

The Preparation and Physical Properties of UP/Montmorillonite Nanocomposite by UV Radiation Curing

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ABSTRACT: This article describes the preparation and properties of unsaturated polyester (UP)/montmorillonite (MMT) nanocomposite by UV radiation. Benzildimethylketal and 1-hydroxy cyclohexyl phenyl ketone (HCPK) as a photoinitiator in UP were photolyzed under nitrogen condition. Analysis of X-ray diffraction patterns of the composites shows that the interlayer spacing of MMT is substantially increased. The type and amount of photoinitiator affects the level of improvement in mechanical properties, and our results suggest that HCPK is a more efficient photoini-

tiator of UP curing reaction. The interaction between photoinitiators and MMT should be considered to acquire the reinforcement effect of the dispersed MMT nanolayers. The properties of nanocomposite are dependent upon the amount of MMT. The effect of MMT concentration on thermal and dielectric properties is also investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3609–3615, 2006

Key words: nanocomposites; thermogravimetric analysis (TGA); viscoelastic properties

INTRODUCTION

Future growth of unsaturated polyester (UP) application will require development of new preparation techniques, especially radiation curing. The curing of UP resin is a radical copolymerization in which a crosslinked network is formed via chain growth between UP molecules and reactive diluents.¹

The Kinetic chemistry includes a series of three different steps: initiation, propagation, and inhibition. The photoinitiation by UV or visible light is a general trend recently to replace conventional thermal initiation, which has distinct advantages in industrial application, mainly high productivity by fast curing and reducing consumption of energy without emission of volatile organic compounds.² Because of these distinct advantages, the introduction of UV-radiation process and its performance in system have been widely investigated in recent years.³ Several studies have also concentrated on nanocomposite-based UP and montmorillonite (MMT) prepared by using thermal decomposed radical initiator and/or additional catalyst.^{4–7}

In the present study, we prepare UP/MMT nanocomposite by UV radiation crosslinking using different type of photoinitiators (PIs). The effect of PI on physical properties of nanocomposite is investigated.

EXPERIMENTAL

Materials

The two radical-type PIs were used in this study: 2,2'-dimethoxyphenyl acetophenone (BDK) and 1-hydroxycyclohexyl phenylketone (HCPK), all from Ciba Specialty Chemicals. They were introduced in UP/MMT mixture at a concentration of 2 wt % before curing.

Cloisite 30B (CEC = 90 mequiv/100 g) is an organically treated MMT (Southern clay products, TX), which was used as clay. UP resin was synthesized by direct esterification of three comonomers obtained from Duksan chemical (Seoul, Korea): maleic anhydride (MA), phthalic anhydride (PA), and propylene glycol (PG). High concentration styrene (Yakuri Pure Chemicals Co., Japan) was chosen as a reactive diluent.

Three comonomers were placed in a 1000 mL beaker (PG : PA : MA = 1 : 0.3 : 0.5 by molar ratio), which was allowed to heating at 100°C for 1 h without agitation. The mixture was stirred vigorously at 160°C for

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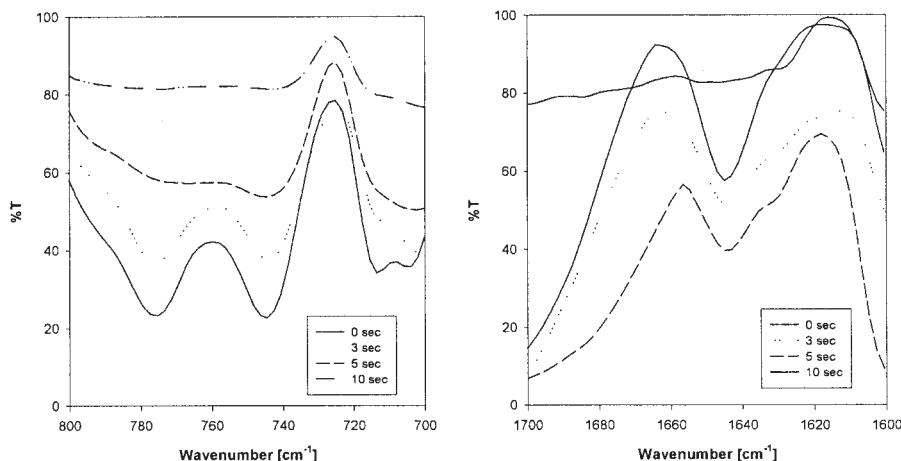


