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THERMOANALYTICAL EVALUATION OF READILY AVAILABLE REFERENCE POLYMERS
Thermoplastics

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Abstract

A commercial set of polymers has been characterized by TG-DTA, DSC, TMA, FTIR spectroscopy and X-ray diffraction analysis (XRD). Thermal and mechanical stability, as well as the polymer glass transition temperature, T_g, and melt temperature, T_m, have been documented. There is a good correlation between measured T_g and T_m values and published data. The degree of polymer crystallinity for polyethylene has been verified by XRD. The credibility and stability of these reference polymers is based on a comparison of their thermal properties, over a wide range of temperatures from two versions of a reference set, published in 1979 (A) and 1994 (B). The thermal properties and crystallinity of these polymers have stood the test of time and are reliable, readily available and consistent.

Keywords: reference polymers

Introduction

There is an ongoing need in the plastics industries for readily available reference polymers. Appropriate and well characterized polymers are needed as technical society (ASTM) [1–2], academic and industrial references for a variety of applications, such as engineering processing [3] and design of plastics [4], composites [5] and coatings. Property and temperature calibration of thermoanalytical techniques, with an established polymer set, are of utmost importance in presenting reliable data and developing quality assurance protocols [6]. Control charting thermal methods with quality polymers can lead to ISO certification.

The objectives of this study are to: select appropriate and readily available reference polymers for thermal analysis; develop a data base of characteristic thermal properties; determine the precision and accuracy of a thermal measurement based on a number of thermoanalytical methods. The selection of reliable polymers is dependent on the stability of the polymers over a period of time.

The Society of Plastics Engineers sponsors an Educational Resin Kit® that meets the stability and the broad polymer base criteria, see Table 1 [7]. The Resin Kit® distributed in 1979 contained 43 polymers, while the 1994 version had 50 polymers. There is a wide variety of polystyrenes, olefins and nylons in these kits. A

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Table 1 List of polymers, Resin Kit (sponsored by the Society of Plastics Engineers, Inc.) set A, 1979 and set B, 1994

Resin Kit #		Society of Plastics Engineers Educational Resin Kit	
A 1979	B 1994	Polymer	Code
1	1	polystyrene general purpose	PS
2	2	polystyrene medium impact	PS
3	3	polystyrene high impact	PS
	4	styrene acrylonitrile	SAN
5	5	acrylonitrile–butadiene–styrene	ABS
6	6	ABS medium impact	
7	7	ABS high impact	
8	8	styrene butadiene	SBR
9	9	acrylic	
10	10	modified acrylic	
11	11	cellulose acetate	CA
12	12	cellulose acetate butyrate	CAB
13	13	cellulose acetate propionate	CAP
14	14	nylon (tranparent)	
15	15	nylon 66	Ny66
16	16	nylon 6	Ny6
17	17	thermoplastic polyester	PBT
18	18	thermoplastic polyester	PETG
19	19	phenylene oxide	PO
20	20	polycarbonate	PC
21	21	polysulfone	PS
22	22	polybutylene	PB
23	23	ionomer	
24	24	low density polythylene	LDPE
25	25	high density polythylene	HDPE
26	26	polypropylene copolymer	EP
27	27	polypropylene	PP
28	28	polyaryl-ether	
29	29	flexible polyvinyl chloride	PVC
30	30	rigid polyvinyl chloride	PVC
31	31	acetal resin	
32	32	acetal resin copolymer	
33	33	polyphenylene sulfide	
34	34	ethylene vinyl acetate	EVA
35	35	synthetic elastomer	
36	36	urethane elastomer	
37	37	urethane elastomer	
	38	polypropylene/flame retardant	

Table 1 Continued

Resin Kit #		Society of Plastics Engineers Educational Resin Kit	
A 1979	B 1994	Polymer	Code
39	39	polyester elastomer	
	40	ABS+flame retardant	
41	41	polyallomer	ABS-PVC
42	42	styrenic terpolymer	
43	43	polymethyl pentene	
	44	PP+talc	
	45	PP+$CaCO_3$	
	46	PP+mica	
	47	nylon 66+glass	
	48	thermoplastic rubber	
	49	medium polyethylene	
	50	ABS/nylon alloy	MDPE
40		ABS-PVC alloy	

number of polymers selected for this study were crystalline, since structural variation can be monitored by XRD.

