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Oxidative behavior of polymers by thermogravimetric analysis, differential thermal analysis and pressure differential scanning calorimetry

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Abstract

Oxidative behavior of commercial engineering plastics, polyolefins and elastomers has been evaluated by simultaneous thermogravimetric analysis (TGA)–differential thermal analysis (DTA) and pressure differential scanning calorimetry (PDSC). There is a good correlation between the measured stability by PDSC in oxygen and DTA/TGA in air and nitrogen for olefin polymers. The thermo-oxidative properties of engineering plastics, polyolefins and elastomers are reliable and precise.

Glass-filled Nylon 66 and reinforced polypropylene were studied in an air oven at 300°C as a function of time by Fourier transform infrared (FTIR) spectroscopy. The mechanism for thermal oxidation was different for these two polymers. Polyolefin oxidation was delineated by rapid carbonyl formation, while Nylon 66 showed minimum carbonyl in the FTIR.

An interesting outcome of this study is that polyethylene and polypropylene have significantly high heats of combustion. At high temperatures and pressures, it appears that these polymers can be used as sources of fuel. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Polymers; Thermogravimetric analysis

1. Introduction

The engineering plastics studied represent those synthetic polymers that are capable of being formed into load-bearing shapes and that have high performance properties which permit them to be used in the same manner as more traditional materials [1–3]. Higher mechanical properties are associated with these polymers that show enhanced thermal, chemical, electrical and oxidative stabilities.

The elastomers evaluated in this study represent high-profile seal and gasket-type polymers. They were included to give a broader perspective to the polymer oxidation testing described in this research.

There continues to be an ongoing need in academic or industrial polymer research for reliable and precise oxidation tests of engineering thermoplastics, polyolefins and elastomers. A key factor in establishing new oxidation tests is the selection of appropriate polymers from a single source. The polymers from the ResinKit Company, Society of Plastics Engineers (SPE) Education Kit, were used and are described in detail elsewhere [4,5]. A number of polymers from this resource have been characterized by TGA-DTA, TGA, differential scanning calorimetry and thermal mechanical analysis in an inert nitrogen atmosphere [5]. The thermal properties of these polymers were reliable and consistent. The oxidative stabilities of the olefin reference polymers in this SPE kit were also evaluated by DTA in air and PDSC in oxygen [6–8].

The determination of oxidation induction time (OIT) by differential thermal analysis, DSC and

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TGA was reviewed by Bair [9,10]. The OIT of polyethylene, as a film, powder or insulated wire, has been determined and it was observed that thin films acted as the optimum sample.

Various thermal-oxidative induction time methods were described by Bair and form the basis of the new ASTM E1858-97, 'OIT of Hydrocarbons by DSC and PDSC' [6,7].

The new ASTM standard test method, E1858, was used to determine the oxidative behavior of the reference polymers. The OIT at selected isothermal temperatures and oxygen pressures measured the polymer oxidation properties [7]. The OIT of a number of polyolefins is precise. The OIT protocol was used to verify a new DTA-TGA air-oxidation temperature test which defines the oxidation onset temperature (OOT) during a programmed heating of the polymer [8].

Bair discussed the technique where a polymer sample is heated at a programmed heating rate in oxygen, at atmospheric or an elevated pressure [9,10]. The most effective antioxidant system produced the highest degradation temperature. An OOT method is currently under study by ASTM E37 on 'Thermal Methods' [8]. Differentiating polymer oxidative stability by OIT is more effective than by OOT. The isothermal OIT method takes into account the degradation rate. The scanning OOT method is somewhat confounded, since the degradation rate increases rapidly with temperature.

TGA was also used to determine an 'OIT' [9,10]. Polyethylene containing an antioxidant exhibited an induction period prior to a weight gain. The oxidation induction period is typically proportional to the type and amount of antioxidant. Polyethylene with 0.03% of a phenolic antioxidant increased the induction period by 33 min. The TGA curves were otherwise identical.

The degradation mechanism, oxidative or thermal, varied widely for the polymers studied by DSC or DTA/TGA. Two Nylon 66 polymers and two polypropylenes were further studied under isothermal temperature conditions in an air oven and the resulting polymer film was monitored by FTIR spectroscopy.

