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DSC STUDY OF THERMAL DECOMPOSITION OF PEROXIDE AND AZO DERIVATIVE MIXTURES IN THE PRESENCE OF LDPE

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The thermal decompositions of azodicarbamide (AZDICA), 2,2'-azobisisobutyronitrile (AIBN), benzoyl peroxide (Bz_2O_2), dicumyl peroxide (DICUP) and α,α'-bis(t.-butylperoxy)-m/p-diisopropylbenzene (PEROXIMON F) in binary and ternary mixtures containing low density polyethylene (LDPE) have been studied by means of DSC alone. Binary mixtures including 2% by weight of Bz_2O_2 or DICUP develop a decomposition heat of 64.2 and 59.1 J/g mixture, respectively.These values are higher than those measured for the decomposition of the pure peroxides. In all the ternary mixtures studied, containing LDPE, a peroxide and an azoderivative, the absolute enthalpic values attributed to the peroxide are lower than those obtained from the LDPE-peroxide mixtures. The enthalpy changes observed have been interpreted on the basis of interactions of the peroxide radicals with the polymer support and with the azo derivative.

In previous works, the thermal decompositions of Bz_2O_2 DICUP and PEROXIMON [1] and the behaviour of Bz_2O_2 and AIBN mixtures [2] were studied by means of DSC.

The aim of this work is to study, by means of DSC, the thermal decompositions of azodicarbonamide and its mixtures with the above-mentioned peroxides in the presence of low-density polyethylene (LDPE). Some experiments have been carried out on mixtures containing AIBN instead of AZDICA.

Experimental

The following reactants were used:

LDPE as grains having the following characteristics: $\bar{M}_w = 156700$, as measured by means of GPC; crystallinity = 29.7%, as measured by means of DSC. Benzoyl

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peroxide purified by crystallization of a Carlo Erba product: % peroxide >98. Dicumyl peroxide, AKZO Chemie: % peroxide = 95. α,α'-bis(t.-Butylperoxy)-m/p-diisopropylbenzene, Montefluos S.p.A., containing 35% para and 65% meta isomer: % peroxide = 95. 2,2′-Azobisisobutyronitrile, Fluka, 98% purity. Azodicarbonamide, Fluka, 98% purity.

DICUP, PEROXIMON F, AIBN and AZDICA were used without further purification.

DSC curves were obtained on a Perkin–Elmer DSC–2 instrument linked to a Perkin–Elmer Thermal Analysis Data Station 3600. Samples of 3–6 mg of the compounds or their mixtures were weighed in aluminium pans on the balance of a Perkin–Elmer TGS–2 instrument. The pans were closed by covers in which a small hole had been made to allow gas generated by reagent decomposition to escape.

The DSC instrument was preset at 308 K and the sample was heated to 67 K at 5 deg/min (dynamic test). Indium was used as the standard for calibrating the temperature axis and the enthalpy output. All experiments were carried out in nitrogen atmosphere.

Results

Table 1 summarizes the characteristics of the DSC curves of the pure compounds AIBN, AZDICA, Bz_2O_2, DICUP and PEROXIMON F [1].

The DSC instrument was present at 308 K and the sample was heated to 67 K at exothermic (458–488 K, duration: 6 min), gives $\Delta H = -171$ kJ/mole, which is more negative than that measured by other authors ($\Delta H = -130$ kJ/mole) [3] Two endothermic peaks, due probably to transformations of the primary decomposition products of AZDICA, follows. The first of these peaks (495–552.5 K, duration:

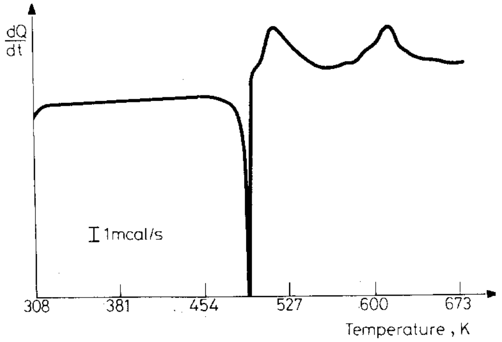


Fig. 1 DSC curve of AZDICA at 5 deg/min

11.5 min) yields $\Delta H = 133$ kJ/mole, and the second (559–650 K, duration: 18.2 min) $\Delta H = 145$ kJ/mole.

