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DTA IDENTIFICATION OF POLYCAPROLACTONE

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Polycaprolactone (PCL) is a new material used in orthopedics. It is characterized by an endothermic melting peak at about 61°C, an endothermic decomposition peak at about 380°C and an exothermic peak at about 453°C. These three observed phenomena and the corresponding thermodynamic data made it easily possible to identify PCL among the other polymers previously examined with Differential Thermal Analysis (DTA).

Introduction

Polycaprolactones, (2-Oxepanone homopolymer $(-O-(CH_2)_5-CO-)_n$), or its blends with polyurethanes, is a new material used in orthopedics for confection of small splints applied on sensitive areas [1, 2]. It becomes malleable and stretched after a few minutes in hot water (60°), and remains supple for four minutes (adequate for moulding and application on the skin according to patient limb shape). The cast is certainly the most common orthopedic material. Unfortunately it is heavy and does not last when placed in presence of a liquid. It must be used in thick coatings and is not washable. PCL avoids these inconveniences. The patients appreciate its comfort, its lightness and its cleanness. PCL standards were studied by DTA in order to distinguish this family from the other ones previously described [3–5]. One may thus identify unknown samples used, for example, in orthopedics.

Equipment and material used

We used DTA-Netzsch type 6.233.0-02 with a heating rate of 2 deg/min (as high as 600°), air circulation, and sample about 150 mg.
Polycaprolactone chosen as reference are Polysar C (white plate, 3 mm thickness) and Orfit S (pink plate, 2 mm thickness, alveolate), supplied by Promoplastiques - France.

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Five unknown samples (splints) were studied by DTA: *A* (white, 3 mm thickness), *B* (white, 3 mm thickness), *C* (white, 3 mm thickness, alveolate), *D* (pink, 3 mm thickness, alveolate), *E* (white, 2 mm thickness).

Reference materials for DTA

Two DTA curves of PCL samples chosen as reference materials are shown in Fig. 1. In Table 1 the average temperature of each peak are represented. These values were computed from 14 assays and 2 different samples.

Table 1 Polycaprolactone chosen as reference

Sample	Assay	Residue after pyrolysis (%)	Melting endo peak (°C)	Decomp. endo peak (°C)	Exo peak (°C)
Polysar C	1	15.7	61	380	446
	2	14.5	62	380	456
	3	15.1	61	379	445
	4	15.4	62	380	450
	5	16.1	61	383	434
	6	16.5	62	375	438
	7	*	58	*	*
	Average	15.6	61.0	379.5	444.8
Standard	Deviation	0.715	1.41	2.59	7.96
Orfit S	1	0.1	62	381	464
	2	0	61	382	465
	3	0	62	384	463
	4	0	62	384	467
	5	0	61	379	462
	6	0.3	64	377	444
	7	*	59	*	*
	Average	~0	61.6	381.2	460.8
Standard	Deviation		1.51	2.79	8.42
Average from 14 assays and 2 samples			61.3	380.3	452.8
Standard deviation			1.44	2.71	11.44
Relative standard deviation (%)			2.35	0.712	2.53
Polysar C (After soxhlet Extraction)	1	0	61	397	455
	2	0.4	60	388	464
	Average	0.2	60.5	392.5	459.5

* Assay to make melting conspicuous

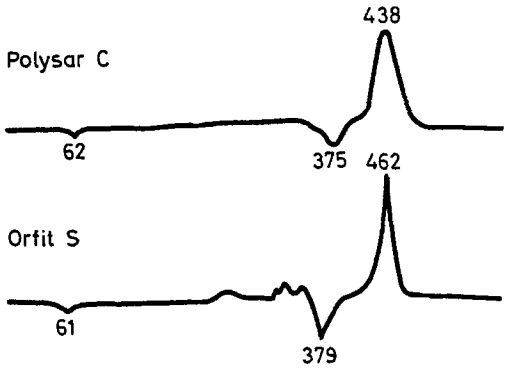

Fig. 1 DTA curves of polycaprolactone chosen as reference

After benzene extraction by Soxhlet method of Polysar C and evaporation of benzene, the residue was submitted to DTA analysis, we obtained no residue after pyrolysing. Temperatures of melting peak, endothermic decomposition peak and exothermic peak were near those of original Polysar C. The filler (15.6%) present in Polysar C have practically no influence on thermodynamic data.

Polycaprolactone was characterized by the presence of an endothermic peak attributed to melting at 61° (on cooling it appears as an exothermic crystallization peak), and in addition an endothermic decomposition peak at 380° and an exothermic peak at 450° could be observed. Enthalpy values of endothermic melting peak is not so large for identification.

Characterization of PCL among previously studied plastic materials

Plastic materials are classified in three groups. The first group (polyolefines, polyamides, polyethers, terephtalic polyesters, polyvinylalcohol, ethylene vinyl acetate copolymers) is characterized by the presence of an endothermic melting peak, the presence or the absence of an endothermic decomposition peak and the presence of one or several exothermic peaks of which the last is considered.

The second group (polyvinyl chloride, polyvinyl acetate, polyvinyl butyral, polymethacrylic esters, polystyrene and copolymers) is characterized by the absence of an endothermic melting peak, the presence of an endothermic decomposition peak, the presence of one or several exothermic peaks of which the first and the last are considered.

The third group (polyacrylonitrile, PVC high viscosity, polyimides, polydimethylsiloxane, cellulose) is characterized by the absence of en-

dothermic peak and the presence of several exothermic peaks of which the first and the last are considered.