The energetics of oxidation and thermal degradation of polypropylene has been extensively studied [9,10]. In an oxidizing atmosphere polypropylene can undergo oxidative cross-linking reactions followed by

polymer degradation as chain scission. Thermal scission of the C–C chain bonds is accompanied by a transfer of hydrogen at the site of the scission, and followed by a decomposition of the polymer. For polypropylene, the hydrogen on the tertiary carbon is more reactive and is abstracted. The methyl group is small and does not hinder a hydrogen transfer. This mechanism leads to chain fragmentation and rarely yields a monomer [11]. The resulting hydrocarbon polymer residue will be highly oxidized, noted by an enhanced carbonyl absorption in the Infrared spectra of polypropylene [12].

Nylon 66 degrades, both thermally and oxidatively, to yield water, carbon dioxide and ammonia [13]. Kamerbeek [14] suggests the following reactions to elucidate observed thermal-oxidative degradation properties: two carbonyl end groups react to form a condensation product, carbon dioxide and water. A carbonyl group can yield branched structures with $>C=N$ and water [14]. Also two amino end groups could react to form a condensation product and ammonia. It is also possible that the latter reaction could yield branching through the reaction of a secondary amine with a carboxylic end group. The FTIR spectra of the Nylon 6,6 films were compared to the spectra before, and after, exposure to a high temperature air environment [15].

2. Experimental procedures

A TAI 910 pressure differential scanning calorimeter was used to determine the OIT, ASTM E1858-97. The PDSC procedure is described in detail in the ASTM standard [6,7].

A Seiko-Haake RTG 220, thermogravimetric analyzer (TGA)-differential thermal analyzer (DTA) was used for the air oxidation study. The experimental conditions are as follows: 10 mg sample size, 250 ml/min air-flow rate, 10°C/min heating rate, the maximum temperature was 500°C and the sample holder comprised aluminum and platinum pans. The polymer melt temperature, DTA OOT, the exothermic oxidation onset temperature, the TGA onset temperature, and the derivative TGA peak temperature were the parameters recorded, tabulated and compared.

A Mattson 2000 FTIR microscope was used to analyze the polymers exposed in an air-flow oven at

300°C. The samples were exposed for different periods of time at the high temperature and then the effect of oxidative degradation was recorded by FTIR spectroscopy

The SPE sponsored Educational ResinKit was used as a resource for the polymers studied here and in other publications [4–6].

3. Results and discussion

A scanning temperature technique by TGA-DTA ranked the oxidative stability of the engineering plastics and elastomers in an air environment (see Tables 1 and 2). In general, there is a good correlation between the derivative peak TGA temperature and the DTA peak temperature. Pan type, aluminum or platinum, produced only minor differences in values.

Some of the crystalline polymers had significantly lower TGA extrapolated onset temperatures in air when compared to their values in nitrogen (see Tables 1–3). Polyphenylene sulfide was the most oxidatively (air) stable crystalline polymer. The Nylon 66 polymers and the acetal polymers degraded thermally

(endothermic decomposition) in air. The urethane elastomers were significantly more oxidatively (air) stable than the synthetic elastomer or the thermoplastic rubber, Table 1.

The oxidative behavior of non-crystalline engineering plastics by the scanning TGA-DTA technique is summarized in Table 2. Polycarbonate and polysulfone were the most stable among the polymers studied. Polyvinyl chloride, both flexible and rigid version, were the least oxidatively stable. The non-crystalline polymers had moderate changes in the TGA extrapolated onset temperatures in air versus their values in nitrogen (see Tables 2 and 3).

Only a select number of the polymers examined by TGA-DTA were also evaluated by isothermal PDSC (see Table 3 and Figs. 1–6). High-density polyethylene and mica-filled polypropylene were previously studied by the PDSC technique and their OIT values were in excellent agreement [6]. The polyacetals, homopolymer and copolymer, along with high-density polyethylene were the most oxidatively stable under high-pressure oxygen at 175°C. It is interesting to note that the acetals and polyethylene were more stable in nitrogen than in air. They were strongly attacked by

