

# Electrical and Thermal Properties of Kraft Paper Reinforced with Montmorillonite

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**ABSTRACT:** Kraft-montmorillonite composites (K-MMT) with different weight percent of MMT and different stirring time were prepared successfully. The electrical properties and thermal stability of K-MMT were investigated. The breakdown voltage of K-MMT (9 wt % MMT, stirring 12 min) was increased to 60 kV/mm from 50.3 kV/mm of blank Kraft. With the increase of MMT, the relative permittivity had a corresponding reduction. The relative per-

mittivity was in the range of 2.29–2.42 at 50 Hz. The thermal stability of K-MMT, Kraft, and MMT were also measured. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** Kraft-montmorillonite; breakdown voltage; relative permittivity

## INTRODUCTION

Kraft (cellulose insulation) is widely used in oil-filled transformers from distribution to large power units.<sup>1,2</sup> Despite some of the shortcoming of cellulose, Kraft continues to be the insulation of choice in virtually all oil-filled transformers because of its low cost and reasonably good performance. With the electrical trade increased, transformer insulation has to be developed almost concurrently. The blend of mineral fillers to paper pulp, prior to the formation of the sheet, has been practiced since the eighth century.<sup>3</sup> The most notable improvement to Kraft is the invention for thermally upgraded Kraft. The process is to add stabilizers to Kraft, such as nitrogen-containing chemicals like dicyandiamide.<sup>4</sup> The thermal upgrading process raises the continuous operating temperature from 90°C to 110°C. Ferrito and Stegehuis<sup>5</sup> added high-temperature synthetic fibers to Kraft to raise the operating temperature and mechanical integrity of Kraft. As is known, the relative permittivity of Kraft is twice that of oil. If the relative permittivity can be reduced,

the insulating distance in transformers can be decreased because uniform electric field distributions can be made in paper-oil-paper composite insulation systems. The polymethylpentene fibers were added to Kraft to reduce the relative permittivity.<sup>6</sup> The high breakdown voltage is an extremely important property to transformer insulation. At present, the use of oil-immersed Kraft is the most common approach. Yet the study to improve the breakdown voltage by modifying Kraft independently is rarely reported.

Composite reinforced on a molecular scale is a relatively new class of materials in which an inorganic clay mineral is dispersed in an organic polymer. Depending on the organization of the silicate layers in a polymer matrix, two types of morphology can be achieved in nanocomposites: intercalated or exfoliated. Montmorillonite (MMT) as a mineral filler was used in epoxies,<sup>7–9</sup> polyethylene,<sup>10–16</sup> and polypropylene.<sup>17–19</sup> These new materials show dramatic improvements in physical properties and barrier properties.

In this article, MMT was added to Kraft for the first time. Kraft-MMT composite (K-MMT) materials were produced. The formation of K-MMT by changing content of MMT and stirring time of mixture (pulp and MMT) were explored. It was noteworthy that breakdown voltage of K-MMT composite had an obvious rise. And the relative permittivity expressed a beneficial down. Meanwhile, the thermal stability of K-MMT also had slight increase.

## EXPERIMENTAL

### Materials

The pulp board (softwood pulp, Taizhou Xinyuan Electrical Equipment, Taizhou/China) used for

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making paper handsheets was beaten to about 400 canadian standard freeness (CSF) in a Valley beater. A natural MMT (Nanomer I.31PS, Nanocer, Chicago/Illinois) clay surface modified with octadecylamine and silane coupling agent was used as the reinforcement filler. The oil for immersing handsheets was conventional transformer mineral oil (25#, Sichuan Chuanrun, Chengdu/China).

