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GASES EMITTED DURING THERMAL DECOMPOSITION OF A POLYPROPYLENE FILM AND A POLYURETHANE ADHESIVE

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Abstract

The thermal decomposition of a polypropylene film, a polyurethane adhesive, as well as a polypropylene coated with a polyurethane adhesive have been studied by a thermogravimetric (TG) analysis, at a heating rate of 5°C a minute with air flow. During the thermal analysis different decomposition steps which correspond to different weight loss rates were obtained on thermal curves. Gases were collected between the different decomposition steps and then analyzed. The results reported deal with the conversion of carbon into oxides and aldehydes–ketones, and also with that of nitrogen into hydrogen cyanide and isocyanates. The findings lead to a better understanding of the hazards and risks of toxic emissions that may be generated by the gas formation following heating of these materials.

Keywords: polymers, polypropylene film, polyurethane, TG

Introduction

The thermal behaviour of polymers is a subject of high interest because of their increased use in modern technology. It is necessary to heat them during the manufacture of polymer containing materials, their destruction by incineration, or their recycling.

Thus, before such treatments, we have to determine the best conditions of heating and the risks to the environment subsequent to the release of gases formed. We associated thermogravimetric techniques with that of analysis of the gases emitted during the thermal decomposition, within the temperature ranges corresponding to different decomposition rates. We analyzed two polymers: polypropylene and polyurethane, as well as polypropylene film coated with polyurethane adhesive.

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Experimental

Sample

The study was performed on typical packaging materials which may include polypropylene films and polyurethane adhesives. The polypropylene film was transparent. The polyurethane adhesive was delivered as a semi-rigid block with small cavities. The polypropylene film coated with polyurethane adhesive was stripped from the substrates by using an acid treatment. We were able to experimentally determine the proportion of the two polymers: for 100 mg of polypropylene film coated with adhesive, polyurethane represented 8 mg and the polypropylene film 92 mg.

Thermogravimetric analysis

The samples were cut with a pair of scissors into small fragments which then introduced into the platinum crucible of a TG – ADAMEL apparatus. The sample weights varied between 100 and 200 mg. The TG analysis was conducted at a heating rate of 5 deg·min^{-1}. An air flow drew the emitted gases towards impingers at an average rate of 30 ml a minute.

Gas sampling

The platinum crucible inside the TG apparatus oven is covered by a metallic funnel with an evacuation fitted with a three-way valve. This makes it possible to selectively feed the gas emission into one of the three impingers through a "Pulse pomp environment INC" pump.

The selection differed according to the nature of the collected gas.

– for acid gases (CO_2, HCN), the collection flasks contained a sodium hydroxide solution without carbonate, in which was placed a glass bubbler. A soda lime cartridge deprives air of its carbon dioxide before entry in the TG apparatus.

– The carbonyl compounds were collected on silica cartridges (Sep–pack C18) coated with 2,4-dinitrophenylhydrazine (DNPH) in acetonitrile [1].

– The isocyanates were collected in impingers charged with 1-(2-methoxyphenyl)piperazine in acetonitrile [2].

– For carbon monoxide assays, gas was collected in a teflon collection bag equipped with a valve.

Gas determination methods

Carbon dioxide fixed as sodium carbonate was assayed by a potentiometric method in the presence of excess sodium hydroxide.

– Hydrogen cyanide fixed as sodium cyanide was assayed by a visible spectrophotometric method according to the König reaction [3].

– Carbonyl compounds fixed as hydrazones were separated and assayed by high performance liquid chromatography.

– The isocyanates converted to stable derivatives by 1-(2-methoxyphenyl) piperazine were analyzed by high performance liquid chromatography.

– The carbon monoxide reacted on palladium and cacotheline, the derivative formed was determined by visible spectrophotometry [4].

Results and discussion

TG curves obtained from each sample are reproduced on Figs 1, 2 and 3. Assay results are shown in Tables 1 to 3.

The carbon conversion during thermal analysis was analysed by assaying the carbonyl compounds and carbon oxides (mono and dioxide). The ratio of aldehydes-ketones was very low. Formaldehyde and acetaldehyde were the most prevalent (Table 1). Carbon monoxide and dioxide formed simultaneously. Their formation depended on many concomitant factors:

