JAE-YOUNG LEE*), MI-JA SHIM**)
SANG-WOOK KIM*)1)

Thermal decomposition of a system consisting of epoxy resin and butadiene-acrylonitrile rubber with blocked carboxyl end-groups

Summary — The rate of thermal decomposition and the kinetic parameters for diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline (MDA)/MDA-endcapped carboxyl terminated butadiene acrylonitrile rubber (CTBN) system were investigated using the data of thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses and the Kissinger and Flynn & Wall expressions. The rate constant of thermal decomposition was decreased and the activation energy increased by the addition of MDA-endcapped CTBN. It means that the thermal stability of the DGEBA/MDA system was improved by the MDA-endcapped CTBN.

Key words: epoxy resin/butadiene — acrylonitrile rubber system, activation energy of thermal decomposition, rate constants of thermal decomposition.

Syntheses of advanced polymers and the thermal stability of polymers have been studied by many workers due to increasing demands for heat-resistant polymer materials. Many expressions have been proposed to estimate the thermal stability of the synthetic polymers; amongst them the Flynn & Wall, Kissinger, Toop's, and Freeman & Carroll expressions are well-known [1-12], with the assumption that the thermal decomposition rate of the polymer was proportional to the rate of weight loss.

In this study, the characteristics of thermal decomposition for a cured epoxy resin were studied using the Kissinger expression [1—4], written as

$$-\ln\left(\frac{\beta}{T_m^2}\right)=\frac{E_d}{R}\cdot\frac{1}{T_m}-\ln\left(\frac{A_d R}{E_d}\right) \qquad (1)$$

where β is the heating rate, T_m the temperature at which maximum decomposition rate took place on the derivative thermogravimetric (DTG) curves, E_d the activation energy of thermal decomposition, R the gas constant, and A_d the pre-exponential factor. The relationship of $-\ln(\beta/T_m^2)$ vs $1/T_m$ was plotted to get the E_d and A_d values.

The Flynn & Wall expression [4, 6] was also used as follows

$$E_d=\frac{-R}{0.457}\,\frac{d(\log\beta)}{d(T^{-1})} \qquad (2)$$

where E_d, β and R have the same meaning as in the Kissinger eq. (1) and T^{-1} was the reciprocal of absolute temperature at a selected weight loss fraction. The linear relationship of log β vs T^{-1} at a selected weight loss fraction was plotted and the E_d value was calculated from the slope. The selected weight loss fractions varied from 0.05 to 0.4 and the E_d value for each weight loss fraction was obtained. These values were compared with the results of Kissinger eq. (1).

EXPERIMENTAL

Diglycidyl ether of bisphenol A (DGEBA, Epon 828 grade) supplied by Shell Co. was used as a base resin, and 4,4'-methylene dianiline (MDA) was used as a curing agent. MDA was also called as 4,4'-diaminodiphenyl methane. Carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) manufactured by B. F. Goodrich Co. under the trade name of Hycar 1300x8 was used as a toughener [1, 5, 10].

The end chains of CTBN were capped with MDA to give better compatibility between epoxy resin and CTBN particle. The CTBN and MDA was linked by the formation of amide group through the condensation reaction between the carboxyl groups of CTBN and the amine groups of MDA. The procedure to synthesize the MDA-endcapped CTBN was as follows. CTBN and MDA were well-mixed in the reactor at the molar ratio of 1 to 2.

---

*) Department of Chemical Engineering, The University of Seoul, 90 Jeonnong-Dong, Dongdaemun-Gu, Seoul 130-743, Korea.

**) Department of Life Science, The University of Seoul, 90 Jeonnong-Dong, Dongdaemun-Gu, Seoul 130-743, Korea.

[1] To whom correspondence should be addressed.

The mixture reacted at 160°C for 1 hr with removing the condensed water by vacuum pump. The synthesized compound was stored at -5°C.

DGEBA, MDA (30 phr) and MDA-endcapped CTBN (0, 5, 10, 15 and 20 phr) were well mixed under 80°C and cured at 150°C for 1 hr after curing at 80°C for 1.5 hr. The cured sample was analyzed by thermal gravimetric analyzer (TGA) at the heating rates of 5, 10, 15 and 20°C/min. Nitrogen gas flowed into the sample tube at the rate of 40 ml/min to prevent the oxidation of the sample. The obtained TGA data were introduced into the Kissinger and Flynn & Wall expressions, and the activation energies of thermal decomposition and pre-exponential factors were calculated.