### Preparation

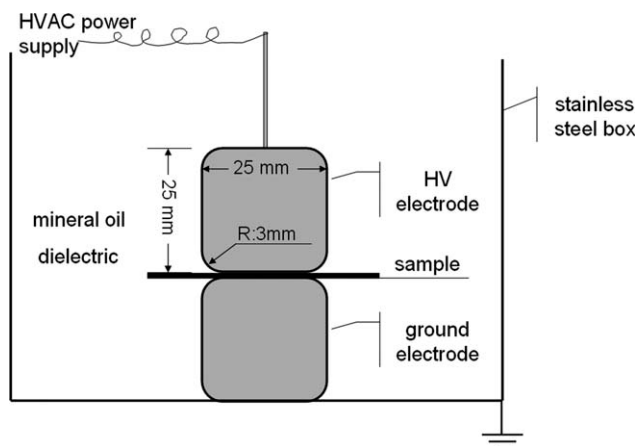
Firstly, the MMT was dissolved in absolute ethanol (1 : 100 wt %) and the slurry was homogenized by vigorous agitation with a magnetic stir bar for 10 min. Secondly, the pulp was diluted to 0.4 wt % in deionized water and various wt % MMT were added. The mixtures were stirred for 3 min at 3000 rpm in fiber disintegrate device and were used to prepare for handsheets. Thirdly, each wet handsheet was pressed at 15 MPa for 5 min at 80°C, and afterward dried at 105°C for 7 min under vacuum. Handsheets with a target basis weight of 120 g/m<sup>2</sup> were produced. Lastly, some handsheets were immersed in oil, with the following main steps: (1) handsheets were cut into 4 cm in diameter of the circle samples and put into different glass bottles according to different kinds of paper. (2) All samples were put into the vacuum chamber and were dried at 90°C for 48 h. After that, the temperature of the vacuum chamber was adjusted to 40°C. (3) The mineral oil at 40°C was infused into the glass bottles in the vacuum chamber to immerse samples for 24 h.

### Characterization

After the preparation of the handsheets, some samples were immersed in mineral oil to measure breakdown voltage, density, and relative permittivity. Some other samples that were not immersed in mineral oil were used to measure tensile strength, scanning electron microscope (SEM), thermal gravimetric analysis (TGA), and X ray diffraction (XRD).

Breakdown voltage was measured by self-made equipment according to IEC 60241-1:1998. Electrodes were made from copper. The diameters of high voltage (HV) electrode and ground electrode were both 25 mm. Oil was used as the dielectric in the surrounding of the equipment. The test power supply was HV alternating current power. Its boot speed was 500 V/s and frequency was 50 Hz. The breakdown voltage of each sample was measured seven times.

Mechanical property was measured by an electronic pull tester (AT-L-2, ANMT Instrument). The tensile speed was 10 mm/min. The length of the samples was 100 mm, and the width 15 mm. The tensile strength of each sample was measured 10 times.



**Figure 1** Diagram of the dielectric test electrode.

Relative permittivity under different frequencies ( $10^{-2}$ – $10^7$  Hz) at room temperature was measured by broadband dielectric spectroscopy equipment (Novocontrol Concept 80, GmbH, Germany). The oil in the surface of oil immersed paper was cleared before the samples were measured. The measuring electrodes were two copper plates with 4 cm diameter. The density of oil immersed paper was measured by Archimedes method.

Microstructure was carried out with a Rigaku X-ray generator (Cu K $\alpha$  radiation with  $\lambda = 1.5406$  Å) (Tokyo, Japan) at the room temperature and a field-emission scanning electron microscope (FEI Nova 400 nano SEM, Hongkong). The diffractograms were scanned in the  $2\theta$  range of 2.0°–90° at a rate of 2°/min. The sample was torn into two pieces and sputtered gold onto its internal surface before SEM observation.

The thermal stability was measured on a TA Instruments Q50, at a heating rate of 10°C/min. Each sample (8 mg) was heated up to 600°C under a flow of 50 mL/min nitrogen or oxygen. The content of MMT in the handsheet was evaluated by the final residue quality at 600°C.