Figure 1 FTIR spectra in the 700–800 cm^{-1} and 1600–1700 cm^{-1} region of nanocomposite (PP, HCPK; [MMT], 3 wt %).

several hours. The agitation was stopped when the acid value of the resin was found to be 35 and then the resin was moved to beaker at room temperature for 1 day.

UV-radiation curing

The resin was mixed with MMT (1, 3, and 5 wt %) at 80°C for 10 min by using mechanical mixer, followed by the addition of diluent with 0.01 wt % hydroquinone as a inhibitor to prevent from the reaction during mixing stage. Finally, 0.3 mmol of PI was added to the mixture and stirred for 5 min at 80°C above melting temperature. In our experimental scale, 0.3 mmol was the minimum amount of PI that was suitable to get sufficient conversion of nanocomposite. The formulated mixture was cast onto a glass plate at a thickness of 70 μm . The curing was performed in placing the plate onto a medium pressure Fe-doped UV lamp (UVA spot 400/T, Dr. Honle). The intensity of the lamp was 30 mW/cm^2 and was received from catalogue. The temperature was controlled at 25°C to prevent from the influence of temperature.

Measurements

Weighted samples were transferred to soxhlet apparatus and the extraction performed in methylene chloride. We took the weight loss of samples as the gel content, which depends on the degree of crosslinking.

$$\text{Gel content (\%)} = W/W_0 \times 100$$

where W is the weight of sample after extraction and W_0 is the weight of sample before extraction.

Infrared spectra of samples were also recorded on a spectrometer, with a resolution of cm^{-1} in the transmission mode was used for conversion measurements

of styrene and polyester $\text{C}=\text{C}$ bonds during the curing reaction. The sample was placed in the potassium bromide plate, which was mounted on a sample holder located in FTIR

The layer spacing of MMT was measured on a Philips X'pert-APP monochromic X-ray diffractometer with Cu $\text{K}\alpha$ radiation ($\gamma = 1.54056 \text{ \AA}$) at a generator voltage of 35 kV and current of 25 mA. 2θ scanning was in 0.02 steps at a speed of 2/min from 1.2° to 10°.

Rheological measurements were made with a UDS 200 rheometer. (Paar Physica Inc. Germany) Tests were conducted with torsional mode under condition of 1 Hz and 0.03% strain at a temperature range from 25 to 400°C. The glass-transition temperature (T_g) of the nanocomposite was taken as the maximum $\tan \delta$ peak point during the rheological test, which was calculated from G''/G' ratio.

Tensile tests were performed by using Instron model 4465 testing machine (Canton), according to ASTM D790 with a crosshead speed of 50 mm/min.

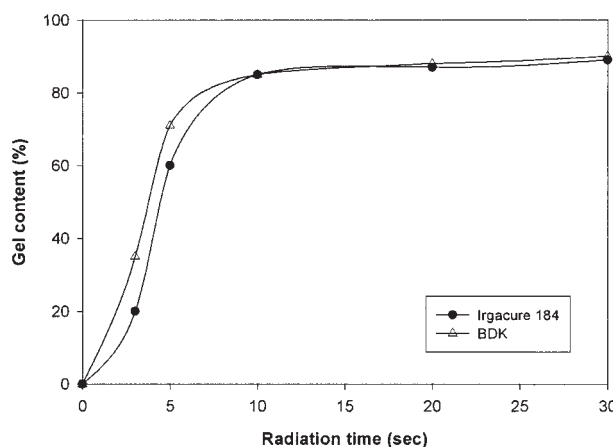


Figure 2 Influence of photoinitiator type on the gel content of nanocomposite.