Experimental

The Resin Kit® crystalline polymers were examined as plaques in an XRD system [8]. The XRD conditions included examining the reference polymer with copper k-alpha radiation, at room temperature (22°C) after calibrating the system with alpha-quartz.

A robotic TG/DTA system [9] was operated as follows: 10–15 mg of sample, heating rate 20°C min^{-1}, nitrogen flow rate at 100 cc min^{-1} and the evaluation of the calibrant, calcium oxalate hydrate and ASTM temperature calibration E1582 [10].

The TMA [9] experimental conditions were: 2–5 mg sample, 2–4 mm in height, heating rate 5°C min^{-1} in a nitrogen atmosphere, gas flow rate 100 cc min^{-1} and an ASTM temperature calibration E1363 [11].

The DSC [12] method used 5–15 mg sample, heating rate 5°C min^{-1} in a nitrogen atmosphere, gas flow rate 50 cc min^{-1} and heat flow calibration employing ASTM E794 [11].

A piece of selected polymers from set A and B were pressed at 500 to 3500 pounds over four hours. The approximate thickness of the pressed polymers are 0.5 mm. Infrared spectra of the pressed polymers were collected with a FTIR spectrometer [13]. Each sample was scanned 200 times at a 4 cm^{-1} resolution. A standard polystyrene infrared curve was used to calibrate the FTIR response.

Results and discussion

The polymers in the two resin kits, set A, 1979 and set B, 1994 are in most cases, from the same material [7]. Therefore, comparing set A and B is a way of evaluating the specific resin kit polymer stored for fifteen years at or near room temperature under laboratory conditions. All of the XRD, FTIR and thermal data was collected in 1996, some DSC data was reported in 1980 [14].

The percent standard deviation, std.dev.%, in all of the TG tables was based on all trials for the cited polymer. This statistical value was used to ascertain the overall variation between sets A and B.

Polyethylenes and polypropylenes

The structural stability of the olefins, polyethylene (PE) and polypropylene (PP) was tested by examining the XRD structure, Table 2. The XRD% crystallinity varied from 96% for high density polyethylene (HDPE) to 40% for ethylene vinyl acetate copolymer (EVA). There was less than 4% relative change for three of the four polyethylenes studied. Medium density polyethylene (MDPE) was not available in set A.

Table 2 Characterization of crystalline polymers by XRD*

Polymer	RK#	Peak area		XRD	set A/B
		set A	set B	% crystallinity	relative %
		d=4.15 Å			
HDPE	25	27100	28100	96	96
MDPE	49	na	23100	82	na
LDPE	24	17300	17800	64	96
EVA	34	11100	11300	40	98
		d=3.91 Å			
Acetal	31	22100	23000		96
Acetal copolymer	32	23200	25100		92
		d=4.33+4.14+3.84 Å			
nylon 6	16	21900	23700		92
nylon 66	15	21600	23800		91
nylon 66+glass	47	na	5710		na

RK# – Resin Kit#, kit sponsored by the Society of Plastics Engineers
Peak area – counts/sec/degree 2θ
* – all data collected in 1996
Set A – Resin Kit, 1979
Set B – Resin Kit, 1994
d – interplanar distance, major diffraction peak(s) in Å
na – not available.

The FTIR curves of low density polyethylene and homopolymer polypropylene from set A and B were identical, that is, there was no sign of polymer aging, Figs 1 and 2.