## RESULTS AND DISCUSSION

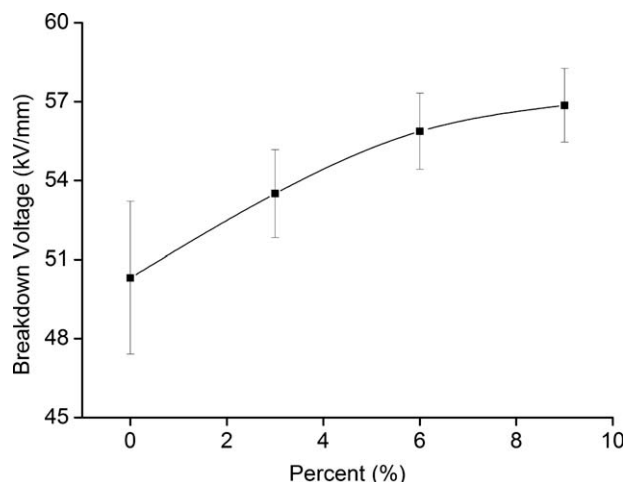
### Electrical properties

Breakdown voltage and relative permittivity with different contents of MMT

The content of MMT in handsheets were 3, 6, 9, and 0%, which were designated K-3%MMT, K-6%MMT, K-9%MMT, and Kraft, respectively.

The test power supply was 50 Hz high voltage alternating current (HVAC) supply. The output voltage ranges were 0–50 kV and the boot speed was 500 V/s. The test electrodes were self-made.

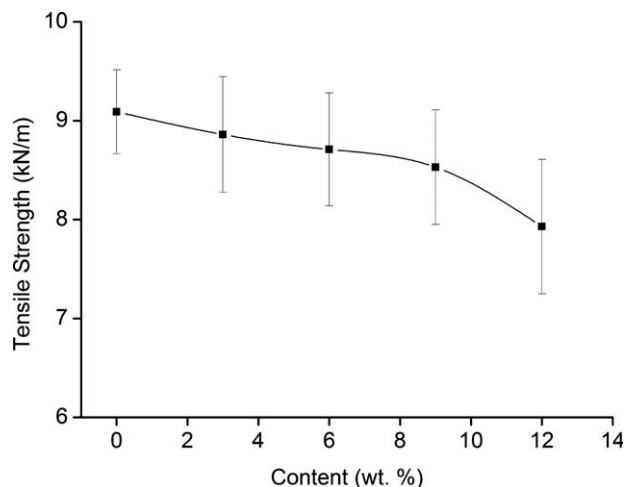
The diagram of electrodes for measuring breakdown voltage of handsheets is shown in Figure 1. The diameter and height of HV electrode and



**Figure 2** Effect of MMT content on the breakdown voltage of oil immersed handsheets mixed with MMT.

ground electrode were both 25 mm. A copper bar connected HV electrode with HVAC power. In this testing, mineral oil was used for dielectric in the stainless steel box.

Relations between breakdown voltage and different MMT contents in handsheets (immersed oil) are shown in Figure 2. The breakdown voltages of K-MMT were higher than that of Kraft obviously. Furthermore, with the MMT added, the breakdown voltages got much higher steadily. The breakdown voltage of Kraft was 50.3 kV/mm. And the breakdown voltage increased to 56.9 kV/mm when MMT content reached 9 wt %. However, the tensile strength of handsheet was reduced with the addition of MMT (Fig. 3). The main reason was the existence of weak interface between the fiber and MMT. The tensile strength of Kraft, K-3%MMT, K-6%MMT, K-9%MMT, and K-12%MMT was 9.09 kN/m, 8.86 kN/m, 8.71 kN/m, 8.53 kN/m, and 7.93 kN/m, respectively. The tensile strength had a sharp decline from K-9%MMT



**Figure 3** Effect of MMT content on the tensile strength of oil immersed handsheets mixed with MMT.

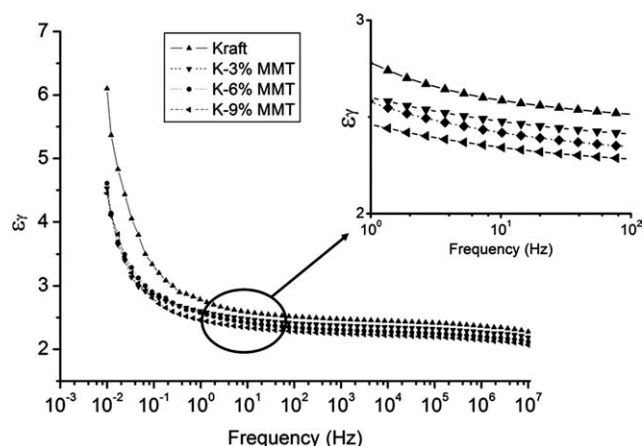
to K-12%MMT. Therefore, the maximum content (optimum content) was set at 9 wt % in this test.