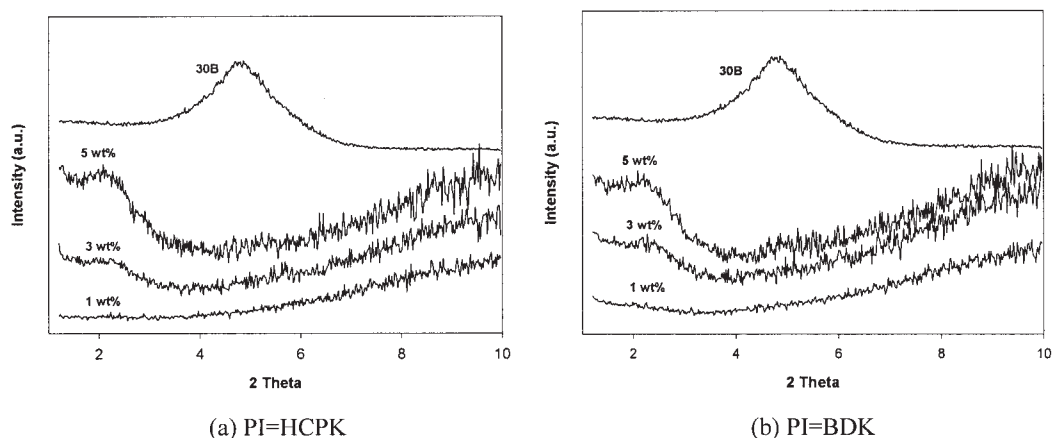


Figure 3 XRD patterns of nanocomposite with various MMT content. (a) PI = HCPK and (b) PI = BDK.

The results were taken from the mean value of those five measurements.

Dielectric properties were measured by digital loss factor analyzer (Vettiner, France) with circular electrode having a surface area 20 cm^2 (radius of 50 mm). The frequency is fixed at 60 Hz and amplitude of test signal is 10 V . The sample dimensions were $10 \times 10 \times 2 \text{ cm}^3$. From the measured capacitance C , we calculate the dielectric constant (ϵ_r)⁸

$$C = (\pi r^2) \epsilon_0 \epsilon_r / d$$

where ϵ_0 is the vacuum dielectric constant, and r and d are the surface area and thickness of sample, respectively.

Thermal decomposition temperature of samples was investigated with TGA (951 thermogravimetric analyzer, Du Pont instruments). The test was carried out from 25°C to 1000°C using a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere.

RESULTS AND DISCUSSION

The consumption of polyester monomer was monitored by measuring the variation in absorbance at 1650 cm^{-1} , which corresponds to the stretching modes of the $\text{C}=\text{C}$ bond in polyester. Absorbance at 775 cm^{-1} was chosen as the consumption of styrene monomer. Figure 1 shows the most of reaction is completed less than 10 s.

Figure 2 shows the gel content of nanocomposite using different type of PI. It can be seen that the gelation occurs at very early stage of radiation and reached at 90% in 10 s. However, the gelation did not proceed because the mobility in polyester chain decreased, and the remaining $\text{C}=\text{C}$ bonds may be buried in the microgel structure in early stage.⁹

According to other published data for UP prepared by thermal initiation, the premature gelation occurs at

very low conversion ($<5\%$), which may be attributed to the spherical structure formed among the polyester molecules in the early stages and also be affected by curing temperature.⁹ However, for our UV radiation system, the thermal effect was not involved and the reaction was completed in much earlier than thermal initiation. Thus, the required time to maximum gelation is nearly identical to the time to overall maximum conversion.

The type of PI was slightly influenced on gelation time, the shorter using BDK as PI than HCPK as shown in Figure 2.