Table 2 lists the enthalpy values of the individual additives heated in the presence of LDPE. In the case of AZDICA, the DSC curve shows only one endothermic peak instead of the two found in the DSC curve of the pure compound. Column V shows the ΔH values calculated on the basis of the data in Table 1. It may be noticed that for the peroxides the found ΔH are clearly higher in absolute value than those calculated. In the case of AZDICA, the found ΔH are lower in absolute value than those calculated for either the exothermic or the endothermic peak. In the case of AIBN, the found values are in good accordance with the calculated heats.

Figure 2 shows a typical DSC curve of a DICUP–LDPE mixture.

Data on the behaviour of peroxide + azo derivative + LDPE systems are given in Table 3. The DSC curves of these 3-component systems are characterized by 3 peaks, in addition to that due to the polymer fusion. A typical example is reported in Fig. 3. The first peak is attributed to the component which decomposes at the lowest temperature, without taking into account possible phenomena of induced decomposition. The expected values for the compound decomposition, calculated

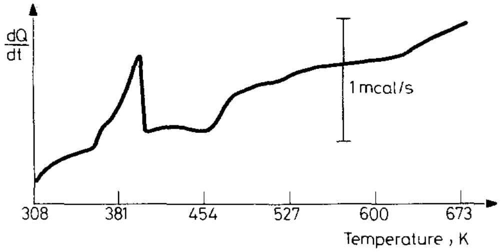


Fig. 2 DSC curve of a DICUP–LDPE mixture at 5 deg/min. Molar ratio DICUP/LDPE = 1/473

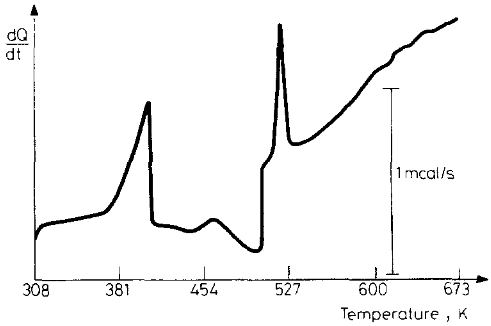


Fig. 3 DSC curve of a DICUP–AZDICA–LDPE mixture at 5 deg/min. Molar ratio DICUP/AZDICA/LDPE = 1/11.6/424.7

Table 1 Results from DSC analysis of azoderivatives and peroxides decompositions. Range of scanned temperature: 308–673 K. Heating rate: 5 deg/min

Compound	1st peak			2nd peak			3rd peak		
	range, K	time, min	ΔH, kJ/mole	range, K	time, min	ΔH, kJ/mole	range, K	time, min	ΔH, kJ/mole
AIBN	355–376	4.2	− 16.5	380–409	5.8	−115.6			
AZDICA	458–488	6.0	−171.0	495–552	11.4	133.0	559–650	18.2	144.9
Bz_2O_2	372–434	12.4	−399.3						
DICUP	395–461	13.2	−218.3						
PEROXIMON F	403–471	13.6	−318.0						

Table 2 Results from DSC analysis of the thermal behaviour of binary mixtures. The first peak is due to LDPE fusion. Range of scanned temperature: 308–673 K. Heating rate: 5 deg/min

Mixture mmoles in 100 g		2nd peak					3rd peak				
		range, K	time, min	ΔH_{found}, J/g mixture	$\Delta H_{calc.}$*, J/g mixture	$\Delta\Delta H$**, J/g mixture	range, K	time min	ΔH_{found}, J/g mixture	$\Delta H_{calc.}$*, J/g mixture	$\Delta\Delta H$**, J/g mixture
LDPE 3500	Bz_2O_2 8.3	464–498	6.8	−64.2	−33.0	31.2					
LDPE 3500	DICUP 7.4	431–474	8.6	−59.1	−16.1	42.9					
LDPE 3500	AZDICA 17.2	467–507	8.0	− 8.3	−29.4	−21.1	525–536	2.0	3.3	22.9	19.6
LDPE 3536	AIBN 6.1	429–502	14.6	− 7.4	− 8.0	− 0.6	558–583	5.0	−4.8		

* ΔH values calculated on the basis of the pure peroxide or azoderivative

** $\Delta H_{calc.} - \Delta H_{found}$

Table 3 Results from DSC analysis of the thermal behaviour of ternary mixtures. The first peak is due to LDPE fusion. Range of scanned temperature: 308–673 K. Heating rate: 5 deg/min