The MMT was a kind of layered silicate with large specific surface area and its average particle size was micron scale. The current could run into MMT layers through the samples under HV. It indicated that MMT acted as a barrier to hinder the current in the samples and ultimately resulted in the rise of breakdown voltage.<sup>20</sup>

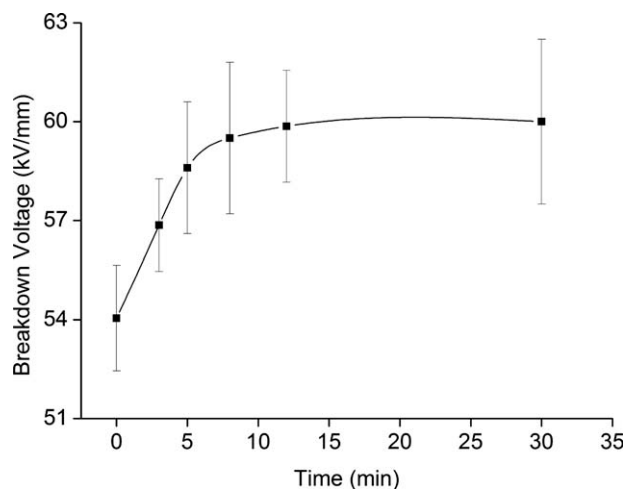
The frequency dependence of relative permittivity of the handsheets with the different mass fractions of MMT filler is shown in Figure 4. The variation trend of the four kinds of samples was similar. The changes of relative permittivity were gentle between 1 Hz to  $10^7$  Hz and severe under 1 Hz. Whereas the relative permittivity of K-MMT (K-3%MMT, K-6%MMT, K-9%MMT) composites were lower than that of Kraft in various frequencies. And at 50 Hz, the relative permittivities were from 2.53 down to 2.29–2.42. Furthermore, for K-MMT composites, the relative permittivity had a slight decrease with higher content of MMT. The existence of MMT improved the distance of fiber chains. And the oil (relative permittivity 2.2) content of handsheets would become large in the immersed handsheets for replacing some air voids. As known, the density represented amount of free volume; meanwhile, relative permittivity depended on the amount of free volume. The density of the oil immersed handsheets dropped to  $0.87 \text{ g/cm}^3$  (K-9% MMT) from  $0.88 \text{ g/cm}^3$  (Kraft). The experimental data definitely supported the result of relative permittivity test.

Breakdown voltage and relative permittivity with various stirring time

Breakdown voltages of K-9%MMT with different stirring time (about 0 min, 3 min, 5 min, 8 min,



**Figure 4** Variation of relative permittivity with different frequency and content of MMT in the oil immersed handsheets mixed with MMT.



**Figure 5** Effect of stirring time on the breakdown voltage of oil immersed handsheets mixed with MMT.

12 min, and 30 min at 3000 rpm separately) were investigated.

The breakdown voltage that rose violently at the initial stirring stage (before 8 min) is shown in Figure 5. But the rise became slower after 8 min and that could be ignored in 12 min later. It indicated that 12 min was the limit time for stirring it well and longer time has no effect for mixing.

Figure 6 shows the SEM images of the cross-sectional surface of K-MMT composites. The layer structures of the MMT could be observed clearly. In other words, the MMT was composed successfully into the kraft. Meanwhile, the MMT had a good dispersibility with the extension of mixing time.

