

# Unusual Effect of Filler ( $\text{CaCO}_3$ ) on Thermal Degradation of Polyurethane

S. K. DOLUI

Central Building Research Institute, Roorkee 247667, India

## SYNOPSIS

The thermal degradation of polyurethane is exothermic in nature. The addition of  $\text{CaCO}_3$  inverts the exothermicity to endothermic behavior in the presence of air. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The addition of fillers and additives in plastic is well recognized to impart desired properties to the virgin plastic such as improvement of strength,<sup>1-4</sup> fire retardancy,<sup>5</sup> UV resistance,<sup>6,7</sup> and for cost effectiveness.<sup>8</sup> Polyurethane is widely used to manufacture foam,<sup>9,10</sup> elastomer,<sup>11,12</sup> coatings,<sup>13</sup> fibers,<sup>13</sup> etc. The toxic emissions from polyurethane on burning and thermal degradation are very objectionable and injurious to health.<sup>14,15</sup> During a study of effects of various fillers such as  $\text{CaCO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{FeSO}_4$  on emissions from polyurethane on thermal degradation, we have observed that  $\text{CaCO}_3$  drastically changes the degradation pattern of polyurethane (PU) in thermal degradation. It inverts the exothermic behavior of PU to endothermic characteristic. This could help in hindering fire propagation in polyurethane.

We have used two polyurethane samples (1) polyurethane made from epoxy-based polyol and hexamethylene diisocyanate received from Krishna Products Ltd., India (Product code AY15 & AB15, without pigment and fillers) (PU-1) and (2) polymer prepared<sup>16-18</sup> from castor-oil-based polyol and toluene diisocyanate (mole ratio of components: glycerol : castor oil : TDI = 1 : 1 : 2.4; nitrogen content in product 5.5%; solvent EA) (PU-2). Both the polymers are two component systems. Fillers  $\text{CaCO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{FeSO}_4$  all are AR grade.

## Film Preparation

Both the components were mixed first in a vessel fitted with a stirrer. To the mixture, various fillers were added, 4% separately in each set, and mixed thoroughly. The mixture was poured over a glass plate and kept as such at room temperature (25°C) for 24 h, then in an oven at 60°C for 5 h for final curing.

## Thermal Analysis

Simultaneously thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were recorded with a thermal analyzer from Stanton Red Croft, London, in air at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

Results are summarized in Table I and show that addition of  $\text{CaCO}_3$  changes the exothermic characteristics of polyurethane. Other fillers,  $\text{Fe}_2\text{O}_3$  and  $\text{FeSO}_4$ , could not produce any change in degradation pattern except the number of steps (Fig. 1). The degradation behavior of PU-1 and PU-2 is almost the same in trend toward filler addition. Unmodified PU decomposes in two steps and modified PU decomposes in three steps. In the TGA/DTA curve for PU-1, the junction of steps 1 and 2 (temperature 500°C) shows a small valley (endo) but it is well above the base line.  $\text{CaCO}_3$ -modified PU shows endothermic degradation (step 2) that is far below the baseline. Other fillers,  $\text{Fe}_2\text{O}_3$  and  $\text{FeSO}_4$ , do not pro-

**Table I Thermal Degradation Results<sup>a</sup>**

Sample	Degradation Pattern		Nature <sup>c</sup> ( $\Delta T$ )	% Wt. Loss	Remarks
	Steps <sup>b</sup>	Temp. Range (°C)			
PU-2	1	235-500	Exo	73	
	2	500-650	Exo	27	
PU-2+	1	236-375	Exo	37	
	2	375-525	Exo	40	
Fe <sub>2</sub> O <sub>3</sub>	3	525-650	Exo	23	
	1	237-390	Exo	51	
PU-2+	2	390-530	Endo	25	Huge endotherm below baseline
	3	530-655	Exo	24	
PU-1+	1	235-437	Exo	54	
	2	437-530	Endo	30	Huge endotherm below baseline
3	550-650	Exo	16		

