

Control of Gaseous Emission During the Curing of Novolac Phenolic Resin in Friction Materials Production: Production Cycle, Physical Properties and Tribological Properties Improvements

Diego Adolfo Santamaria Razo
ITT Italia Srl

Diego Pellerej
ITT Corporation

ABSTRACT

Thermosetting resins such as Novolac phenolic resin are commonly used as binders in the production of friction materials. It is known that the reactions between the Novolac resin and hexamethylenetetramine (used as catalyst) produce volatile compounds as ammonia. Emitted gases give rise to pores in the friction material. This forces producers to create specific pressure-no pressure cycles to avoid cracking of the material during production.

The contribution of this paper deals with the reduction of volatile compounds emission during curing by modifying the composition of the mix formula using two approaches:

The first one consists in adding to the formulation suitable fillers that are able to absorb volatile compounds and not to release them for temperatures up to 200°C. These substances must have high surface area and acidic properties to effectively absorb ammonia and other volatile compound and shall be chosen between commercial fillers already used in the formulation of brake pad to minimize the effect of their introduction in the production cycle and cost. The following materials were investigated: a zeolite (HY) and a clay (montmorillonite) that are known to fulfill the above-described requirements.

The second way for volatile removal consists in modifying the surface properties of fillers already present in the formulation of brake pads by chemical functionalization, a technique that is widely used to design adsorbents suitable for chosen substances. Carbon was chosen to be functionalized, that is present in brake pad formulation as graphite and carbon black. In particular active carbon, that is already known for its adsorbent properties, has been functionalized with sulphonic groups.

Both approaches were then compared to evaluate gas removal by means of thermogravimetric analysis. Adsorbent powders were then introduced in the friction lining formulation. A reference material was produced and compared to materials produced with the use of the best adsorbent raw materials. Production cycle and tribological properties were then evaluated and compared.

A suitable technique to produce adsorbent materials has been evaluated. It has been then used as a method to control gaseous emissions during the curing of Novolac phenolic resins with positive results. An important improvement in the production process of friction linings has been developed. Industrial development has to be evaluated and its impact on production costs has to be studied. Low cost functionalization has to be evaluated with raw materials producers.

CITATION: Santamaria Razo, D. and Pellerej, D., "Control of Gaseous Emission During the Curing of Novolac Phenolic Resin in Friction Materials Production: Production Cycle, Physical Properties and Tribological Properties Improvements," *SAE Int. J. Mater. Manf.* 7(1):2014, doi:10.4271/2013-01-2058.

INTRODUCTION

Agglomerates have been developed to be used as friction linings since a very long time (1, 2), it is the best way to find a compromise between a relatively high friction coefficient and a good wear resistance (3, 4). Suitable tribological characteristics are to be found through formulation of many different raw materials. All available ingredients can be categorized in different groups: polymer matrix or binder, reinforcing materials, friction modifiers and fillers (5, 6). Many efforts and extensive researches have been done to understand the influence of each group in the friction material behavior (7, 8, 9, 10, 11, 12). It is complex to understand the role of each ingredient without taking into account the interaction they have between all of them.

Novolac phenolic resins (PR) are the main polymeric matrix used in the friction material market (13, 14, 15, 16), even if several modified resins are available to improve heat and wear resistance. Novolac PR and hexamethylenetetramine (HMTA used as catalyst) generate gaseous emissions during the polymer curing. Those gases pass through the material and give rise to pores. Pores influence friction material physical characteristics and thus tribological properties, conditioning the material production process. Gas emission forces producers to create specific pressure-no pressure cycles to avoid cracking of the material during production and to control tribological properties (17). They are introduced in the production process in order to allow gas to exit the stamp during PR curing.

Gas emission cannot be avoided, it is an obligatory waste of the PR chemical endurance. Gas absorbance is a suitable technique to reduce the consequences of vapors presence and it can be achieved by using the surface area (empty space) available on the fillers surface. On the one hand there are high surface area ingredients (as zeolites and montmorillonite) and on the other there is the possibility of modifying the chemical characteristics of some fillers surfaces. This modification is called functionalization and it can be used to obtain absorbent fillers. Absorbent fillers can be obtained through the surface modification of fillers already present in the formulation of brakes by chemical functionalization, a technique that is widely used to design absorbents suitable for chosen substances. It has been proved that functionalized CNT can be used for such an objective (18), anyhow those materials are quite far away to be used at industrial level and more suitable fillers have to be evaluated.

Active carbons were chosen to be used as volatile adsorbent thanks to their high surface area and the possibility to be functionalized with sulphonic acidic groups, it is done with the aim of make them suitable for removal of volatile emitted during the curing (19). Furthermore carbon is already present in brake pad formulation as graphite and carbon black.

MATERIALS AND METHODS

Phenolic resin and fillers were pyrolysed in controlled conditions in a Thermogravimetric (TG) Mettler Toledo TGA/SDTA851e equipment in the range 50-1000°C at the heating rate of 10°C/min in argon flow. TGA curves are reported up to 300°C as it is intended to be the working temperature of the gasses trapping fillers.

The HY zeolite (referred to hereafter as HY) with a Si/Al ratio of 10.2 and a surface area of 730 m²/g was purchased at Zeolyst.

Montmorillonite K-10 (referred to hereafter as Mont) with a surface area of 250 m²/g was purchased at Sigma-Aldrich

Active Carbon (referred to hereafter as AC) was purchased at AcqueNYMCOspa.