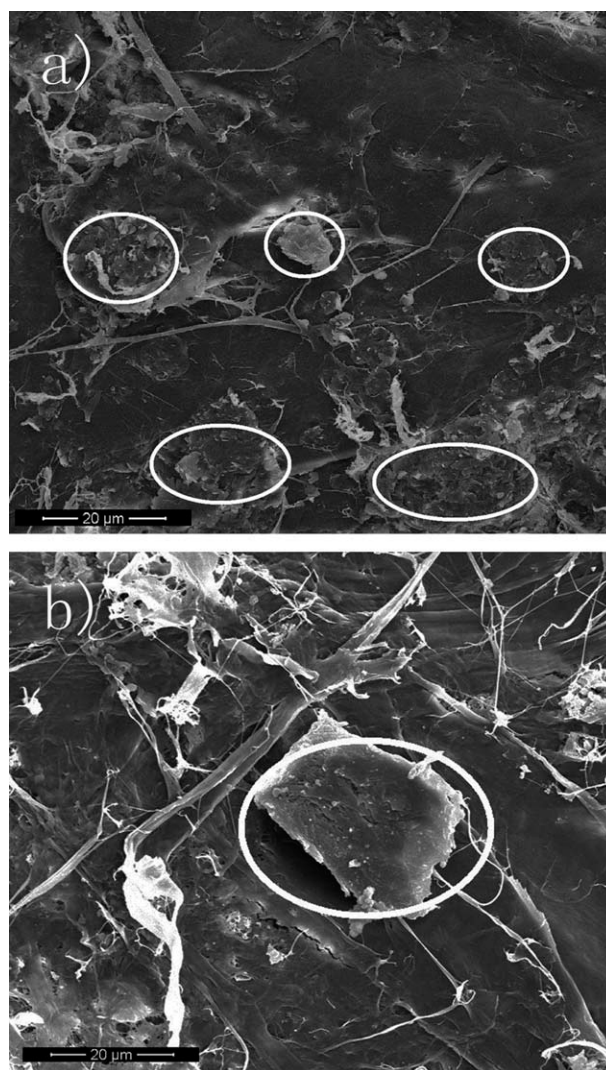
Figure 7 shows the peak at  $2\theta = 4.14^\circ$  is the only extra peak between K-9%MMT (stirring 12 min) and Kraft (spectrum a, b). So the presence of this peak resulted in mixed MMT in handsheets. The diffraction spectra of K-9%MMT (stirring 12 min), MMT (spectrum b, c) exhibited a peak at  $2\theta = 4.32^\circ$ ,  $2\theta = 4.14^\circ$  separately, corresponding to the mean interlayer spacing of the (001) plane for MMT. This also supported the result for the presence of MMT in the composites.

In a word, good dispersibility was a significant cause for the increase of breakdown voltage.

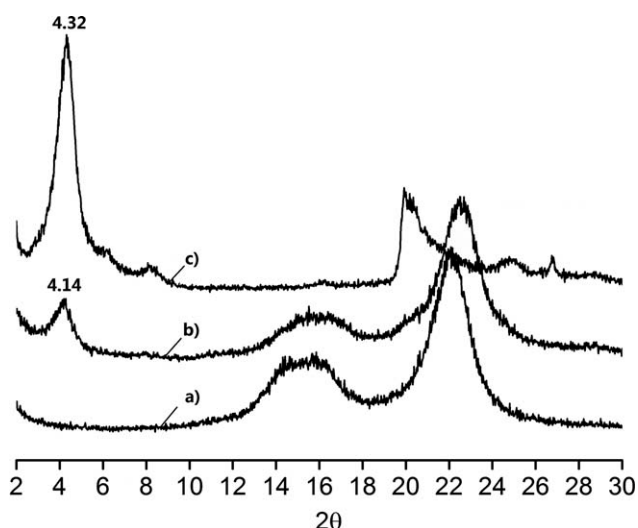
Variation of relative permittivity with different frequencies and stirring time for K-9%MMT is shown in Figure 8. With the change of stirring time, the relative permittivities were nearly the same for K-9%MMT at various frequencies. It indicated that the stirring time had a negligible influence on the relative permittivity. Therefore, the effect of mixing time on breakdown voltage was more important than on the relative permittivity.