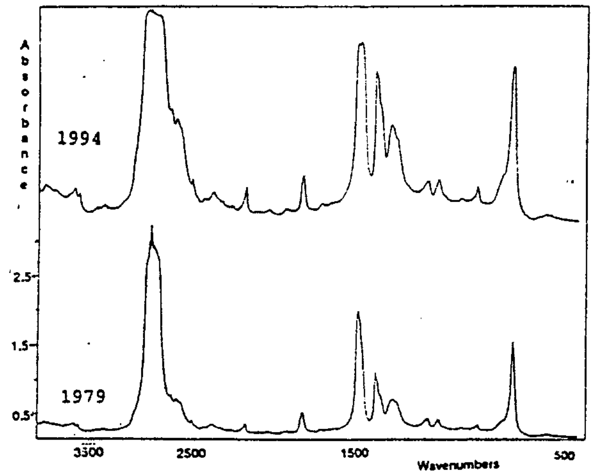

Fig. 1 FTIR of low density polyethylene, #24, set A and set B

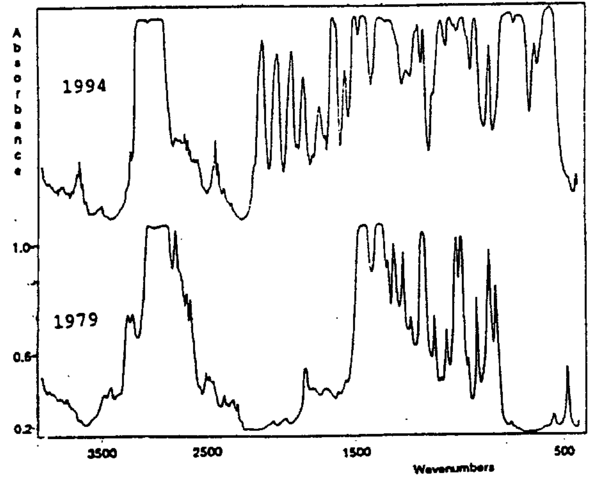

Fig. 2 FTIR of polypropylene homopolymer, #27, set A and set B

The interplanar distances, *d* Å, for polypropylene from 3.15 to 6.39 Å were identical for set A and set B (Table 2). The XRD structures of PE and PP did not vary from set A to set B, a 15-year period, which is supported by the FTIR data.

The TG decomposition temperatures, as measured by the extrapolated onset temperatures, T_{0e}, for PE and PP had less than a 2% standard deviation, Table 3. The repeatability of HDPE set A and set B was excellent, however, the sets did differ by as much as 17°C with an overall 1.87% standard deviation.

Table 3 Polymer decomposition of polyethylene, polypropylene and styrene polymers by TG

Polymer	RK#	trial	TG* set A T_{oe} /°C	TG* set B T_{oe} /°C	Std. Dev. %
1 Polyethylene – low density	24	1	459	454	0.68
2		2	457	452	
3 Polyethylene – high density	25	1	475	458	1.87
4		2	473	460	
5 Polypropylene – copolymer	26	1	447	447	0.19
6		2	449	448	
7		3	448	449	
8 Polyethylene – homopolymer	27	1	432	429	0.32
9		2	429	430	
10 Polystyrene – general purpose	1	1	403	408	0.59
11		2	404	407	
12 Polystyrene – medium impact	2	1	na	421	0.00
13		2	na	421	
14 Polystyrene – high impact	3	1	420	422	0.31
15		2	421	423	
16 Styrene acrylonitrile – copolymer	4	1	403	403	0.12
17		2	403	404	
18 Acrylonitrile-butadiene-styrene-transparent	5	1	399	399	0.24
19		2	400	401	
20 Acrylonitrile-butadiene-styrene-med. impact	6	1	410	412	0.32
21		2	409	411	
22 Acrylonitrile-butadiene-styrene-high impact	7	1	409	413	0.44
23		2	410	412	
24 Styrene butadiene – copolymer	8	1	424	424	0.22
25		2	426	425	

RK# – Resin kit#
TG* – all data collected in 1996
Set A – Resin Kit, SPE, 1979
Set B – Resin Kit, SPE, 1994
T_{oe} – extrapolated onset temperature, °C.

The melt temperatures, T_m, of the polyethylenes are summarized in Table 5. There is a good correlation between various thermal methods that can determine the T_m, that is, the extrapolated onset temperature by DSC [14], peak temperature by DTA and extrapolated onset temperature by TMA. The coefficient of expansion, COE, below the T_m is also recorded in Table 5.