RESULTS AND DISCUSSION

TG and DTG curves for DGEBA/MDA/MDA-endcapped CTBN (10 phr) system at two different heating rates are shown in Fig. 1. It is seen that the sample maintained its stability to thermal stress until about 300°C and abruptly decomposed at about 350°C. Shapes of TG curves are similar regardless of the heating rate, however the curve at the rate of 15°C/min appeared at higher temperature than that of 5°C/min. Decomposition temperatures T_d for 5 and 15°C/min were 356.4 and 376.1°C, respectively. T_d could be obtained from the point where weight loss abruptly increased. By the derivation of TG curves, DTG curves could be displayed. Shapes of the DTG curves are similar and only one peak of DTG curve means that the thermal decomposition took place in one stage regardless of the heating rates.

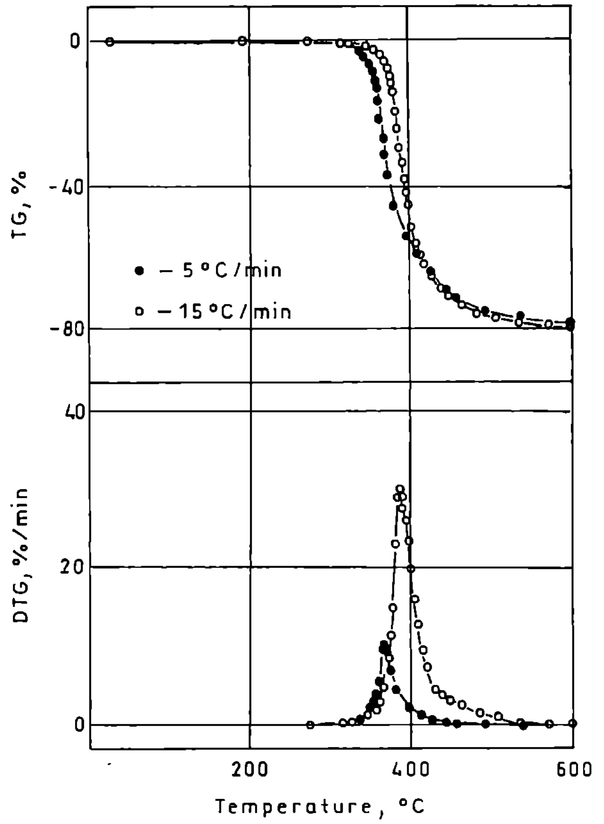

Fig. 1. TG and DTG curves for DGEBA/MDA/MDA-endcapped CTBN (10 phr) system

DTG curves for DGEBA/MDA/MDA-endcapped CTBN (10 phr) system at various different heating rates are shown in Fig. 2. All curves were similar, i.e. the thermal decomposition occurred in one stage. The maximum values of the DTG curves were increased with the increase of heating rate and the temperatures, at which the maximum DTG values appeared, occurred at higher points. To get the activation energy and the pre-exponential factor for thermal decomposition of the system, the relationship between $-\ln(\beta/T_m^2)$ and $10^3/T_m$ was listed in Table 1 and displayed in Fig. 3. The linear expression was as follows:

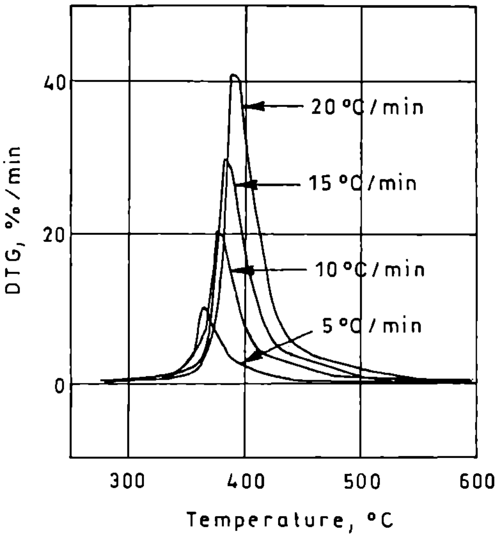

Fig. 2. DTG curves for DGEBA/MDA/MDA-endcapped CTBN (10 phr) system

$$-\ln\left(\frac{\beta}{T_m^2}\right) = 21.90 \cdot 10^3 \frac{1}{T_m} - 23.01 \qquad (3)$$