Mixture mmoles in 100 g						2nd peak	
			range, K	time, min	ΔH_{found}, J/g mixture	$\Delta H_{calc. as DICUP}$, J/g mixture	$\Delta H_{calc. as DICUP + LDPE}$, J/g mixture
LDPE	DICUP	AZDICA					
3429	7.4	17.2	412–464	10.4	−13.7	−16.1	−59.1
3357	7.4	34.4	417–462	9.0	−12.4	−16.1	−59.1
3143	7.4	86.0	415–460	9.0	−17.0	−16.1	−59.1
						$\Delta H_{calc. as PEROXIMON F}$ J/g mixture	
LDPE	PEROXIMON F	AZDICA					
3429	5.9	17.2	474–505	6.2	− 4.3	−18.8	
3143	5.9	86.0	408–472	12.8	−27.9	−18.8	
						$\Delta H_{calc. as AIBN}$ J/g mixture	$\Delta H_{calc. as AIBN + LDPE}$ J/g mixture
LDPE	DICUP	AIBN					
3500	3.7	6.1	429–471	8.4	−10.9	− 8.0	−7.4
3429	7.4	12.2	415–468	10.6	−23.1	−16.1	
LDPE	PEROXIMON F	AIBN					
3429	5.9	12.2	429–477	9.6	−32.7	−16.1	

Table 3 continued

Mixture mmoles in 100 g			3rd peak				
			range, K	time, min	ΔH_{found}, J/g mixture	$\Delta H_{calc.\,as\,AZDICA}$, J/g mixture	$\Delta H_{calc.\,as\,DICUP+LDPE}$ J/g mixture
LDPE	DICUP	AZDICA					
3429	7.4	17.2	466–509	8.6	−11.2	− 29.4	− 8.3
3357	7.4	34.4	466–508	8.4	−36.2	− 59.0	
3143	7.4	86.0	466–503	7.4	−85.6	−147.4	
LDPE	PEROXIMON F	AZDICA					
3429	5.9	17.2	505–534	5.8	−12.2	− 29.4	− 8.3
3143	5.9	86.0	478–502	4.8	−60.1	−147.4	
						$\Delta H_{calc.\,as\,DICUP}$ J/g mixture	$\Delta H_{calc.\,as\,DICUP+LDPE}$ J/g mixture
LDPEI	DICUP	AIBN					
3500	3.7	6.1	471–497	5.2	− 9.7	− 8.1	
3429	7.4	12.2	475–538	12.6	−18.6	− 16.1	−59.1
						$\Delta H_{calc.\,as\,PEROXIMON F}$ J/g mixture	
LDPE	PEROXIMON F	AIBN					
3429	5.9	12.2	485–563	15.6	−17.3	− 18.8	

Table 3 continued

	Mixture mmoles in 100 g		4th peak				
			range, K	time, min	ΔH_{found}, J/g mixture	$\Delta H_{\text{calc. as AZDICA}}$, J/g mixture	$\Delta H_{\text{calc. as AZDICA + LDPE}}$, J/g mixture
LDPE	DICUP	AZDICA					
3429	7.4	17.2	524–541	3.4	5.3	22.9	3.3
3357	7.4	34.4	514–528	2.8	15.4	45.9	
3143	7.4	86.0	506–527	4.2	40.0	114.6	
LDPE	PEROXIMON F	AZDICA					
3429	5.9	17.2				22.9	3.3
3143	5.9	86.0	504–525	4.2	44.4	114.6	
LDPE	DICUP	AIBN					
3500	3.7	6.1					
3429	7.4	12.2					
LDPE	PEROXIMON F	AIBN					
3429	5.9	12.2					

on the basis of the measurements on the single product or its mixtures with LDPE, are reported in columns V and VI, respectively. Columns X and XI, XV and XVI show the corresponding data for the peak attributed to AZDICA.

Discussion

In the presence of the polymer, AIBN, Bz_2O_2 and DICUP start to decompose at temperatures higher than those measured for the pure compounds, whereas little change is observed in the case of AZDICA.