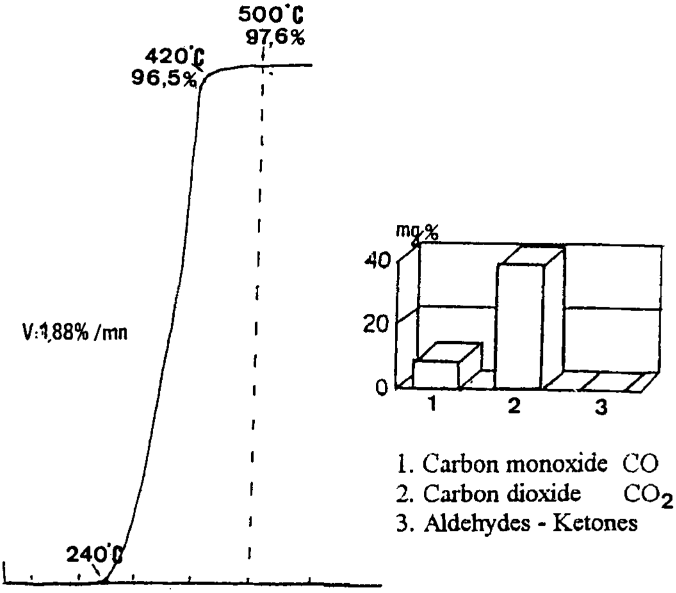


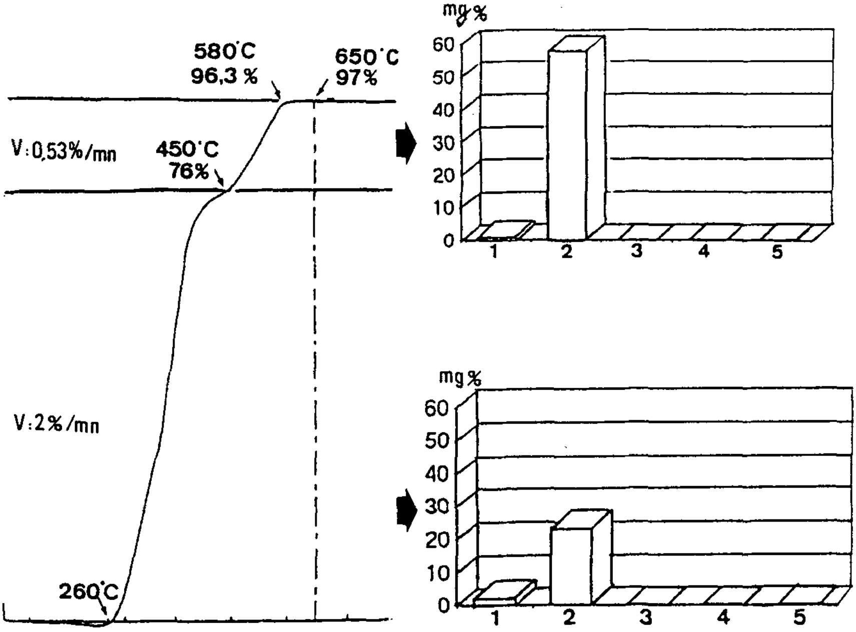
Fig. 1 Polypropylene

– the endogenous and exogenous oxygen ratio (for, an increase in air flow leads to an increase in the carbon dioxide ratio)

– the temperature

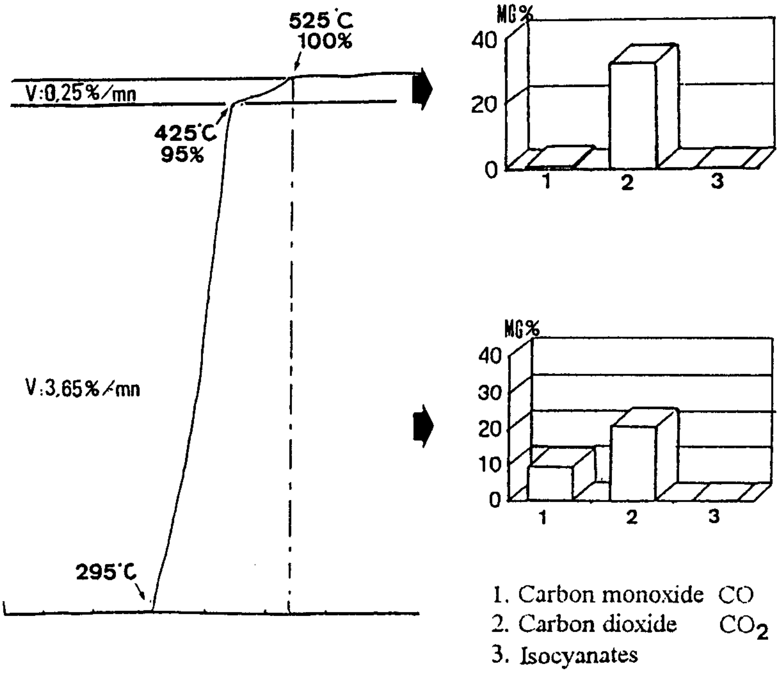
– the decomposition rate within a temperature range determined on the TG curve: the lower the rate, the more contact with O_2. This leads to a better combustion reaction and larger carbon dioxide formation.

We observed that, for both polyurethane and the polypropylene film coated with polyurethane adhesive, the amount of carbon dioxide formed was lower in the first collection zone (high decomposition rate) than in the second one (low decomposition rate). Therefore, the opposite occurred for carbon monoxide. Finally, the amount of carbon transformed into carbon monoxide and dioxide has been determined experimentally and separately for the two polymers and for the polypropylene film coated with polyurethane. For the latter, the experimental result obtained (Table 2) was higher than the total calculated from experimental results obtained on the original compounds (15.2 mg/100 mg).