The activation energy could be obtained from the slope and the pre-exponential factor was calculated from

Table 1. $-\ln(\beta/T_m^2)$, $10^3/T_m$ and kinetic parameters for DGEBA/MDA/MDA-endcapped CTBN (10 phr) system using the Kissinger expression

β, °C/min	T_m, K	$-\ln(\beta/T_m^2)$	$10^3/T_m$, K^{-1}	A_d, sec^{-1}	E_d, kJ/mol
5	638.55	11.309	1.566	3.59x10^{12}	182.1
10	650.05	10.652	1.538		
15	657.65	10.269	1.520		
20	664.15	10.001	1.506		

the intersection. The activation energy was found to be 182.1 kJ/mol, i.e. within the range of covalent bond energy, and the pre-exponential factor was $3.59\text{x}10^{12}$ sec^{-1}, as shown in Table 1.

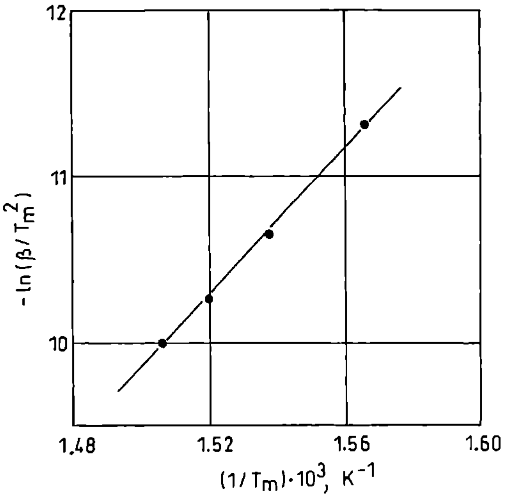

Fig. 3. Kissinger plot for DGEBA/MDA/MDA-endcapped CTBN (10 phr) system

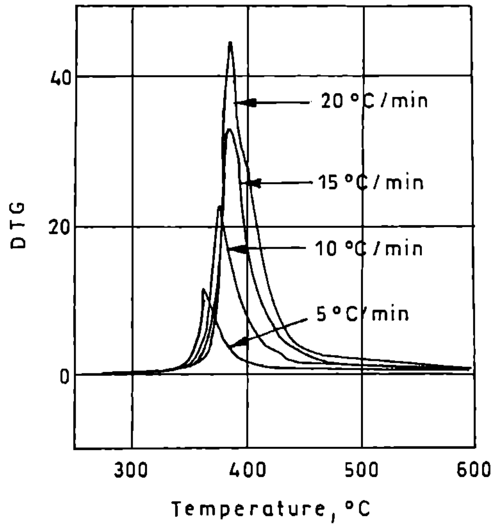

Fig. 4. DTG curves for DGEBA/MDA/MDA-endcapped CTBN (0 phr) system

Table 2. $-\ln(\beta/T_m^2)$, $10^3/T_m$ and kinetic parameters for DGEBA/MDA/MDA-endcapped CTBN (0 phr) system using Kissinger expression

β, °C/min	T_m, K	$-\ln(\beta/T_m^2)$	$10^3/T_m$, K^{-1}	A_d, sec^{-1}	E_d, kJ/mol
5	635.95	11.301	1.572	7.49×10^{10}	161.6
10	648.75	10.648	1.541		
15	660.25	10.277	1.514		
20	662.35	9.996	1.510		

DTG curves for DGEBA/MDA system without MDA-endcapped CTBN at four different heating rates are shown in Fig. 4. The thermal decomposition occurred in one stage regardless of the heating rate. However, the curves were shifted to higher temperature and the DTG value was also shifted to higher values with the increase in heating rate. The temperatures at which the maximum rate of thermal decomposition took place were listed in Table 2 at the various heating rates. The values of $-\ln(\beta/T_m^2)$ and $10^3/T_m$ were also calculated and listed in Table 2. To get thermal decomposition kinetic parameters, the relationship of $-\ln(\beta/T_m^2)$ vs $10^3/T_m$ was plotted in Fig. 5. The straight line expression was as follows

$$-\ln\left(\frac{\beta}{T_m^2}\right) = 19.43 \cdot 10^3 \frac{1}{T_m} - 19.26 \tag{4}$$