Table 4 Polymer decomposition of acetal and nylon polymers by TG

Polymer	RK#	trial	TG* set A T_{oe} /°C	TG* set B T_{oe} /°C	Std. Dev. %
1 Acetal resin – homopolymer	31	1		359	0.42
2		2		356	
3		3		357	
4 Acetal resin – copolymer	32	1		377	0.26
5		2		378	
6		3		379	
7 Nylon – transparent	14	1	454	455	0.27
8		2	452	453	
9		3	454	452	
10 Nylon – type 66	15	1	419	412	0.68
11		2	412	414	
12		3	417	416	
13 Nylon – type 6	16	1	432	429	0.32
14		2	429	430	
15		3	431	432	

RK# – Resin kit#
TG* – all data collected in 1996
Set A – Resin Kit, SPE, 1979
Set B – Resin Kit, SPE, 1994
T_{oe} – extrapolated onset temperature, °C.

The melt temperatures of polypropylenes, homopolymer, copolymer and with fillers is given in Table 5. There is a good correlation between the DSC (set A) and DTA (set B) T_m values. The TMA T_m values for the homopolymer and copolymer were typically higher than the DTA values. The DTA method is sensing the polymer melt temperature prior to the low stress TMA mechanical polymer melt temperature. An alternate interpretation is that the DTA heating rate of 20°C min^{-1} and the TMA 5°C min^{-1} is influencing the measured values. The PP filled polymers had similar DTA and TMA T_m values.

Polystyrenes

The FTIR structures of 'high impact' polystyrene (impact properties are cited in the Resin Kit® company literature [7]) from set A and B were identical, Fig. 3. There were no additional IR peaks for the two polystyrenes. The polystyrenes in the Resin Kit® are not crystalline.

The TG of styrene and styrene co- or ter-polymers (styrene acrylonitrile copolymer), SAN and acrylonitrile butadiene styrene terpolymer, ABS, are presented in

Table 5 Characterization of polymers by DSC, DTA and TMA*

		Transition temperature/°C					
		DSC	DTA	TMA			
Polymer	RK#	Set A	Set B				
		T_m, T_{oe}	T_m, T_p	T_g, T_{oe}	T_t, T_{oe}	T_m, T_{oe}	COE
1 HDPE	25	121	123			127	120
2 MDPE	49	na	121			126	115
3 LDPE	24	91	93			99	136
4 EVA	34	84	88			87	93
5 PP	27	145	147			154	
6 PP copolymer	26	133	137			147	
7 PP+flame retardant	38	na	151			153	
8 PP+talc	44	na	152			154	
9 PP+calcite	45	na	153			154	
10 PP+mica	46	na	151			153	
11 PS-general purpose	1			90	136		54
12 PS-medium impact	2			90	140		56
13 PS-high impact	3			84	140		57
14 ABS-medium impact	6			96	142		55
15 ABS-high impact	7			92	141		52
16 SAN-copolymer	4			98	144		53
17 SB-copolymer	8			68	111		103
18 Acetal	31			42			91
19 Acetal-copolymer	32			65			80
20 Acetal-copolymer	32			64			78
21 Nylon 6	16			51			34
22 Nylon 66	15			44			30
23 Nylon 66+glass	47			40			13

* – all data collected in 1996
RK# – Resin Kit sponsored by the Society of Plastics Engineers, Inc.
Set A – Resin Kit, 1979
Set B – Resin Kit, 1994
T_g – glass transition temperature, °C
T_m – melting temperature, °C
T_t – transition temperature, marked change in CEO, °C
COE – coefficent of linear expansion (mm/mm/°C)
T_{oe} – extrapolated onset temperature, °C
T_p – peak temperature, °C
na – not available.

