at 800°C compared to the straight PF, although the maximum degradation temperature of the modified resin was much lower than that of the straight PF.

Figure 4 shows the variation of the storage modulus $E'$ and the loss factor (tan $\delta$) of the friction materials based on the modified and the straight PF resins with increasing temperature. The storage modulus $E'$ represents elastic behavior, and the temperature of the tan $\delta$ peak corresponds to the glass transition temperature ($T_g$). The variation tendency of the storage modulus of both friction materials was similar (Fig. 4(a)). The modulus decreased rapidly to about 650–700 MPa when the temperature was increased to room temperature. After that, the modulus slowly decreased to 100–200 MPa with increasing temperature, followed by a slight increase. When the temperature was higher than 420°C, the modulus of both friction materials was near 0 MPa. It is noteworthy that the modulus of the modified PF pad was almost twice as high as that of the straight PF pad at the high temperature of 280–350°C. That is to say, the distortion of the modified PF pad was higher than that of the straight PF pad at 280–350°C, although the maximum degradation temperature of the modified PF (470°C) was much lower than that of the straight PF (628°C).

Tan $\delta$ peaks of the modified PF pad appeared at 3°C, 209°C, 398°C and 425°C, and those of the straight PF pad appeared at 2°C, 190°C, 345°C and 424°C. The peaks at low temperatures, 2°C and 3°C, could be attributed to the energy loss of rubber ingredients, the peaks at 190°C for the straight PF pad and 209°C for the modified PF pad could be attributed to the movement of the PF macromolecular main chains. The peak at 424°C for the straight PF and 425°C for the modified PF may be attributed to the distort of benzene ring, and the peak at 345°C for the straight PF and 398°C for the modified PF may be ascribed to the bridge bond between the latex particle and the PF rigid main skeleton chain. The higher tan $\delta$ temperatures for the modified PF pad imply that the crosslinking density of the modified resin was higher than that of the straight PF after the curing process and post-heat treatment. It is well known that the tan $\delta$ value is related to the damping property of the composite. Figure 4(b) indicates that the damping stability of the modified PF pad with increasing temperature was better than that of the straight PF pad.

It has been reported (7–9) that the damping properties of most fiber reinforced composites are mainly offered by the polymer matrix. In this work, hybrid fibers were used as reinforcement in both of the brake pads. The fibers with various length-diameter ratios may form random reticulations, and the effect of the reticulate structure on the damping properties cannot be ignored. Combining Figs. 3(a) and Fig. 4, it is thought that although the initial heat degradation temperature of the modified PF pad was about 360°C, both the multi-functional groups and fibers (broken) contributed to the strength and damping properties, and inhibited severe heat fade of the pad at high temperature.

### 3.2 Physical and Mechanical Properties

Table 2 presents physical and mechanical properties of the brake pads and the required values regulated by TB/T
Braking Performance of a New Organic Brake Pad

3118-2005. All the test samples were cut from the pads. The mechanical properties of the pads fully satisfy the required values in TB/T 3118-2005. It is noteworthy that the impact strength of the modified PF pad was twice as high as that of the straight PF pad, and was much higher than the required value of 3 kJ/m². This result may be due to the interaction between the modified matrix binder and the other ingredients being quite strong.

3.3 Brake Test Results

The braking performance of the pads was evaluated on a full-scale bench tester. Figure 5 gives the instantaneous friction coefficient vs. braking speed under dry conditions at an applied load of 21.0 kN; the sloping lines in the figures indicate the tolerances for the instantaneous friction coefficients under dry friction required by TB/T 3118-2005. The results showed that the modified PF pad met the corresponding requirement, and the friction coefficients under various braking speeds were very stable, proving the modified PF pad can achieve reliable and stable braking. For the straight PF pad, although the friction coefficient at the speeds higher than 30 km/h was within the range required by TB/T 3118-2005, the fluctuation amplitude of the friction coefficients was large, and the friction coefficient at low speed of 0–20 km/h exceeded the range.

Under wet conditions, the friction coefficients of the modified PF pad under various prescriptive braking speeds were also more stable than that of the straight PF pad. Although both pads satisfied the TB/T 3118-2005 regulation, the fluctuation amplitude of the friction coefficients of the modified PF pad was again much smaller than that of the straight PF pad under all the tested initial speeds.