The activation energy was calculated from the slope ($19.43\text{x}10^3$ K) multiplying by the gas constant (8.314

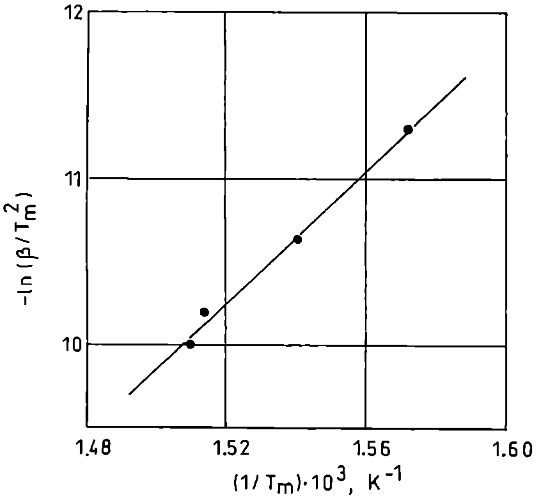

Fig. 5. Kissinger plot for DGEBA/MDA/MDA-endcapped CTBN (0 phr) system

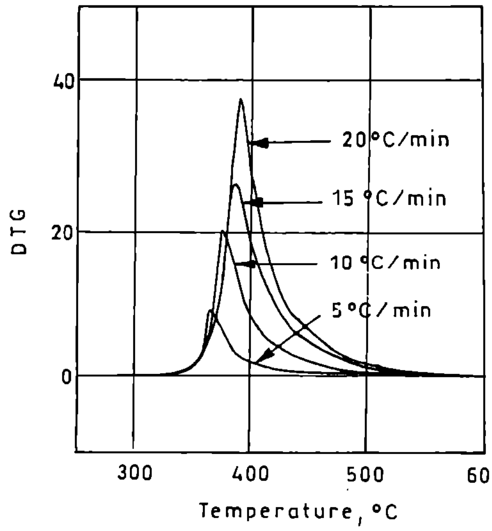

Fig. 6. DTG curves for DGEBA/MDA/MDA-endcapped CTBN (20 phr) system

J/mol-K), and pre-exponential factor was obtained from the intersection which was equal to $-\ln(A_d R/E_d)$. E_d = 161.61 kJ/mol and A_d = 7.49x10^{10} sec^{-1} were obtained, see Table 2.

The DTG curves for DGEBA/MDA/MDA-endcapped CTBN (20 phr) system at various heating rates are shown in Fig. 6 and the relationship of the heating rate on the temperature of the maximum decomposition from the DTG curve is shown in Fig. 7. The activation energy for the system was 192.7 kJ/mol and the pre-exponential factor was 4.27x10^{13} sec^{-1}.

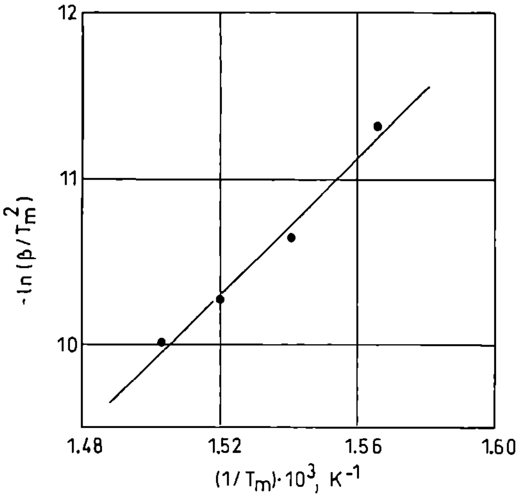

Fig. 7. Kissinger plot for DGEBA/MDA/MDA-endcapped CTBN (20 phr) system

The kinetic parameters for DGEBA/MDA system with various MDA-endcapped CTBN are shown in Table 3. To compare the rate constant of thermal decomposition for the systems, the activation energies and pre-exponential factors obtained by the Kissinger equation were introduced to the Arrhenius equation

$$k = A_d \exp(-E_d/RT) \quad (5)$$

T a b l e 3. Kinetic parameters for DGEBA/MDA system with various MDA-endcapped CTBN