### Thermal stability

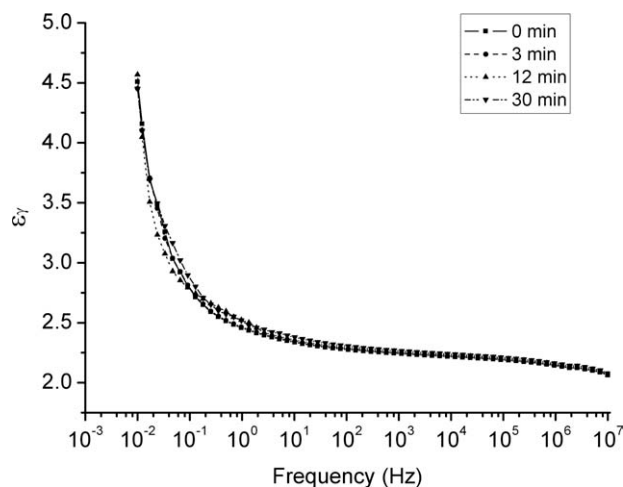
Thermal stability of Kraft, K-9%MMT (stirring 12 min), and MMT were investigated by thermogravi-



**Figure 6** SEM images of the cross-sectional surface of K-MMT composites, (a) stirring 0 min, (b) stirring 12 min.



**Figure 7** XRD spectra for (a) Kraft; (b) K-9%MMT (stirring 12 min); (c) MMT.

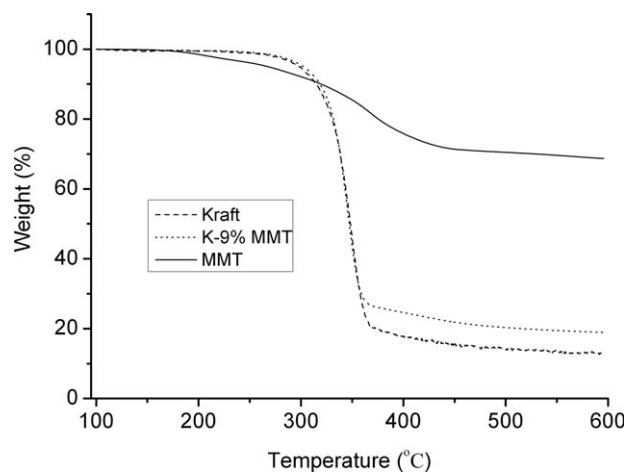


**Figure 8** Variation of relative permittivity with different frequency and stirring time for the oil immersed hand-sheets (K-9%MMT).

metry (TG) under nitrogen and oxygen flow. Figure 9 shows the TG traces recorded at 10°C/min in nitrogen for the above three samples. TG curves of Kraft and K-9%MMT (stirring 12 min) showed that the process occurred in a single weight-loss step. On the other hand, TG curve of MMT had three weight-loss steps (Table I).

The presence of MMT filler led to slight changes in thermograms. In particular, the degradation temperature of K-9% MMT (stirring 12 min) was higher than that of Kraft at 5% weight loss value. In the range of weight loss (30–90%), the two handsheet samples displayed a similar behavior and the influence of the MMT filler on the thermal stability was negligible. At higher temperatures an increased final residue was noticed for K-9%MMT (stirring 12 min), due to the presence of the inorganic filler (MMT) which had high final residue (Char yield<sub>600°C</sub>). The content of MMT in the handsheet could be calculated by the final residue (Char yield<sub>600°C</sub>).

