QI Analysis by Microwave Absorption

Morten Sørlie and Knut Tørklep
Elkem a/s, R&D Center, N-4620 VÅGSBYGD, Norway

Introduction

The quality of coal-tar binder pitches is greatly influenced by their content of carbonaceous particulate matter; i.e. primary quinoline insolubles and mesophase spherolites |1|. A correct estimate of the amount of these phases in binder pitches has always been a problem for a pitch end user, as some mesophase may dissolve in quinoline, and the goodness of the optical method is limited by the resolution of the microscope. In thermally treated pitches the primary QI content has traditionally been an information reserved the pitch distillers, knowing the amount of primary QI in the parent tar and the pitch yield.

While using a microwave unit as a rapid way of heating green anode paste for viscosity measurements, we observed that pitch specimens also were heated when exposed to the radiation, although to a much smaller degree. This led to the present investigation of whether the dissipation of microwave energy can be used as a quick method for directly determining the amount of primary QI in pitch. To our knowledge no direct method for determining the primary QI content in a pitch also containing mesophase has been reported until now.

Theory

Materials can reflect, absorb, or be transparent to microwave radiation. The main absorption mechanisms are dipolar, Maxwell-Wagner polarization (also termed space charge or interfacial polarization), and ohmic losses. Dipolar losses are due to molecules with permanent dipoles, while Maxwell-Wagner polarization arises from a charge build-up in interfaces between components in a heterogenous system. The power (Δp) dissipated in a volume of material is described by the expression

$$\Delta p = kfE^2\epsilon'\tan\delta \qquad (1)$$

where k is a constant, f the frequency, E the electric field strength, ϵ' the dielectric constant and $\tan\delta$ the loss tangent. The absorbed power in a sample may be measured directly by calorimetry, or the loss factor, $\epsilon'\tan\delta$, obtained from separate measurements in a suitable resonator (not reproduced here). Primary QI particles in pitch can be expected to absorb microwave energy by ohmic or Maxwell-Wagner losses. These tar vapour pyrolysis particles bear some resemblance to soot or carbon black. It is well known from the rubber vulcanization industry that non-polar latexes can be efficiently cured in microwave generators if certain types of carbon black are added |2,3|.

Experimental

A Precision Microwave unit from GCA Corporation, operating at a frequency of 2450 MHz, was used in the present work. Energy absorption in pitch samples was measured in a simple differential calorimeter constructed from two dewars, a differential thermocouple (K type), a shaking machine, and an analogue voltmeter calibrated to be accurate to within 0.5 µV. Readings were made by connecting a recorder.

The EMF differential associated with the dissipated microwave energy was determined by extrapolating the recorder trace back to the point of adding the exposed sample. The absorbed power per unit weight, ΔP (in kW/kg), was calculated from the equation

$$\Delta P = (\Delta\mu V/(40TG))(1.15G+4.18H) \qquad (2)$$

where $\Delta\mu V$ is the EMF differential, T the time of exposure (s), G sample weight (g), and H the amount of water (g) in the dewar containing the exposed sample. The constants 40, 1.15, and 4.18 are thermocouple temperature coefficient (µV/°C), and heat capacities of pitch and water (J/g°C), respectively.

Absorption of microwaves is primarily volume-dependent, not weight-dependent, but as the variation in pitch density was within 3 %, the uncertainty introduced by choosing the more practical weight unit was small.

Results

The absorbed energy increases with increased exposure to microwaves for two "as received" binder pitches (A, B) and one pitch (C) with some of its own QI added (Figure 1), thereby increasing the calculated content of primary QI and mesophase to approximately 22 % and 5 %, respectively. The relative exposure is the product of the exposure time and the fraction of the maximum power output of the unit. Heat losses to surroundings and other time-related errors appeared negligible.

Absorbed power as function of total QI for three pitches with re-added QI is shown in Figure 2. The "as received" pitches were the same as in Figure 1.

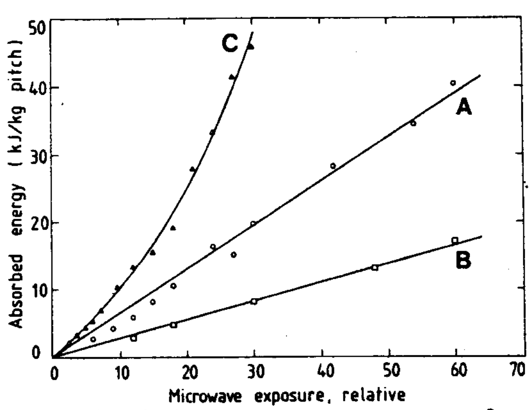

Figure 1. Absorbed microwave energy as a function of microwave exposure.