Polycaprolactone belongs to the first group, the polymers of which have a melting point above 100° except ethylene vinyl acetate copolymer (EVAC) for 27% PVAC (polyvinylacetate), which has an endothermic melting peak at 75°; furthermore, EVAC has no endothermic decomposition peak.

Polycaprolactone is different from all the first group polymers, because it has a lower melting point.

Identification of unknown samples

Figure 2 presents the DTA curves of the five unkown samples used in orthopedics and Table 2 contains the collected results. Other techniques can be used such as IR method (film or powder), or X-ray method but DTA don't request preliminary pulverisation or solubilisation.

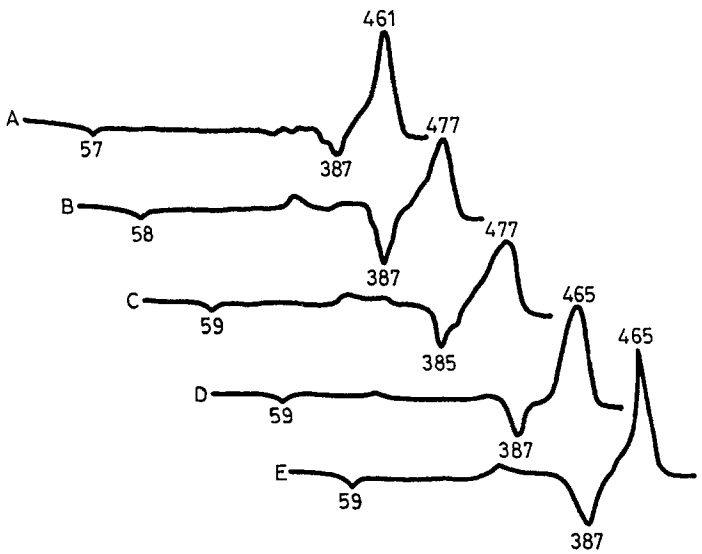

Fig. 2 Unknown samples

Samples *A, B, C, D, E* were polycaprolactone because endothermic peaks (melting and decomposition) are very near those of polycaprolactone chosen as reference; exothermic peak also. In all cases, temperatures of references peaks are between m ± 2SD of unknown samples. If such a match is not observed another method has to be applied for an identification [3].

Table 2 Unknow samples

Sample	Assay	Residue after pyrolysis (%)	Melting endo peak (°C)	Decomp. endo peak (°C)	Exo peak (°C)
A	1	12.2	59	391	452
	2	12.3	57	387	461
	3	12.5	59	382	454
	4	*	60	*	*
	Average	12.3	58.8	386.7	455.7
Standard	Deviation	0.15	1.26	4.51	4.72
B	1	0.5	62	389	470
	2	0.2	58	387	477
	3	0.3	61	387	467
	4	0.1	59	390	470
	5	*	59	*	*
	Average	0.28	59.8	388.3	471.0
Standard	Deviation	0.17	1.64	1.50	4.24
C	1	0	59	394	478
	2	0	59	385	477
	3	*	60	*	*
	Average	0	59.3	389.5	477.5
Standard	Deviation		0.58		
D	1	20.9	55	387	460
	2	20.8	59	387	465
	3	20.5	63	385	468
	4	*	60	*	*
	Average	20.7	59.3	386.3	464.3
Standard	Deviation	0.21	3.30	1.15	4.04
E	1	0	59	387	465
	2	0	58	389	463
	3	0	58	392	466
	4	*	59	*	*
	Average	0	58.5	389.3	464.7
Standard	Deviation	0	0.58	2.52	1.53

* Assay to make melting conspicuous

Saponification and esterification indexes

Table 3 shows the indexes computed for standard and unknown samples. Three of them (samples *B, C, E*) had high values. This may be due to the presence of copolymere reacting with potash.

Table 3 Saponification and esterification index

Sample	Saponification index (KOH mg · g^{-1})	Esterification index (KOH mg · g^{-1})	Residue after pyrolysis (%)
PCL chosen as reference			
Orfit S	402	402	0
Polysar C	376	373	15.6
Polysar C (after soxhlet extraction)	438	438	0
Unknown			
A	396	396	12.3
B	529	529	0.3
C	549	549	0
D	291	290	20.7
E	528	528	0

(Each number is the computed average from three or four assays)

Conclusion

The DTA curve of Polycaprolactone is distinct from that of the other polymers previously studied. DTA makes it possible to characterize orthopedic unknown samples.

* * *

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References

1 T. Pennet, Eur. Patent No. 263, 552 (1986).
2 T. Pennet, Belg. Patent No. 905, 981 (1986).
3 J. Kaloustian, A. M. Pauli and J. Pastor, Analusis, 15 (1987) 101.

4 J. Kaloustian, A. M. Pauli and J. Pastor, J. Thermal Anal., 34 (1988) 465.
5 J. Kaloustian, A. M. Pauli and J. Pastor, Proceedings of the 15th JEEP (Grenoble), (1989) 63.

Zusammenfassung — Polycaprolacton ist ein neuartiger Kunststoff, der in der Orthopädie als Knochenersatz Verwendung findet. Die Charakterisierung und Identifizierung kann durch thermoanalytische Messungen (DTA) auf Grund von endothermen Vorgängen bei 61 und 380°C und eines exothermen Vorgangs bei 453°C erfolgen.