The higher ΔH values measured for the peroxide decompositions in the presence of LDPE than in its absence must be related with the reactions which can take place between the primary radicals formed from the peroxide decomposition and the polyhydrocarbon (PH). The simplest scheme is that which requires LDPE cross-linking:

$$\mathrm{ROOR} \rightarrow 2\,\mathrm{RO}^{\cdot} \tag{I}$$

$$\mathrm{RO}^{\cdot} + \mathrm{PH} \rightarrow \mathrm{P}^{\cdot} + \mathrm{ROH} \tag{II}$$

$$2\,\mathrm{P}^{\cdot} \rightarrow \mathrm{P-P} \tag{III}$$

In this case reaction (II) is exothermic and a ΔH value in the range -33 to -55 kJ/mole is foreseeable, depending on whether a primary or a secondary hydrogen reacts [4].

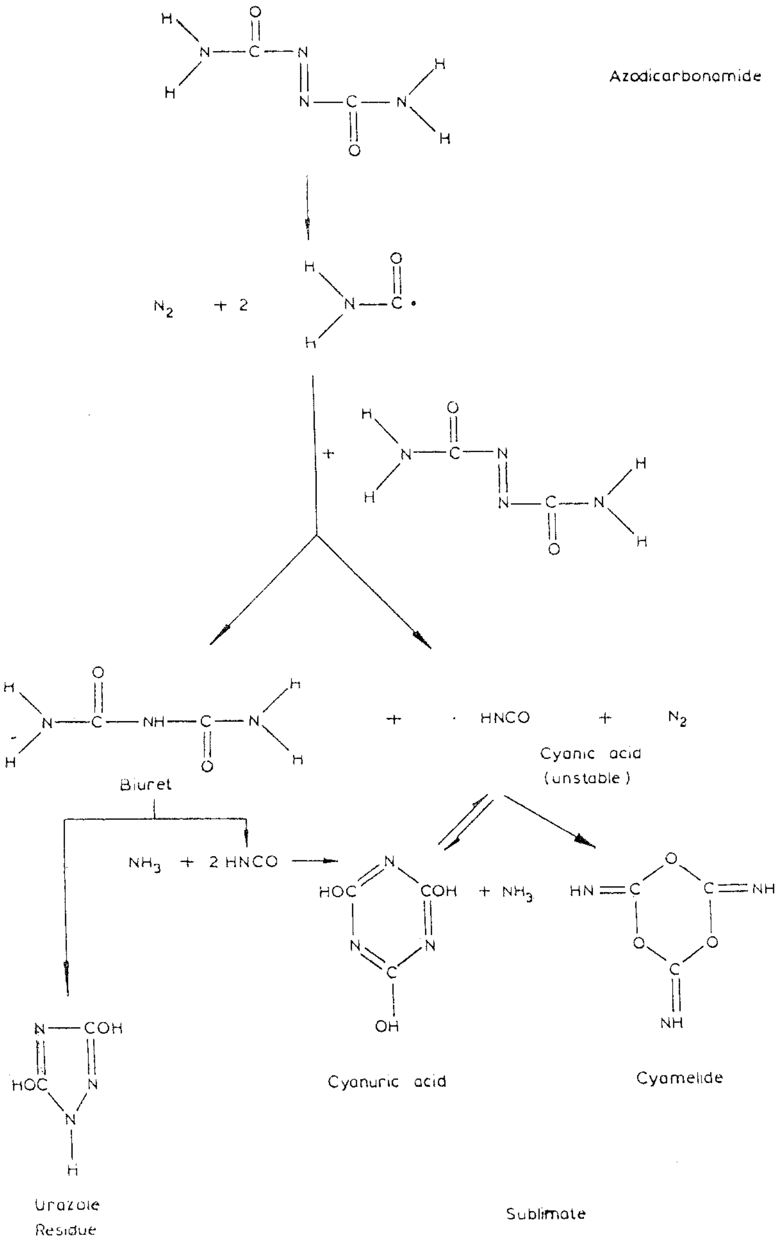
The absolute ΔH values found for the LDPE–AZDICA mixture are clearly lower than those calculated; the difference between the calculated and found values is -21.0 J/g mixtures for the second peak and $+19.6$ J/g mixture for the third peak. These differences are probably related to a possible change in the chemism of the decomposition reaction.

Bhatti et al. [5] state that AZDICA decomposes according to the following scheme (see p. 1198).