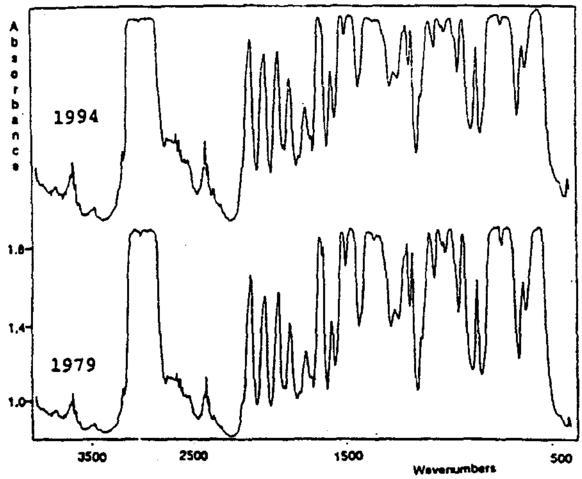

Fig. 3 FTIR of high impact polystyrene, #4, set A and set B

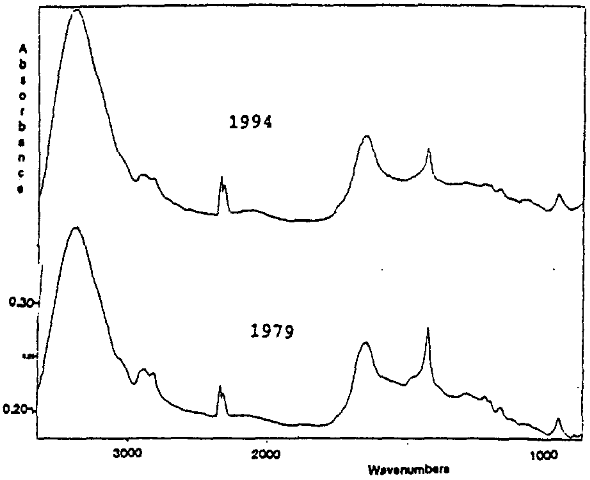

Fig. 4 FTIR of nylon 66, #16, set A and set B

Table 3. The relative overall % standard deviation for these polymers was less than 1 % for sets A and B. Three of the eight styrene polymers had T_{0e} values from 399 to 408°C, two polymers from 409 to 413°C and three polymers from 420 to 425°C. High impact PS and the SB copolymer were the most thermally stable.

The 'high impact' polystyrene (PS) and styrene butadiene (SB) copolymer had the lowest TMA T_g, Table 5, 84 and 68°C, respectively. The other polystyrenes had T_g values from 90 to 98°C. The COE values were essentially the same, with the SB copolymer the exception. A transition temperature, T_t, was noted in all the styrene polymers at 136 to 144°C. The SB copolymer was again the exception with a T_t of 111°C.

Acetal polymers

The acetal homopolymer and copolymer XRD structure varied by less than 8% for set A and B, Table 2. The TG decomposition temperatures had less than 0.5% standard deviation for set B polymers, Table 4. The acetal copolymer T_g and COE values were repeatable, Table 5.

Polyamides: Nylons

The XRD structure of nylon 6 and 66 varied slightly from set A to set B (Table 2). The variation was 8–9% for the aged period. The addition of 33%w glass to nylon 66 (67%w) reduced the peak area (relative crystallinity) to 24% of the pure nylon 66. The addition of the glass has diminished the crystalline content in Nylon 66.

The FTIR structures of nylon 66 from set A and B were identical (Fig. 4). TG of the nylons is summarized in Table 4. The overall % standard deviation was less than 1% for these three nylons. Again, this implies marked room temperature stability of the nylons over the 15-year period, 1979 to 1994.

The TMA of nylon 6, 66 and 66 with glass are cited in Table 5. The glass filler significantly lowered the coefficient of linear expansion, COE.

Conclusions

The SPE educational Resin Kit® is a viable source of reference polymers. The more recent kit has 50 polymers that are readily available at a low cost per polymer.

The crystalline polymers, olefins, acetals and nylons have been characterized by XRD and the relative percent crystallinity has varied at <10% over the 15-year period from 1979 (set A) to 1994 (set B). The FTIR curves of a styrene polymer, a polyethylene, a polypropylene and a nylon confirm their storage stability from set A to set B.

More than half of the available polymers (set B) have been characterized by TG. Decomposition temperatures varied by less than 1% standard deviation, or typically <5°C at 400°C. DSC (set A, 1980) and DTA (set B, 1996) polymer melt temperatures were in good agreement.

A number of polymers evaluated in this study by thermoanalytical and structural methods are recommended as reference or standard polymers: polyethylenes, polypropylenes, polystyrenes, nylons and acetals.

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