Discussion

The curves in Figure 1 are least square polynomials with no constant terms, i.e. they are forced to pass through the origin. Their slopes equal the power absorbed (kW/kg pitch). There is no significant deviation from linearity for the two "as received" pitches (A, B) within the experimental error. Visual inspection of these two curves indicates, however, a slight non-linearity at low exposures. Absorption in the C pitch with artificially increased QI content is clearly non-linear. Variations in the microwave load will not give rise to systematic errors for the pure pitches, except possibly at very low exposures. The reason for the non-linear response in the pitch with re-added QI is unknown, but is of no importance for the purpose of determining primary QI in electrode binders.

The most direct evidence of mesophase transparency to microwaves was furnished by a petrol pitch measurement. The "as received" pitch was almost free of particulate matter. Mesophase formation by heat treatment gave QI contents up to 75 %, but the pitch continued to show complete transparency.

Evidence of pitch matrix transparency is more indirect. The curves in Figure 2 have two significant properties; they are linear and they extrapolate to intercept the ordinate at zero or negative values. If the pitch matrix were not transparent to microwaves, intercepts must have been positive. The reason for negative intercepts is probably mesophase solubility in quinoline. An estimate of this solubility can be made from the non-linearity at low QI contents. The curves will approach linearity asymptotically as the mesophase of the original pitch is "diluted" with extracted mesophase from the same pitch. In principle, the slope of the linear region yields the QI composition, which together with the slope at the origin provides the mesophase solubility. As a first approximation of this slope, we used the secant from the origin to the first point on the curves. Assuming that the QI fraction of pitch A was free from mesophase, the amounts of mesophase in absolute percent dissolved during the quinoline extraction was calculated to 1.5, 4.4, and 2.8 % for pitches A, B, and C, respectively.

The linearity of the curves in Figure 2 shows that microwaves are absorbed by pitch in direct proportion to the primary QI content. The primary QI percentage, pQI, can thus be calculated from the equation

$$pQI = f \cdot \Delta P \qquad (3)$$

where ΔP is the power absorption, and f a constant. If this method is to be absolute, f must be obtained from measurements on a pitch of known composition. Alternatively, f may be calculated from the expression

$$f = 100(QI - mQI)/\Delta P \qquad (4)$$

in which mQI is the mesophase content. In this case, f will be subject to the combined errors of the QI determination and the optical mesophase analysis.

Figure 3 is a scattergram that compares primary QI contents found by the microwave method and those obtained by subtracting optically determined mesophase from the QI content (optical analysis from two laboratories). Two pitches show extreme deviation from the diagonal in Figure 3, i.e. microwaves have been absorbed by the isotropic pitch matrix. After examining 18 binder pitches from seven producers we estimate the accuracy of the method in primary QI determination to be 1 % absolute.

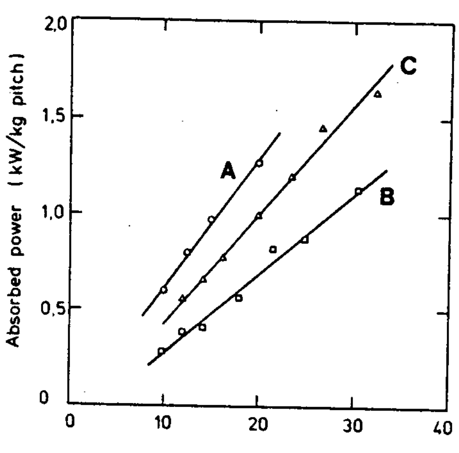

Figure 2. Absorbed microwave power as a function of QI. The QI content has been artificially enriched by re-adding QI to the original pitch.

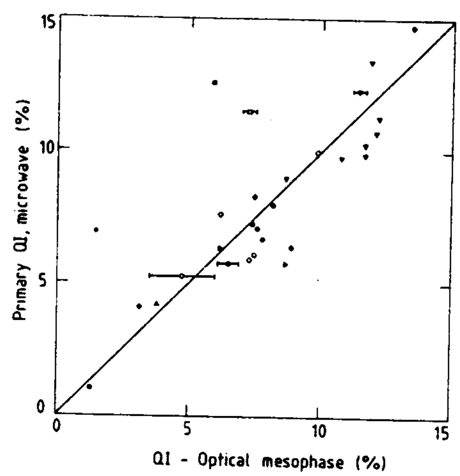

Figure 3. Scattergram showing primary QI measured by microwave absorption compared to values found from the difference between QI and optical mesophase.

Conclusion

The primary QI content in anode binder pitches can be determined with an accuracy of 1 absolute percent by the microwave absorption technique.

The pitch matrix will not absorb microwaves unless being of inferior quality. Combination of microwave, optical and QI determination yields additional and unambigous information on pitch properties.

Mesophase can be estimated as the difference between QI and microwave determined primary QI, thus providing a simple alternative to microscopic analysis.

References

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