The X-ray diffraction (XRD) patterns of the nanocomposites are shown in Figure 3. The peak at 4.8° correspond to the (001) plane in pristine Cloisite 30B. It can be seen that the peak corresponding to the basal spacing of MMT was disappeared in samples with 1 wt % MMT loading. It was expected that interaction between MMT and UP with hydrophilic end group enhances the delamination of MMT. But a small peak at 2.2° ($d = 20.07 \text{ \AA}$) was observed in samples with higher MMT loading and its intensity increased with MMT content. Thus, the clay tactoids are considered not to be exfoliated completely and some remained as aggregates with clay loading up

TABLE I
Viscoelastic Properties of Nanocomposite with Various MMT Content

PI	Clay content (wt %)	T_g ($^\circ\text{C}$)	G'_{No} (MPa)
HCPK	0	273	127
	1	270	142
	3	268	184
	5	269	136
BDK	0	270	124
	1	271	138
	3	266	146
	5	268	140

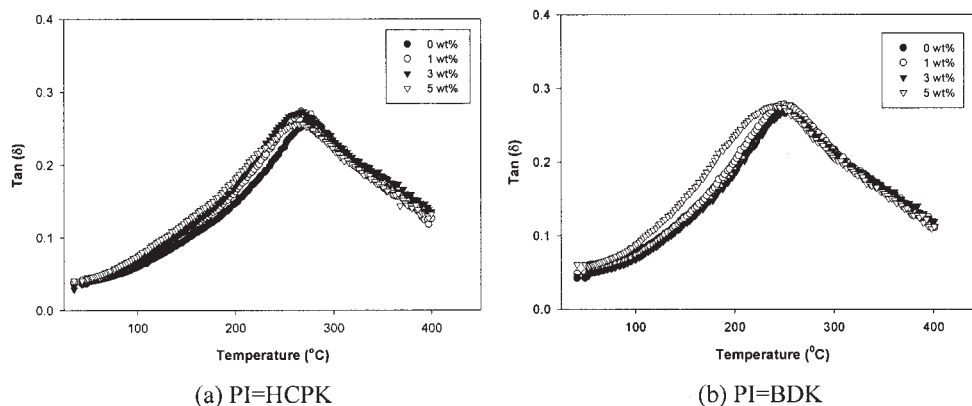
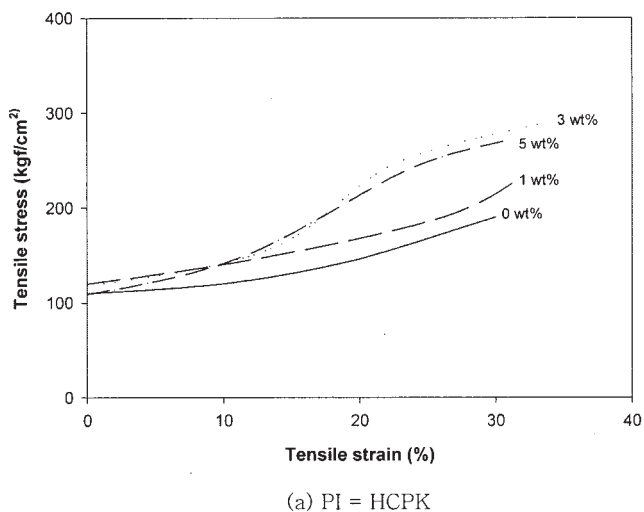
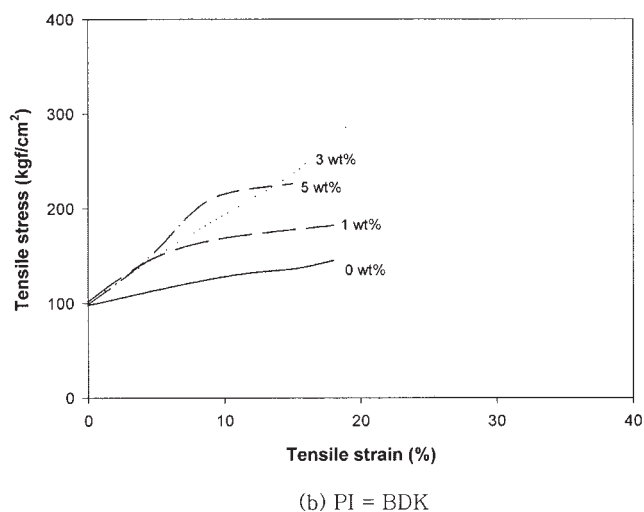


Figure 4 $\tan \delta$ of UP/MMT nanocomposite with various MMT content. (a) PI = HCPK and (b) PI = BDK.