Bhatti et al. [6] agree with Reed [7] that AZDICA decomposition in an open flask produces a solid residue containing 2% of biuret, whereas under the surface of liquid paraffin the biuret content increases to 34%.

These data suggest that in the presence of paraffin, and therefore probably in the presence of polyethylene too, the reactions which lead from biuret to urazole, cyanuric acid and cyamelide, with resulting change in the ΔH values observed, are stopped or limited (see Scheme).

The data reported in Table 3 show that the lower absolute ΔH values than those expected on the basis of the peroxide-LDPE system correspond to the second peak, attributable to the peroxide.


Azodicarbonamide
N2 + 2
HNCO + N2
Cyanic acid
(unstable)
Biuret
NH3 + 2 HNCO
+ NH3
Cyanuric acid
Cyamelide
Urazole
Residue
Sublimate

The DSC curves obtained for the AIBN–DICUP–LDPE and AIBN–PEROXIMON F–LDPE mixtures are characterized by a second peak attributable to AIBN and a third peak attributed to the peroxide. In these cases too, the absolute ΔH values are comparable with those of the pure compounds as obtained from Table 1, but lower than those reported in Table 2 for peroxide-LDPE mixtures. In contrast, the absolute ΔH values attributable to AZDICA in the peroxide-AZDICA–LDPE mixtures correspond to those reported in Table 2.

The low absolute ΔH values attributable to the peroxides decomposing in the presence of an azo derivative are probably related to reactions of the alkoxy radicals with the decomposition products of the azo derivatives.

Conclusions

LDPE markedly affects the ΔH values and the temperatures of decomposition of the peroxides and azo derivatives studied.

The decompositions of Bz_2O_2 and DICUP in the presence of LDPE are characterized by absolute ΔH values higher than those due to the peroxides alone.

AIBN and AZDICA, under the same conditions, give absolute ΔH values which are comparable and lower, respectively, than those obtained in the absence of the polymer.

The exothermic peaks due to the decompositions of Bz_2O_2, DICUP or AIBN in their mixtures with LDPE start at temperatures higher than those characteristic of the individual reagents.

The ΔH values attributed to the peroxides in the ternary mixtures, which are lower in absolute terms than those obtained in the absence of azo derivative, are probably due to an interaction of the primary radicals produced in the peroxide decomposition with the radicals or the final products formed in the azo derivative decomposition.

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Zusammenfassung — Die thermische Zersetzung von Azodicarbamid, 2,2'-Azo-bisisobutyronitril, Benzoylperoxid, Dicumylperoxid und α,α'-Bis(t-butylperoxy)-m/p-diisopropylbenzen in Polyethylen niedriger Dichte enthaltenden binären und ternären Gemischen wurden mittels DSC untersucht. Für 2 Gew.-% Bz_2O_2 bzw. DICUP enthaltende binäre Gemische wurden Zersetzungswärmen von 64,2 bzw. 59,1 J/g erhalten. Diese Werte sind höher als die für die Zersetzung der reinen Peroxide gemessenen. Bei allen hier untersuchten Mischungen von LDPE, einem Peroxid und einem Azoderivat liegen die absoluten Enthalpiewerte höher als die den Peroxiden zuzuschreibenden Werte. Die beobachteten Enthalpieänderungen wurden basierend auf Wechselwirkungen der Peroxidradikale mit dem Polymerträger und dem Azoderivat interpretiert.

Резюме — Методом ДСК изучено термическое разложение азодикарбамида, 2,2-азобисизобутиронитрила, перекиси бензоила, перекиси дикумола и α, α'-бис(трет-бутилперокси)-м/п-диизопропилбензола в двойных и тройных системах; содержащих полиэтилен с низкой плотностью. Двойные смеси, содержащие 2 весовых процента перекиси бензоила или перекиси дикумола, показывают теплоту разложения, соответственно, 64,2 и 59,1 дж на г смеси. Эти значения выше таковых, измеренных при разложении чистых перекисей. Во всех тройных смесях, содержащих полиэтилен низкой плотности, перекись и какое-либо азопроизводное, абсолютные значения энтальпии отнесенные к перекиси, ниже таковых полученных для смесей полиэтилен-перекись. Наблюдаемые изменения энтальпии объяснены на основе взаимодействия перекисных радикалов с полимерной основой и с азопроизводным.