Preparation and characterization of brake linings from modified tannin-phenol formaldehyde resin and asbestos-free fillers

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Because of the inevitable decrease in petroleum reserves and unstable political situation in the Middle East, many scientists have studied the production of phenol-based products from renewable resources [1]. So far, various attempts have been made to replace phenol, in the production of phenol-formaldehyde-type polymers, with natural polymer [1–14].

Tannins were found to be the best replacement for phenol in the production of phenol-formaldehyde-type adhesive due to its higher reactivity to formaldehyde in comparison to the others. Particularly, tannins extracted from the bark of the black wattle tree (*Acacia mollissima*) and the wood of quebracho (*Shinopsis* spp.) were commercialized in New Zealand, Australia and South Africa for making hot- and cold-setting-type adhesives for wood industries [1, 2, 12]. However, to our knowledge, no study has been done on the usage of tannin/modified tannin as replacement for phenol in the production of brake linings.

Moreover, asbestos (which has been commonly used as reinforcement material in the production of automotive friction materials) has been found to be a risk-effective material due to increasing health and environmental consciousness concerning lung cancer and gastrointestinal cancer [15–19]. Therefore, it is compulsory to find out more adequate replacement for asbestos in producing brake linings as well [20–22].

The aim of this study was to characterize the new brake linings prepared with a new binder called modified tannin-phenol formaldehyde resin (MTPFR) and non-asbestos filler such as glass fiber, Kevlar aramid and stone wool as well as others and compare them to ones prepared with synthetic novolac resin (SNR).

The brake linings were formulated with various ingredients as shown in Table I. SNR so-called “novolac”, used as commercial matrix mixed with hexamine (6%, based on weight of novolac), was provided by Yigit Plastic Co., Istanbul, Turkey. Tannin from the bark of the black wattle (*Acacia mollissima* L.) was purchased from ALTIN leather Company established in K. Maras City, Turkey. Some characteristics of the fillers used here are summarized in Table I. Carbon black was used as a coloring agent. Also, cashew nut shell and graphite powders were used as friction modifier and solid lubricant, respectively.

A mixture of oven-dried tannins from the bark of black wattle (*Acacia mollissima* L.), phenol (phenol:tannin ratio 2:1, w/w) and H_2SO_4 (5%, based on wood phenol by weight) was first heated under atmospheric pressure at 140 °C for 1 hr. The resulting solution was then allowed to cool to about 100 °C. The reaction mixture was dissolved with 1,4-dioxane and filtered with a glass-fiber filter (Toyo GA-100). The resulting dioxane-soluble parts were evaporated at 50 °C under vacuum in order to remove dioxane.

Subsequently, 37% aqueous formaldehyde (100 parts), distilled water (50 parts) and 50% NaOH (12.9 parts) were added to the dioxane-soluble parts (100 parts). This mixture was heated at 75 °C for 1 hr under reflux with a constant stirring. Thus, MTPFR was obtained. The MTPFR was mixed with

TABLE I Typical characteristics of the filler used in this study

Filler	Density (g cm^{-3})	Size (mm)	Source
Glass fiber	2.540	Diameter: 10–15 μm; Length: 3–4.75 mm	Izocam Trade and Ind. Inc., Turkey
Kevlar	1.440	Diameter: 11.9 μm	As Balata Inc.
Stone wool	0.105	8–20 μm	Izocam Trade and Ind. Inc., Turkey
Graphite	2.1	8 μm	As Balata Inc., Turkey
Cashew friction dust	–	150 μm	As Balata Inc., Turkey
Silica carbide (SiC)	2.900	0–32 μm	As Balata Inc., Turkey

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TABLE II Composition of non-asbestos fibers-reinforced brake linings

Components	Percentages					
	C25	C25B	K25	K25B	T25	T25B
Glass fiber	25	25	–	–	–	–
Kevlar aramid	–	–	25	25	–	–
Stone wool	–	–	–	–	25	25
SNR (Novolac)	21	11	21	11	21	11
MTPFR	–	10	–	10	–	10
Silica carbide (SiC)	3	3	3	3	3	3
Graphite	7	7	7	7	7	7
Cashew nut shell powder	11	11	11	11	11	11
Other fillers	33	33	33	33	33	33