(a) PI = HCPK



(b) PI = BDK

Figure 5 Mechanical properties of UP/MMT nanocomposite with various MMT content ([P1] = 0.3 mmol). (a) PI = HCPK and (b) PI = BDK.

to 3 wt %. This result is very similar to our previous study for UP/Cloisite 30B nanocomposite by thermal initiation.⁵ The influence of PI type on the XRD patterns was not detected.

The viscoelastic test results are presented in Table I and Figure 4. The enhanced rubbery plateau modulus (G'_{N0}) at 400°C of the nanocomposites in comparison with the unfilled UP can be attributed to the surface adhesion between the polymer and rigid MMT, the nanometer-sized particles restrict the motion of UP molecules at interface even in high temperature. However, the T_g was declined with increase of the MMT content for all PI systems. This small drop in the T_g can be ascribed to the aggregation of MMT.

It is noteworthy that the improvement of plateau modulus is more apparent in nanocomposite using HCPK. This trend is also observed in mechanical properties of nanocomposites as shown in Figure 5. The increase in the tensile strength and high extension rate are observed in HCPK system. On the other hand, Figure 5 also shows more brittle, with low strength and elongation in BDK system, which may be attributed to the poor interaction between PI and MMT in mixture before curing.

To discover the solubility of PI on the properties of nanocomposite, different PI amounts are added to the

TABLE II
Viscoelastic Properties of Nanocomposite with Various PI Content

PI	PI content (mmol)	T_g (°C)	G'_{N0} (MPa)
HCPK	0.3	263	184
	3	265	158
	6	251	130
BDK	0.3	266	160
	3	254	130
	6	246	115

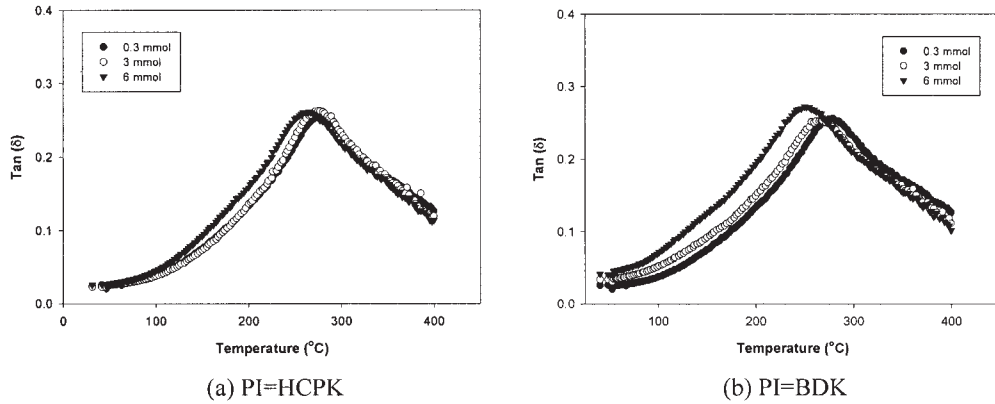


Figure 6 $\tan \delta$ of UP/MMT nanocomposite with various photoinitiator concentrations ([MMT] = 3 wt %). (a) PI = HCPK and (b) PI = BDK.