The MMT was able to increase handsheet thermal stability, as the MMT could act as a barrier to hinder the diffusion of heat and migration of degraded vol-



**Figure 9** Thermal stability for Kraft paper, MMT, and their compound heated at 10°C/min in nitrogen.

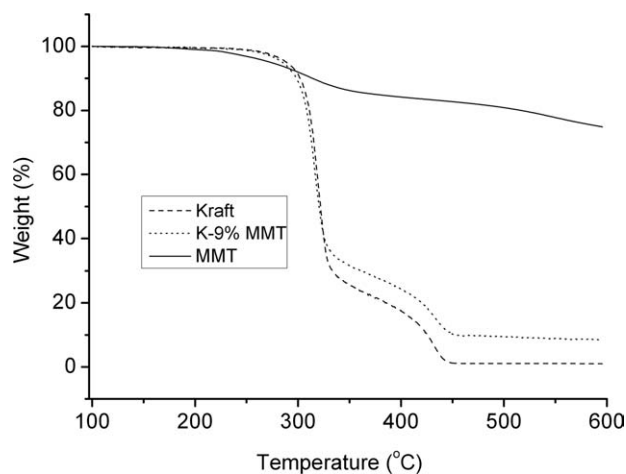
atiles, and then retarded the decomposition rate.<sup>21,22</sup> It had been observed that during Kraft thermal degradation, at moderate temperatures, dehydration processes<sup>23–25</sup> were predominant.

Superior thermal energies (>300°C) caused a radical mechanism operating in the process of depolymerization. In this stage, the presence of the MMT was not able to alter the thermal behavior for K-9%MMT (stirring 12 min).

A second decomposition step of Kraft and K-9%MMT (stirring 12 min) due to the oxidation of the char produced during the first weight loss stage is shown in Figure 10. Moreover, TG curve of MMT still had three weight loss steps as in nitrogen. The presence of MMT filler also improved the handsheet thermo-oxidative stability (Table I). But a decrease at 5% weight loss value was observed for K-9%MMT (stirring 12 min). The 5% weight loss temperature of MMT (273°C) was similar to that of Kraft (289°C). So the two processes of 5% weight loss (MMT, Kraft) exert an influence and the 5% weight loss temperature of K-9%MMT (stirring 12 min) was lower than that of Kraft. From the above, the thermal stability of K-9%MMT (stirring 12 min) had a slight increase in both nitrogen and oxygen atmosphere.

**TABLE I**  
Loss Temperature of 5 wt % ( $T_{5 \text{ wt } \%}$ ), Maximum Decomposition Rate Temperature ( $T_{\text{max}}$ ), and Char Yield at 600°C (Char yield<sub>600°C</sub>) for the Kraft Paper, MMT, and Their Compound

Sample	In nitrogen			In oxygen		
	$T_{5 \text{ wt } \%}$ (°C)	$T_{\text{max}}$ (°C)	Char yield <sub>600°C</sub> (%)	$T_{5 \text{ wt } \%}$ (°C)	$T_{\text{max}}$ (°C)	Char yield <sub>600°C</sub> (%)
Kraft	296	349	12.9	289	319/432	1
K-9% MMT	302	345	18.9	284	316/434	8.4
MMT	267	208/368/563	68.7	273	187/313/549	74.8



**Figure 10** Thermal stability for Kraft paper, MMT, and their compound heated at 10°C/min in oxygen.

### CONCLUSIONS

Kraft-MMT composites (K-MMT) with different wt % MMT and various stirring time were prepared successfully. Microstructure revealed that the MMT was composed successfully into the kraft and had a good dispersibility with the extension of mixing time.

The electrical property and thermal stability of K-MMT were investigated. The breakdown voltage of K-MMT (immersed oil) increased with the increase of MMT content. However, the tensile strength had a sharp decline supposing MMT content was more than 9 wt %. Therefore, the maximum content (optimum content) was set at 9 wt % in this test. It was also obvious that the breakdown voltage depended on stirring time. The breakdown voltage rise became slower after 8 min and that could be ignored in 12 min later. Finally, the breakdown voltage of K-MMT (9 wt % MMT, stirring 12 min) was increased to 60 kV/mm from 50.3 kV/mm of blank Kraft. The relative permittivity of composite decreased with the MMT content adding. But the effect of stirring time on relative permittivity can be ignored. Furthermore, the thermal stability of K-MMT (9 wt % MMT, stirring 12 min) was also improved.

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