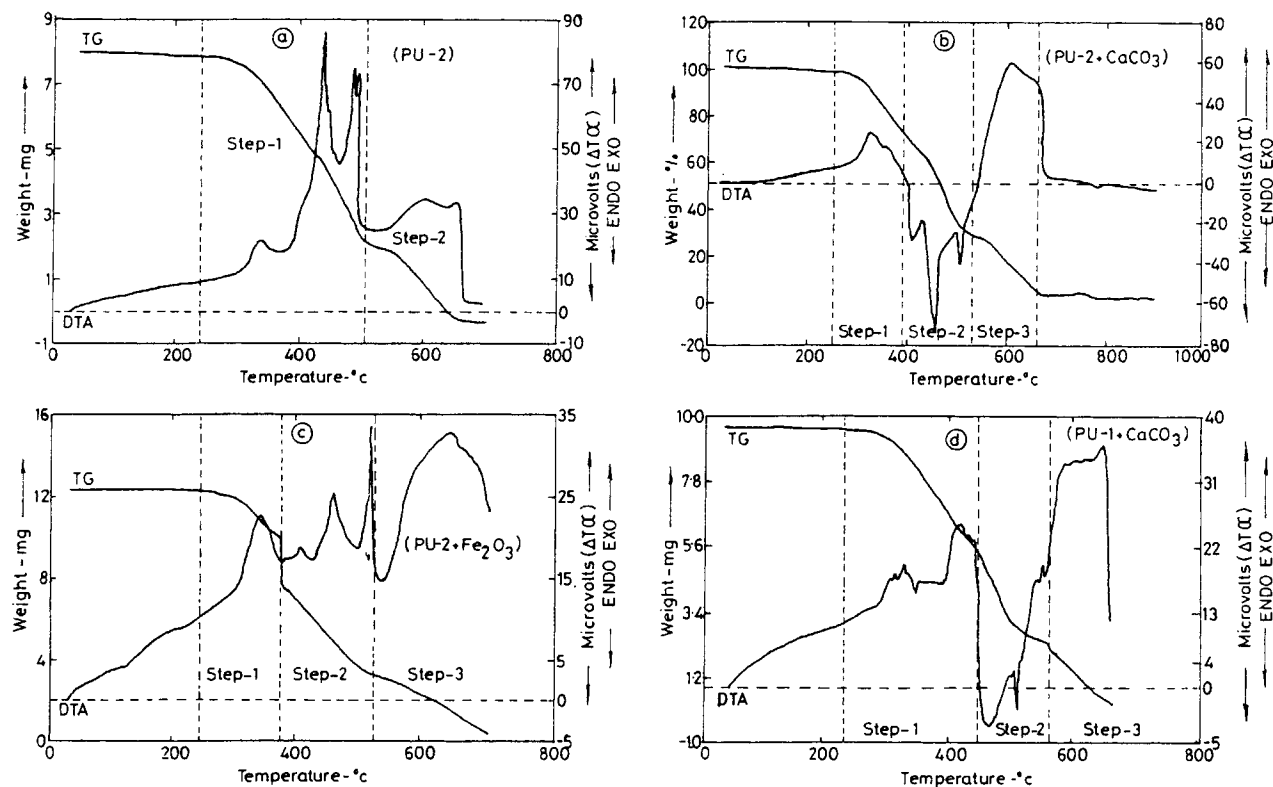
<sup>a</sup> Summarized from TGA/DTA curves.

<sup>b</sup> Steps are separated where plateaux are reached in the weight loss curve.

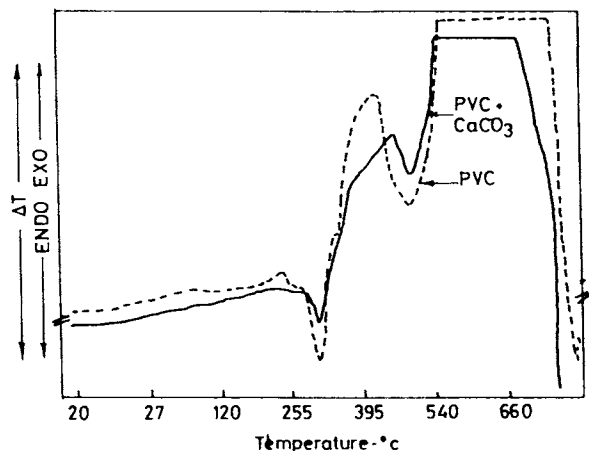
<sup>c</sup> Average trend of heat curve (DTA) in particular region.

duce such a drastic change; in each step, small valleys that are well above baseline are present. Pure CaCO<sub>3</sub> decomposes at 850-860°C (peak temperature) with

an endotherm.<sup>19</sup> It was thought that emission of acidic components such as HCN may cause early decomposition of CaCO<sub>3</sub>. However, the addition of



**Figure 1** TGA/DTA curves of PUs and modified PUs. (a) PU-2: showing two-step degradation (exo) with a small valley (endo) at 500°C; (b) PU-2+CaCO<sub>3</sub>: changes the degradation pattern drastically, depicting three-step degradation with a huge endotherm well below baseline; (c) PU-2+Fe<sub>2</sub>O<sub>3</sub>: showing three-step degradation (overall exo); and (d) PU-1+CaCO<sub>3</sub>: drastic change in degradation pattern, showing three-step degradation with a large endotherm well below baseline.