TABLE III Friction coefficients of the friction materials manufactured with various ingredients versus temperature at the pressure of 3000 kPa

Sample	Temperature (°C)									
	50	100	150	200	250	300	350	400	SD[a]	Mean
C25	0.31	0.38	0.44	0.48	0.50	0.52	0.48	0.44	0.069	0.444
C25B	0.33	0.41	0.45	0.48	0.52	0.53	0.49	0.46	0.065	0.459
K25	0.32	0.38	0.46	0.48	0.51	0.51	0.50	0.45	0.068	0.451
K25B	0.34	0.41	0.44	0.49	0.50	0.51	0.51	0.49	0.061	0.461
T25	0.34	0.37	0.42	0.50	0.52	0.54	0.49	0.45	0.072	0.454
T25B	0.33	0.39	0.45	0.47	0.50	0.52	0.51	0.49	0.066	0.458

[a] Standard deviation.

TABLE IV Density, Brinell hardness and specific wear rate of the brake linings from MTPFR and SNR

Sample	Density (gr cm^{-3})	Brinell hardness	Specific wear rate $\times 10^8$ (cm^3 Nm^{-1})
C25	1.919	23	10.2
C25B	2.019	22	8.97
K25	2.118	27	5.79
K25B	2.145	29	5.43
T25	2.214	36	9.23
T25B	2.219	43	8.17

asbestos-free fillers and other friction modifiers listed in Table II to make brake linings.

For preparing brake lining samples, various components of the formulations (see Table II) were mixed. A cold gauge pressure of 0.1 MPa was first used to prevent the leakage of material from the mould before gelation of the resin. And then, the mixture obtained in each case was loaded into a mould and hot pressed at about 170 °C under a gauge pressure of 0.15 MPa for 15 min. The test specimens were cut from molded composite plates.

Friction and wear tests were performed on a friction-material-testing machine designed in our laboratory, which consisted of a cast-iron disk with a nominal diameter of 280 mm. The machine was equipped with an air cooler, and an electric heater to control the bulk disk temperature. The test specimen was fixed on the disk through a mechanic arrangement. This was attained by subjecting the specimens to run at a counter face speed of 6 m s^{-1} and load of 3000 kPa as described in Turkish standard (TS) 9076. Frictional force was measured at the end of each application, and friction coefficient was then calculated by following the procedure described in TS 555. Moreover, at the beginning and end of the wear test, the weight of the specimen was measured and the corresponding weight loss noted. Subsequently, specific wear rate and wear amount per unit were determined by following TS 555.

Furthermore, the resistances of the brake linings against distilled water, salty water, engine oil and brake oil were determined by following procedures in TS 9075. In these physical tests, percent weight gain and thickness swelling were determined. Also, Brinell harnesses were determined on a Universal testing machine (Officine Galileo) according to TS 139. Eventually, the microstructures of some brake specimens subjected to friction and wear test were analyzed by a using scanning electron microscope (SEM; LEO 440).

As shown in Table III, friction coefficients show a slight increase with increase in temperature from 50 to 300 °C. There is a subsequent decrease with further increments. Both types of brake linings filled with three different asbestos-free fillers used here show similar friction coefficients at a pressure of 3000 kPa. The friction coefficients calculated for both types of brake linings are found to exceed the requirements described in TS 555 regarding the friction coefficient levels (0.37–0.42) of brake linings. However, the Kevlar filler gives somewhat higher friction coefficient when compared to other fillers.

It is evident from Table IV that the Brinell hardness and densities of brake linings prepared from MTPFR were slightly higher than those of prepared from SNR for the two types of fillers studied here (Kevlar aramid and stone wood). It is also interesting to note from the same table that the values of specific wear determined for the brake linings from MTPF resin are clearly greater than those from SNR. Furthermore, the brake linings containing Kevlar aramid fiber exhibit lower wear rate more than these containing the other fibers used.