MDA-endcapped CTBN, phr	A_d, sec^{-1}	E_d, kJ/mol	k at 300°C, sec^{-1}
0	7.49x10^{10}	161.6	1.39x10^{-4}
5	7.83x10^{15}	222.6	0.40x10^{-4}
10	3.59x10^{12}	182.1	0.90x10^{-4}
15	1.58x10^{13}	188.5	1.03x10^{-4}
20	4.27x10^{13}	192.7	1.16x10^{-4}

The rate constants, k at 300°C were calculated and compared in Table 3. The rate constants of the system with MDA-endcapped CTBN were lower than that of the system without MDA-endcapped CTBN. It means that the thermal stability of the DGEBA/MDA system was improved by the addition of MDA-endcapped CTBN, however the decomposition rate was increased with the inrease of MDA-endcapped CTBN content. It is due to the presence of CTBN domains formed during the cure reaction. When the sample is heated, the domain absorbs the heat by flowing, however it decomposes at lower temperature than the matrix.

The TG curves for DGEBA/MDA/MDA-endcapped CTBN (10 phr) system at the heating rates of 5, 10, 15 and 20°C/min are shown in Fig. 8. The curves shifted to right-hand side with the increasing heating rate. The temperatures at the conversion α=0.05 for the different heating rates were measured from the cross points of dotted lines and the TG curves. The following values were obtained; 347.42°C, 353.46°C, 366.13°C, and 377.36°C at 5, 10, 15 and 20°C/min, respectively. These data were converted to log β and $10^3/T$ to get the activation energy of thermal decomposition shown in Table 4. The data at other values of α were also in Table 4. The fixed conversions have been selected within the range from 0.05 to 0.4, because the values at a lower than 0.05 are affected by volatilization of some low molecular weight molecules.

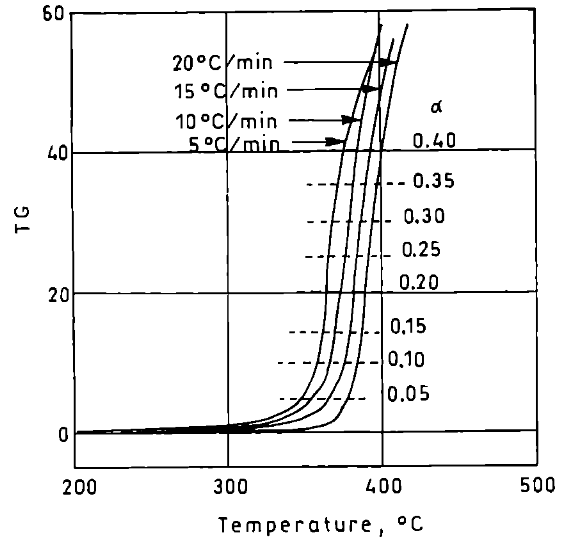

Fig. 8. TG curves of DGEBA/MDA/MDA-endcapped CTBN (10 phr) system for Flynn & Wall expression

To get the activation energy of thermal decomposition, the relationships of log β vs $10^3/T$ were plotted in

T a b l e 4. The relationship between log β and T^{-1} for DGEBA/MDA/MDA-endcapped CTBN (10 phr) system

log β	$1/T$ x 10^3, K^{-1}							
	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4
0.699	1.611	1.586	1.575	1.569	1.563	1.555	1.548	1.539
1.000	1.596	1.563	1.554	1.545	1.539	1.532	1.527	1.520
1.176	1.564	1.542	1.532	1.526	1.521	1.514	1.506	1.499
1.301	1.537	1.521	1.514	1.510	1.504	1.498	1.491	1.485