**Figure 2** DTA curves of PVC and modified PVC. Addition of CaCO<sub>3</sub> does not produce any change in degradation pattern.

CaCO<sub>3</sub> does not change the degradation pattern of polyvinyl chloride (PVC) where initial dehydrohalogenation is strong. We have verified that the degradation pattern of PVC and polyethylene (PE) remain undisturbed with addition of CaCO<sub>3</sub> (Fig. 2). This behavior of CaCO<sub>3</sub> could be well exploited to make fire-resistant polyurethane. In fire propagation, the degradation step produces maximum heat and makes room for further fire propagation as well as degradation.<sup>5</sup> Generally, either pure CaCO<sub>3</sub> is added to polymer as a filler or CaCO<sub>3</sub> is added with diammonium phosphate in polymer as a fire-resistant additive.

We are not aware of any report that pure CaCO<sub>3</sub> could be added as a fire-resistant additive. The addition of CaCO<sub>3</sub> in PU acts like heat sink at higher temperature. The technique might be applicable to other nitrogen-containing polymers. The reason for this behavior is not known. It is possibly due to the presence of nitrogen in the polymer and the added calcium makes a difference at high temperature. To find out the reason for this behavior, a study is in progress and details will be published shortly.

Thanks are due to Dr. T. S. R. Prasada Rao, director of the Institute, for providing facilities and to M/S Krishna Products, Bombay, for supplying samples. The author is also grateful to Mr. S. K. Malhotra for providing thermograms.

## REFERENCES

1. S. D. Gehman, *Rubber Chem. Tech.*, **30**, 1202 (1957).
2. L. E. Nielsen, R. A. Wall, and P. G. Raymond, *SPE J.*, **11**, 22 (1955).
3. L. E. Nielsen, *Mechanical Properties of Polymers and Composite*, Vol. 1, Dekker, New York, 1974.
4. Qiang Fu and Guiheng Wang, *Polym. Internatl.*, **30**, 309 (1993).
5. *Encyclopedia of Polymer Science and Technology*, H. F. Mark, Ed., Wiley-Interscience, New York, 1987, Vol. 7, pp 81-194.
6. L. P. Cipriani and J. F. Hosler, *Mod. Plastics*, **45**, 406 (1967).
7. R. Zweidler and H. Hausermann, in *Encyclopedia of Chemical Technology*, 2nd ed., Vol. 3, Wiley-Interscience, New York, 1964, p. 738.
8. F. Rodriguez, *Principles of Polymer System*, 2nd ed., McGraw-Hill, Singapore, 1983, p. 261.
9. One-Step Urethane Foam, Bulletin F-40487, Union Carbide Corp., 1959.
10. I. A. Eldib, *Hydrocarbon Process. Petrol. Refiner*, **42**(12), 121 (1963).
11. C. Hepburn, *Polyurethane Elastomers*, Appl. Science, London, 1982.
12. P. Wright and A. Cumming, *Solid Polyurethane Elastomer*, MacLaren and Sons, London, 1968.
13. J. M. Buist and H. Gudgeon, *Advances in Polyurethane Technology*, MacLaren and Sons, London, 1969.
14. J. M. Jouany, C. Boudene, and R. Truhant, *The Physicogram as a Method for the Evaluation of Toxicity of Combustion Products in Controlled Ventilation Experiments*. Polymer Conference, Salt Lake City, 1976.
15. T. Morikawa, E. Yanai, and T. Nishina, *J. Fire Sci.*, **5**, 248 (1987).
16. Z. S. Petrović, I. Javni, and Ž. Jelčić, *Colloid Polym. Sci.*, **267**, 1077 (1989).
17. *Encyclopedia of Polymer Science and Technology*, H. F. Mark et al., Eds., Vol. 11, Wiley-Interscience, New York, 1969, pp. 514, 525, 555.
18. L. H. Sperling, N. Devia, and J. A. Manson, *J. Appl. Polym. Sci.*, **24**, 569 (1979).
19. J. A. Murray, H. C. Fischer, and R. W. Shade, DTA of Lime Stone, 32nd Annual Convention of National Lime Assoc., Virginia, USA, 1950.

Received October 14, 1993

Accepted November 7, 1993