1. Carbon monoxide CO
2. Carbon dioxide CO_2
3. Aldehydes - Ketones
4. Hydrogen cyanide HCN
5. Isocyanates

Fig. 2 Polyurethane



Hydrogen cyanide HCN: 0,009 MG%

Fig. 3 Polyurethane+polypropylene

Table 1 Aldehydes and ketones emitted during the thermalanalysis

Carbonyl compounds	Polypropylene µg/100 mg PP	Polyurethane µg/100 mg PUR
Formol	70	15
Acetaldehyde	10	16
Acrolein	7	2
Acetone	–	2
Propanal	13	7
2-trans-butenal	5	2.4
Isovaleraldehyde	0.1	4.8
Pentanal	–	3
Pentanone	–	7
Total	105	59

As concerns the nitrogen, only hydrogen cyanide and phenyl isocyanate have so far been quantitatively determined. The two forms correspond to a very

Table 2 The conversion of carbon into carbon monoxide and carbon dioxide

Sample	Collection zone / °C	Weight loss / %	Decomposition rate / %mm	CO mg/100mg of sample	CO_2 mg/100mg of sample	Carbon mg/100mg of sample
Polypropylene	200 to500	98	1.88	8.82	39.2	14.5
Polyurethane	250 to 450	76	2	2.35	23.5	
	450 to 650	21.3	0.53	1.22	57.9	
	Total	97.3	–	3.57	81.4	23.7
Polypropylene +Polyurethane	200 to 430	95	3.65	9.5	20.8	
	430 to 550	5	0.25	1	32.2	
	Total	100	–	10.5	53	19

Table 3 The conversion of nitrogen into hydrogen cyanide and isocyanates

Sample	Collection zone / °C	Weight loss / %	Decomposition rate %/mm	HCN µg/100 mg of sample	Phenyl isocyanate µg/100 mg of sample	Nitrogen N µg/100 mg of sample
Polyurethane	250 to 450	76	2	27	78.8	
	450 to 650	21.3	0.53	142	25.9	
	Total	97.3		169	105	100
Polyurethane +Polypropylene	200 to 430	95	3.65	ND	64	
	430 to 550	5	0.25	ND	4.3	
	Total			9	68.2	12.7

small ratio of total nitrogen, i.e. 3.87 mg for 100 mg of polyurethane and 0.306 mg for 100 mg of the polypropylene film coated with polyurethane adhesive. (These results were experimentally determined.) We observed that for 100 mg polyurethane, only 100 μg of nitrogen was found as hydrogen cyanide and phenyl isocyanate, and that for 100 mg of polypropylene film coated with polyurethane adhesive only 12.7 μg of nitrogen was found in two forms (Table 3). The largest part of nitrogen was probably emitted as other forms (amines, ammonia and nitrogen oxides).

Similarly, as for the carbon, we observed that the quantity of nitrogen found as hydrogen cyanide and phenyl isocyanate from a polypropylene film coated with a polyurethane adhesive was higher than the total calculated from experimental results obtained on the original compounds adhesive (8 μg/100 mg). This confirms the observation noted for the carbon compound. It seems that gaseous emissions from the two polymers combined differ from those of the original polymers degraded separately.

Concerning hydrogen cyanide, the amount found (0.169 mg for 100 mg of polyurethane) was small and did not agree with previously published results [5]: 0.95 mg for 100 mg of an expanded rigid polyurethane and 2.31 mg for 100 mg of an expanded flexible PU. But the polyurethane formulations vary as does the initial nitrogen ratio. We noted, as in the earlier work [5], that hydrogen cyanide formation was larger in the second zone of decomposition, which has the slower decomposition rate.

For the isocyanates, the major product was phenyl isocyanate. This result confirms the work of Renman *et al.* [6].

Conclusion

Our results show that thermal decomposition factors (temperature, weight-loss, decomposition rate) as well as the oxygen ratio act on toxic or dangerous gas emission. This shows the interest of analyzing gas emission during thermal analysis. One may determine the thermal behaviour of any material under specific conditions, and the constitution of gas emitted during decomposition. Gas emission analysis makes it possible to establish the toxic risks and the consequences for the environment. Evacuation systems or recycling processes may thereby be adjusted in order to decrease these risks.

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Zusammenfassung — Mittels TG wurden bei einer Aufheizgeschwindigkeit von 5°C/min im Luftstrom die thermischen Zersetzungen eines Polypropylenfilmes, eines Polyurethanhaftmittels und eines mit Polyurethanhaftmittel beschichteten Polypropylens untersucht. Während der Thermoanalyse erhielt man an den Thermokurven verschiedene Gewichtsverlustgeschwindigkeiten, die verschiedenen Zersetzungsschritten entsprechen. Zwischen den einzelnen Schritten wurden die Gase gesammelt und dann analysiert. Die erhaltenen Ergebnisse stehen für die Umwandlung von Kohlenstoff in Oxide und Aldehyde-Ketone sowie für die Umwandlung von Stickstoff in Zyanwasserstoff und Isozyanate. Die Ergebnisse führen zu einem besseren Verständnis der Gefahren und Risiken toxischer Emissionen, die bei der Gasentwicklung im Anschluß an ein Erhitzen dieser Substanzen erzeugt werden.