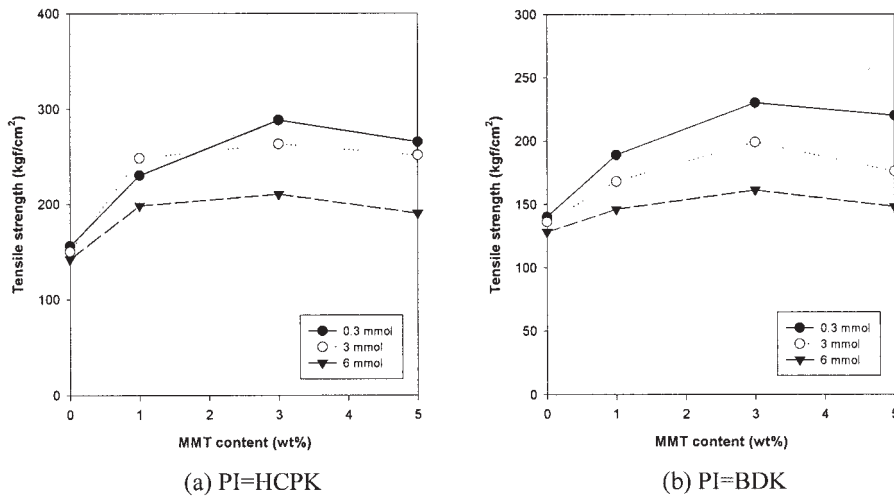


Figure 7 Tensile strength of UP/MMT nanocomposite with various photoinitiator concentration. (a) PI = HCPK and (b) PI = BDK.

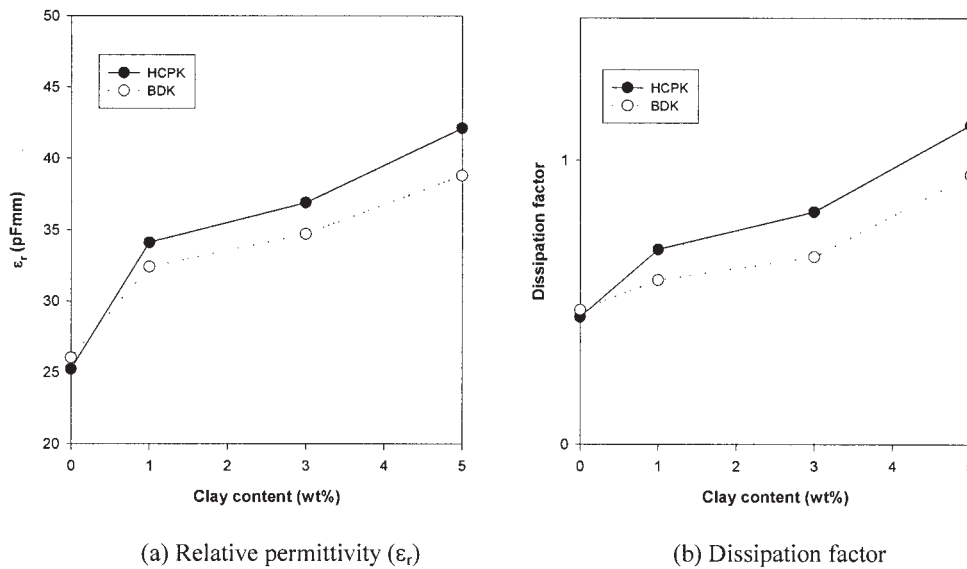


Figure 8 Dielectric properties of UP/MMT nanocomposite with various MMT content ([PT] = 0.3 mmol). (a) Relative permittivity (ϵ_r) and (b) dissipation factor.

TABLE III
 T_i of UP/MMT Nanocomposite with Different Photoinitiator

	MMT content (wt %)			
	0	1	3	5
HCPK	216	220	248	266
BDK	237	257	240	227

mixtures and cured in the same experimental condition. The viscoelastic test results are summarized in Table II and Figure 6, where the properties are affected by initiator content in both PIs system.

Decreasing of properties is more apparent in BDK initiated system, which is also found in tensile strength of nanocomposite in Figure 7.