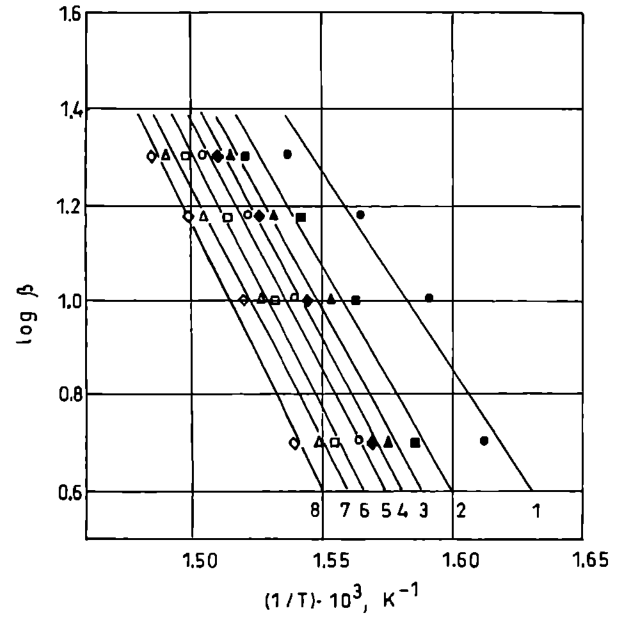

Fig. 9. Isoconversional plots of DGEBA/MDA/MDA-endcapped CTBN (10 phr) system for Flynn & Wall expression; values of α: 1 — 0.05, 2 — 0.10, 3 — 0.15, 4 — 0.20, 5 — 0.25, 6 — 0.30, 7 — 0.35, 8 — 0.40

Fig. 9, and the expressions of the straight lines for various α were obtained, as it is shown in Table 5. The activation energy was increased steeply in the initial stage of thermal decomposition and then it was slowly increased. It means that the molecules of weak bond resistance to thermal stress were destroyed in the initial stage, and then the strong-bond molecules were responsible for the high activation energy values.

The activation energies for the systems with other contents of MDA-endcapped CTBN were calculated using the same method, see Fig. 10. The activation energies for other contents of MDA-endcapped CTBN were also increased steeply in the initial stage and then they were slowly increased for higher values of α. With the increase of MDA-endcapped CTBN content, the activation energies were increased. There was a little difference between the activation energies obtained from the Kissinger expression, calculated at T_m, and those from the Flynn & Wall expression, obtained from the temperatures at a selected weight loss fraction throughout the entire conversion.

T a b l e 5. Activation energy of thermal decomposition for DGEBA/MDA/MDA-endcapped CTBN (10 phr) system using the Flynn & Wall expression

a	Linear expression, Fig. 9	Activation energy, kJ/mol
0.05	Y = -8.333 + 14.183	151.60
0.10	Y = -9.524 + 15.838	173.26
0.15	Y = -10.000 + 16.480	181.92
0.20	Y = -10.309 + 16.886	187.55
0.25	Y = -10.417 + 17.000	189.51
0.30	Y = -10.753 + 17.441	195.62
0.35	Y = -10.638 + 17.191	193.53
0.40	Y = -11.111 + 17.822	202.14

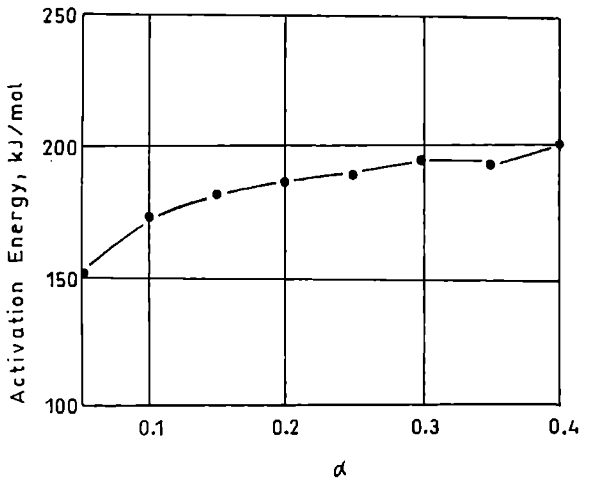

Fig. 10. Decomposition activation energy for DGEBA/ /MDA/MDA-endcapped CTBN(10phr) system by Flynn & Wall expression

CONCLUSIONS

The thermal decomposition of the DGEBA/MDA/ /MDA-endcapped CTBN system took place in one stage regardless of the MDA-endcapped CTBN content. The rate constants of the system with MDA-endcapped CTBN were lower than that of the system without MDA-endcapped CTBN. The activation energy increased steeply in the initial stage of thermal decomposition and then was slowly increased, due to the high bond strength of decomposing molecules. In the case of the system with MDA-endcapped CTBN, the decomposition rate increased with the increase of MDA-endcapped CTBN content.