It is clear from Table V that all the weight gain and thickness swelling values found for the MTPFR-based brake linings are slightly lower than those for SNR-based linings. MTPF resin based brake linings filled with Kevlar aramid show the least percent weight gain

TABLE V Percent weight gain and thickness swelling of the friction materials made from MTPFR and SNR

Sample	Distilled water		Engine oil		Brake oil		Salty water	
	WG (%)	TS (%)	WG (%)	TS (%)	WG (%)	TS (%)	WG (%)	TS (%)
C25	3.326	0.283	2.986	0.196	3.234	0.349	1.957	0.495
C25B	3.118	0.208	2.245	0.256	2.981	0.296	1.893	0.201
K25	1.626	0.451	2.029	0.327	3.238	0.285	1.538	0.477
K25B	1.247	0.405	1.986	0.289	3.006	0.258	1.301	0.226
T25	2.015	0.360	2.628	0.217	3.148	0.276	2.736	0.436
T25B	1.958	0.335	2.544	0.206	3.013	0.213	2.596	0.364

[1] Weight gain.

[2] Thickness swelling.

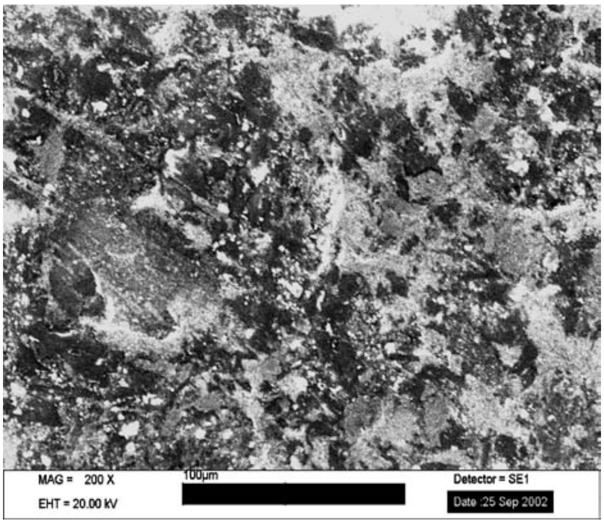

Figure 1 SEM photograph of surface of MTPFR-based brake linings before wearing.

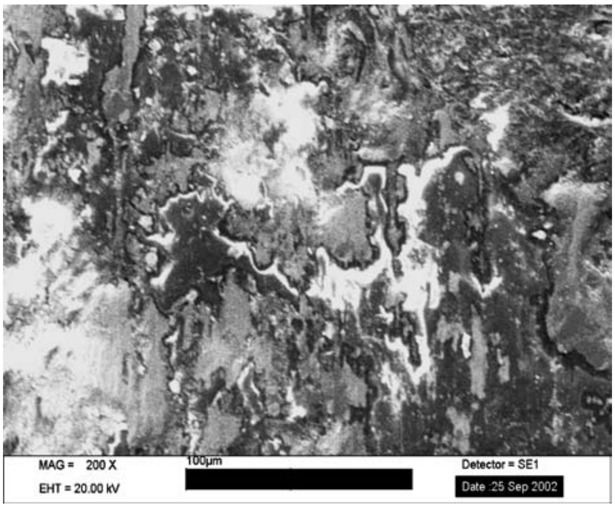

Figure 2 SEM photograph of surface of MTPFR-based brake linings after wearing.

and thickness swelling of the four types of liquids, followed by stone wool and glass-fiber fillers in comparison with the brake linings made from SNR and the same fillers. The MTPFR-based brake linings gave smaller percent weight gain and thickness swelling values when they were soaked in the four types of liquids shown in Table V.

If one compares the unworn surface (Fig. 1) to the worn one (Fig. 2), the latter is of lighter color, and the Kevlar fiber filler remains almost undamaged. Also, no crack or significant damage was observed after a friction test at a maximum temperature of 400 °C at a speed of 6 m s^{-1} for a total time of 1 hr. Furthermore, the light-colored phase can be attributed to the modified friction metal content. It is also interesting to report that no debonding and pullout were found after the friction test.

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