The measurements under dry conditions showed that the disc temperature increased with the braking speed and the load; the highest measured temperature was 206°C for the modified PF pad, and 220°C for the straight PF pad. According to “Newcomb’s model” (10), related to the emergency stop-braking of a train running at 160 km/h, the maximal increase of average disc surface temperature was 263°C. The temperature rises in the tests were lower than that reported in Ref. (10). It is well known that temperature rise in the disc should be as low as possible and it is termed as one of the parameters of counterface friendliness. It can be concluded that the modified PF pad is friendlier to the matched brake disc than the straight PF pad. This result could be due to the latex particles modified resin itself having high flexibility.

Figure 6 shows the wear loss of the modified PF pad and the straight PF pad after the completed braking tests. The wear loss of the modified PF pad was 0.57 cm³/MJ, which was lower than that of the straight PF pad of 0.78 cm³/MJ; both pads met the required value of lower than 1.0 cm³/MJ. On the other hand, no cracks and metal-embedded deposits were observed on the modified PF pad surface after the brake tests, or on the brake disc surface. Patch-like films were formed and adhered firmly to the friction surface of the modified PF pad (Fig. 7(a)). The color of the films was different from that of the pad material. In contrast, obvious cracks were observed on the straight PF pad, as shown in Fig. 7(b). This result implies that the better braking stability and anti-wear property of the modified PF pad may be related to the changes in the microstructure of the surface composition during the braking process.
3.4 Chemical Structure Changes of the Binders at Different Temperatures

It is well known that the surface temperature of brake pads during the braking process can vary from 300 to 900°C. Organic binders in friction materials are most sensitive to the mechanical forces and frictional heat, so tribochemical reactions are unavoidable during braking and affect the braking performance. However, the tribochemical changes are difficult to be detected because of the limitation of in-situ analysis technology for braking interfaces. In order to understand the chemical reactions of binders at frictional interfaces, FTIR and $^{13}$C-NMR analysis of the modified PF and the straight PF resins were carried out under air atmosphere at different temperatures from room temperature (RT) to 600°C.

The FTIR spectra are shown in Figure 8. Table 3 lists the characteristic infrared bands with the assignments for the resins. Compared with the FTIR spectrum at room temperature, the change in the spectrum of the modified resin (Fig. 8(a)) at the maximum weight loss temperature of 470°C (Fig. 3(a)) can be described as follows: the two peaks at 1604 and 1507 cm$^{-1}$ belonging to aromatic ring stretching disappeared; the peak at 1233 cm$^{-1}$ that belongs to phenol –OH became two peaks at 1257 cm$^{-1}$ and 1205 cm$^{-1}$. A new peak at 872 cm$^{-1}$, typical for polyaromatic systems appeared. The above results suggest the formation of methylene links and higher substituted rings. It is interested to note that the modified PF remains in organic structure at 600°C because of the presence of the peaks at 1461 cm$^{-1}$ (C=C in aromatic ring), 1111 cm$^{-1}$ (aliphatic C-H-C) and 518 cm$^{-1}$ (C-H in alkene). On the other hand, the intensity of the peaks at 2925 and 2852 cm$^{-1}$ (aliphatic CH$_2$ asymmetric stretching and symmetric stretching) significantly increased with the increasing temperature up to 470°C, but were nearly absent at 600°C, indicating that the main structure of the modified resin changed toward a polyaromatic structure. This suggestion is also supported by that the original doublet peaks (1604 and 1642 cm$^{-1}$) in the resin became a broad band covering a range of 100 cm$^{-1}$ with the increasing temperature, typical for polyaromatic systems (11–14).
Fig. 8. FTIR spectra of the modified PF (a) and straight PF (b) resins at different temperatures in air. (Color figure available online.)
As for the straight PF resin, a new peak around 1710–1730 cm\(^{-1}\) was observed at the temperatures higher than 340\(^\circ\)C, indicating that an oxidation reaction occurred and carboxylic acid was formed.