ACKNOWLEDGMENT:
This work was supported by SK group in Korea.

REFERENCES

1. Lee J. Y., Choi H. K., Shim M. J., Kim S. W.: *Kor. J. Mater. Res.* 1997, 7, 229.
2. Day M., Cooney J. D., Wiles D. M.: *J. Appl. Polym. Sci.* 1989, **38**, 323.
3. Cooney J. D., Day M., Wiles D., M.: *ibid.* 1983, **28**, 2887.
4. Stivala S. S., Kimura J., Gabbay S. M.: "Degradation and Stabilisation of Polyolefins", ed. Allen N. S., *Applied Science Publishers Ltd*, London 1983, Ch. 3.
5. Lee J. Y., Shim M. J., Kim S. W.: *Mater. Chem. Phys.* 1997, **48**, 36.

6. Flynn J. H.: *Polym. Eng. Sci.* 1980, **20**, 675.
7. Freeman E. S., Carroll B.: *J. Phys. Chem.* 1958, **62**, 394.
8. Lee J. Y., Lee S. H., Park J. H., Shim M. J., Kim S. W.: Proc. of HNTT'96, Dandong (China) 1996, 568.
9. Varhegyi G.: *Thermochim. Acta* 1987, **110**, 95.
10. Lee J. Y., Shim M. J., Kim S. W.: *Mater. Chem. Phys.* 1996, **44**, 74.
11. Maiti S. N., Mahapatro P. K.: *Polym. Compos.* 1990, **11**, 223.
12. Horovitz H. H., Metzer G.: *Anal. Chem.* 1963, **35**, 1464.
13. Toop D. J.: IEEE Trans. Dielectr. Insul. 1972, **EI-7**, 32.

Problematyka ochrony środowiska w przetwórstwie tworzyw sztucznych

W dniu 5 października br. w Instytucie Francuskim w Warszawie odbyło się francusko-polskie seminarium poświęcone problematyce ochrony środowiska w przetwórstwie tworzyw sztucznych, zorganizowane z inicjatywy Stowarzyszenia Polskich Przetwórców Tworzyw Sztucznych i Fédération de la Plasturgie.

Patronat nad Seminarium sprawowało Biuro Radcy Handlowego przy Ambasadzie Francji w Warszawie.

Na program Seminarium złożyły się trzy sesje:

Problematyka zużytych wyrobów z tworzyw sztucznych

- p. Jallon, Fédération de la Plasturgie — *Przepisy i normy Unii Europejskiej. Zagadnienia techniczne i aspekty strategiczne*
- p. Henn, ELF ATOCHEM — *Metody zagospodarowania zużytych wyrobów z tworzyw sztucznych*
- p. Lanfranchi, CGEA — *Systemy zbiórki i sortowania odpadów tworzyw sztucznych*

Problematyka ochrony środowiska w zakładach przemysłowych

- p. Lestage, ADEME (Agencja ds. Środowiska i Gospodarki Energetycznej) — *Obowiązujące przepisy i normy. Plan ochrony środowiska w przedsiębiorstwie*
- p. Jallon, Fédération de la Plasturgie — *ADEGE jako inicjatywa francuskiego przetwórstwa tworzyw sztucznych*

Podejście ekologiczne w projektowaniu wyrobów z tworzyw sztucznych

- p. Jean, ECOBILAN – *Pojęcia podstawowe i zasady*
- p. Couchoud, ELF ATOCHEM — *Podejście ekologiczne w przemyśle opakowań z tworzyw sztucznych*
- p. Jean, ECOBILAN — *EIME - Narzędzie uwzględnienia wymogów środowiska na etapie projektowania wyrobów*

Podsumowania Seminarium dokonał Prezes Polskiego Stowarzyszenia Przetwórców Tworzyw Sztucznych doc. P. Szewczyk, który podziękował francuskim gościom za przybycie i doskonałe przygotowanie referatów. Wyraził też nadzieję na dalszą owocną współpracę.

W godzinach popołudniowych uczestnicy Seminarium mieli możliwość wymiany doświadczeń z francuskimi przedstawicielami przetwórców tworzyw sztucznych w specjalnie zorganizowanym Spotkaniu.