Sulphonated Active Carbon (referred to hereafter as AC-SO₃) was prepared as described in literature (20). In a typical synthesis, AC (5g) was added to fuming H₂SO₄ (150 mL) and soaked at 120°C for 18 hours under nitrogen flow. AC-SO₃ was separated by centrifugation and washed with boiling distilled water until the pH is neutral. The degree of functionalization determined by TGA analysis is 49 mmol of SO₃H per gram of dry carbon.

Graphite was purchased at Durrans.

Surface areas measurement of AC, AC-SO₃ and graphite are in progress.

Adsorbent materials and the resin were mixed in a pestle in different ratios as reported in Table 1.

Table 1. composition of resin-adsorbent mixtures.

SAMPLE NAME	COMPOSITION (in volume)
PR+G_1:1	Phenolic Resin: Graphite=1:1
PR+HY_1:1	Phenolic Resin:Zeolite HY=1:1
PR+HY_2:1	Phenolic Resin:Zeolite HY=2:1
PR+Mont_1:1	Phenolic Resin:Montmorillonite=1:1
PR+AC	Phenolic Resin: Active Carbon=1:1
PR+AC-SO ₃	Phenolic Resin: Sulfated Active Carbon=1:1

Evaluation of the effect of absorbent materials on friction linings has been done by means of AK-Master Efficiency test following the TS 4-16-114 AK-Master procedure; in [Appendix 1](#) a brief explanation of the different sections of the procedure is reported.

A floating caliper with a piston diameter of 22.9 mm has been used, and the gray cast iron rotor dimensions were 256 × 22 mm; the effective radius was 104 mm, dynamometric roll

radius was 308 mm, and the inertia used for dyno-test evaluation was 65 Kg m^2 .

The characteristics of the brake pad used and its production parameters (reference production parameters) are described in [table 2](#).

Table 2. Friction material general characteristics and general description of the reference production process.

Surface area [cm ^{2}]	46.6
Thickness [mm]	18.5
Pressure [MPa]	16
Pressing time [min]	8
Pressure- no pressure cycles [number]	6
Pressing temperature [°C]	160
Static oven temperature [°C]	200
Static oven time [min]	120

A typical commercial formula has been used as reference (Material A), its composition and the composition of the modified materials are described in [Table 3](#).

Table 3. Reference friction material A and modified materials with absorbent fillers.

Raw material	A (Vol %)	E (Vol %)	F (Vol %)	G (% Vol)
Phenolic resin	20	20	20	20
Aramid Fibre	5	5	5	5
Inorganic fibre	5	5	5	5
Graphite	10	0	0	0
Zirconium oxide	20	20	20	20
Vermiculite	15	15	15	15
Sulphides	5	5	5	5
Abrasives	20	20	20	20
HY Zeolite	0	10	10	10

Porosity and density measurements were carried out with the use of a Pentapyc 5200e Gas Pycnometer with a sample of 4.25 cm ^{3} .

The production process describes a pressure time that is composed by different pressure/no pressure cycles (PNPC) to allow gasses to exit the mould. [Table 4](#) describes exactly the PNPC used for this development. The general [formula 1](#) describes a PNPC cycle.

$$C_n(P+N_p)+x=T_p$$

Formula 1

where C_n is the number of PNPC, P is the time under pressure, N_p is the time with no pressure, x is the time that after degassing the mould will apply pressure again and T_p is the total pressure time in minutes of the PNPC.

Table 4. Reference production cycle for friction material and improved production cycle (no degassing process).

Cycle	Reference	Improved	Reduced
Pressure time [min]	8 min	8 min	6 min
Formula	$6(10''+13'')+x''=8'$	480	360
Time under pressure [sec]	$6*10=60$	480	360
Time with no pressure [sec]	$6*13=78$	0	0
x value. Under pressure [sec]	$480-78-60=342$	0	0
Sample	A, E	F	G

RESULTS AND DISCUSSIONS

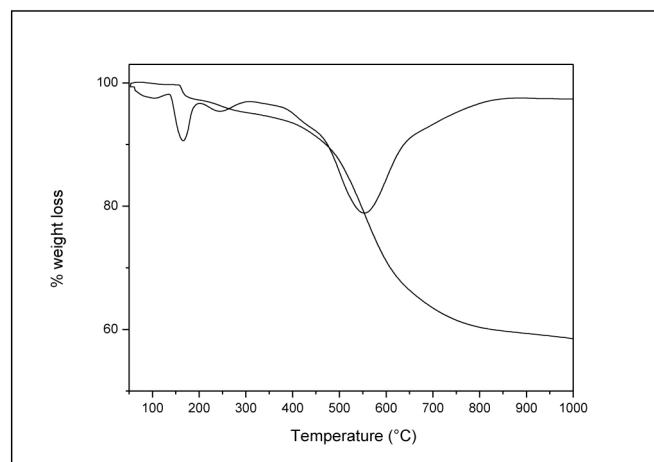


Figure 1. TG and first derivative traces of the phenolic resin

[Figure 1](#) shows the TG trace and the first derivative of the phenolic resin heated between 50 and 1000°C. As clearly discernible in the derivative, there are two principal weight losses during the heating process: the first one (135-190°C) is due to the curing of the phenolic resins; the second weight loss starts beyond 300°C and arise from the thermal degradation of the polymer that continue throughout the thermal heating process.

TGA traces and first derivative of PR-HY_2:1 compared with that of PR-G_1:1 are reported in [Figure 2](#). PR-HY_1:1 sample was not shown since the large amount of water released by the Zeolite at about 100°C does not allow a correct evaluation of weight loss in the region of interest.