Figure 9 shows \(^{13}\)C-NMR spectra of the resins obtained at different temperatures. The carbon resonance assignments are presented in Table 4 based on the literature (15, 16). As shown in Figure 9(a), the main change in the \(^{13}\)C-NMR spectra of the modified resin occurred at 410\(^\circ\)C: the peak, belonging to methylene bridges (chemical shift 36 ppm), obviously increased, accompanied with the disappearance of the non-substituted ortho carbons in aromatic ring (chemical shift 116 ppm). These results indicate that the crosslinking reaction occurred in the modified PF resin, and a three-dimensional network connected with methylene bridges was formed. In the case of the straight PF (Fig. 9(b)), a new peak at 16 ppm, corresponding to methyl carbons, appeared in the spectrum obtained at 410\(^\circ\)C, and the intensity of non-substituted ortho carbons (chemical shift 116 ppm) decreased. The methylene bridges may break to form methyl carbons at high temperature for the straight PF binder.

3.5 Discussion

The reinforcing fiber is one of important ingredients in organic friction materials, since it can provide mechanical strength to the composites. In this study, the modified PF pad reinforced by hybrid fibers showed better braking stability and anti-wear properties than the straight PF pad. The good performance is partially due to the hybrid fibers in the friction materials building random micro-networks, such as aggregating together and fiber entanglement, which can fully utilize the performance of these fibers, and the interaction with the modified matrix binder is quite strong, providing the high mechanical strength and the excellent resistance to the formation of cracks and the extension of cracks in the materials.

On the other hand, a large number of studies (11, 14, 17, 18) have been carried out concerning PF degradation. In an inert atmosphere, structural change of the PF is suggested to occur in three steps. In the first step (< 450\(^\circ\)C), the carbonaceous material of the resins contains structures such as diphenylether, i.e., benzene nuclei joined with methylene bridges. In the second step (450–700\(^\circ\)C), the benzene nuclei directly combine with each other by breaking of \(-\text{CH}_2-\) and \(-\text{O-}\) bridges forming biphenyl groups. In the third step (700–1000\(^\circ\)C), condensation reaction of the aromatic rings occurs to form polycyclic aromatic systems. In an air atmosphere, oxidation is caused and the structural changes start at lower temperature (about 300\(^\circ\)C).

Figures 8 and 9 showed that the degradation reaction of the modified PF resin was different from that of the straight PF resin. At 410\(^\circ\)C (initial decomposition temperature of the modified PF), a large amount of methylene bridges were detected by FTIR and \(^{13}\)C-NMR, suggesting that a three dimensional network with high crosslinking density was formed in the modified resin. Although the highest measured-temperature of the brake disc during the braking tests with the modified PF pad was 206\(^\circ\)C, it is reasonable to believe that the local temperature at the pad-disc interface was much higher than this temperature because of the flash temperatures at the contacting micro-asperities.

From the test and analysis results, it can be concluded that the improved overall properties of the modified PF pad are also due to the chemical structure changes of the modified resin during braking. The breakage of the modified PF
Braking Performance of a New Organic Brake Pad

chains under the frictional heat and the sequential formation of the three-dimensional network structure with high crosslinking density played an important role in improving the braking performance of the modified PF pad. The friction film tribochemically formed on the pad surface was heat-resistant and anti-wear. A polymer matrix that can form a stable and anti-wear tribochemical film during dynamic braking process is more important for brake friction materials than the anti-heat ability of the matrix binder.

4 Conclusions

An organic brake pad based on a modified PF binder and reinforced with hybrid fibers was prepared and investigated. For comparison, a conventional brake pad based on a straight PF binder was also studied. The modified PF pad exhibited higher impact strength, and better braking performance and wear resistance than the straight PF pad.

It is concluded that the better overall properties of the modified PF pad resulted from the chemical structure changes of the modified resin binder during braking and the reinforcing effects of the hybrid fibers. The breakage of the modified PF chains under the frictional heat and the formation of a three-dimensional network structure with high crosslinking density played an important role in improving the braking performance of the modified PF pad. The interactions between the modified matrix binder and the other ingredients were quite strong, and thus the reinforcing material of the hybrid-fibers was effective for increasing the anti-impact properties of the friction material. On the other hand, the friction film tribochemically formed on the pad surface was heat-resistant and wear resistant. A polymer matrix that can form stable and anti-wear films during dynamic braking process is more important for brake friction materials than the anti-heat ability of the matrix binder.

Acknowledgments

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