In Figure 7, the tensile strength of nanocomposite using various amounts of PIs is compared. The samples using HCPK for PI as compared to BDK initiated samples, especially at high PI content, and the results suggest that part of initiator is not resolved or partially miscible with the mixture and the excess may remain even in cured sample. The beneficial influence of the hydroxyl group in HCPK on solubility in UP resin at higher initiator concentration is obtained in mechanical properties; however, the effect of solubility is less pronounced in HCPK initiated systems. As a result, it assumed that HCPK is more efficient PI than BDK in our experimental scale. This may be predominated by the solubility or miscibility with components not by the quantum yield of dissociation or other factors in PI as we know.

Figure 8 shows dielectric properties of nanocomposites. It is found that the relative permittivity (ϵ_r) and dissipation factor ($\tan \delta$) are proportional to the clay loading. This result may be attributed to the presence of clay with higher permittivity, which increases the local interface between matrix resin and MMT, consequently the probability of polarization occurring is

increased. It was reported that good insulator was obtained for current polymer composite with low dielectric losses ($\tan \delta < 10\%$).¹⁰ As shown in Figure 8, $\tan \delta$ of nanocomposites increase with MMT concentration, but all the values are below 3%.

The initial temperatures (T_i) of the thermal degradation are listed in the Table III. From these results, it is observed that T_i is increased with MMT concentration. The thermal stability may be attributed to the barrier effect of MMT to delay the decomposition of UP resin as studied earlier. This behavior is more clear in samples using HCPK for PI, which also corresponds to the rheological and mechanical properties of two systems. On the other hand, the irregular increase of T_i in BDK system reflects the poor solubility in mixture. Figure 9 shows that the thermal stability increased with MMT loading in HCPK system, probably the effect of MMT was not found in BDK system because of the lack of interaction between PI and MMT.

CONCLUSIONS

We prepared UP/MMT nanocomposite by UV radiation curing technique and studied the influence of PI type and MMT concentration on physical properties. From the XRD patterns, it is concluded that the d -spacing of most part of MMT highly expanded in nanocomposite but some remains in aggregates. Increased MMT content leads to an improvement in the rubbery plateau modulus and mechanical properties due to the well adhered hard particles. The dielectric properties of nanocomposite indicate the insulating capability of MMT. From the test results, it is determined that these properties are affected by PI types. HCPK was proved to be more efficient PI than BDK in our experimental scale, indicating that the interaction between PI and MMT plays an important role to selecting PI and determining its efficiency.

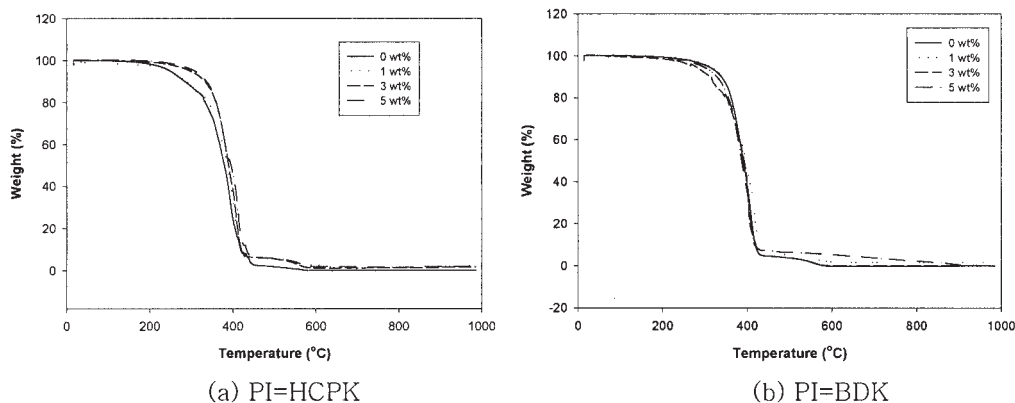


Figure 9 TGA diagram of UP/MMT nanocomposite using different photoinitiator ([PT] = 0.03 mmol). (a) PI = HCPK and (b) PI = BDK.

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