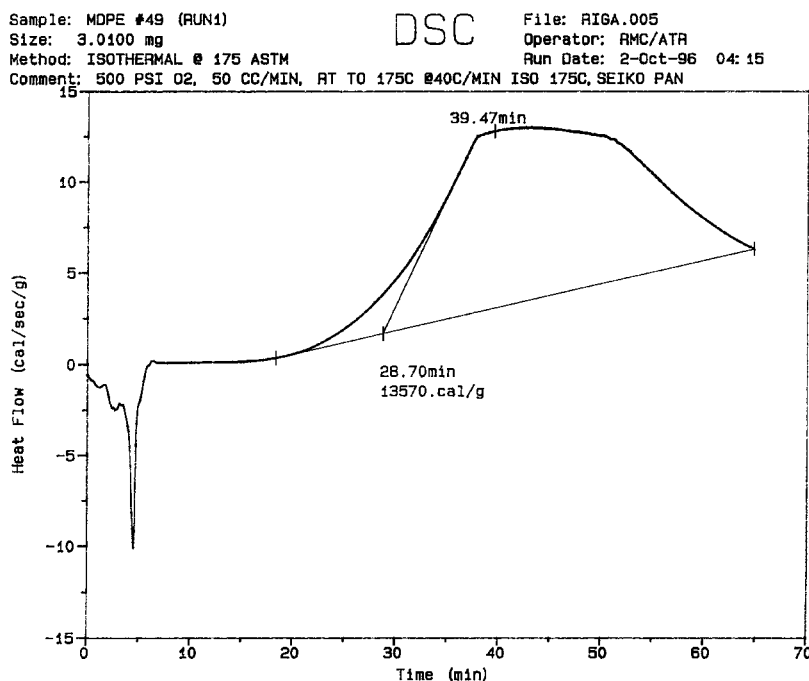


Fig. 1. PDSC of medium-density polyethylene, MDPE, SPE ResinKit #49.

Table 1
Oxidative behavior of engineering plastics and elastomers TGA and DTA: crystalline polymers and elastomers

	ResKit # ^b	TGA, T_{0r} air ^c	DTGA, T_{pr} air ^d	DTA, $T_{0=OOT}$ air ^e	DTA, T_p air ^f	TGA ave T_0 N ₂ (lit)	TGA, wt% residue air/500°C ^g	Pan type ^h
A. Crystalline polymers								
1	25	297	420	216	420	459	2.9	Pt
		393	444	377	439		1.7	Al
2		348	388	228	396		6.0	Pt
		296	386	234	389		5.2	Al
3	15	382	455		447 ^a		9.0	Pt
4	47	396	449		436 ^a	414	38.5	Pt
5	31	255	293		293 ^a	357	0.0	Pt
		269	314		322 ^a		0.0	Al
6	32	283	330		333 ^a	378	0.4	Pt
		292	328		323 ^a		0.2	Al
7	33	481			490		94.4	Pt
		489			492		96.4	Al
B. Elastomeric polymers								
1	36	315	423	265	423 ^a		16.2	Pt
		314	369	315	405		12.7	Al
2	37	320	348	360	404		10.2	Pt
		321	392		382		15.7	Al
3	35	270	439	300	439 ^a		10.4	Pt
4	48	260	442		431 ^a		12.1	Al
		262	407	281	407		17.7	Pt
		268	408	305	411		18.4	Al

^a DTA endotherm.

^b The Resinkit Company, Woonsocket, RI 02895.

^c Thermogravimetric analysis. Temperature in air atmosphere, heating rate of 10°C/min, and heated to 500°C.

^d Derivative TGA peak temperature (°C).

^e DTA extrapolated onset temperature (°C).

^f DTA peak temperature (°C).

^g TGA weight % residue in air at 500°C.

^h Pan type: aluminum (Al); platinum (Pt).

Table 2
Oxidative behavior of plastics by TGA and DTA: non-crystalline polymers^a

	Non-crystalline polymers	ResKit #	TGA temp		TGA wt%		DTGA	DTA		Pan
			T ₀ /°C	residue	T _p	OOT		T _p		
1	Polystyrene high impact	3	378	2.2	416	388	422	Pt		
			340	1.9	403	377	403	Al		
2	Acrylonitrile–butadiene–styrene terpolymer high impact	7	377	10.9	412		408 ^a	Pt		
			370	10.1	414		408 ^a	Al		
3	Acrylonitrile–butadiene–styrene terpolymer medium impact	6	383	12.0	412	381	416	Pt		
			371	11.0	411		408	Al		
4	Styrene–acrylonitrile copolymer	9	359	4.0	401		398 ^a	Pt		
			355	4.4	402		401 ^a	Al		
5	Polyvinyl chloride flexible	29	238	12.2	290	288	460	Pt		
			244	13.6	289	289		Al		
6	Polyvinyl chloride rigid	30	284	19.3	294	284	298	Pt		
			254	19.6	293	245	296 ^a	Al		
7	Polysulfone	21	437	87.9		413	456	Pt		
			485	88.8		453	474	Al		
8	Polycarbonate	20	463	45.2	474	377	456	Pt		
			457	55.3	478	383	464	Al		

^a Legend same as in Table 1.

Table 3
Oxidative behavior of engineering plastics by PDSC

Polymers	ResKit #	PDSC at 175°C		Heat of combustion ^d (kJ/g) (O ₂)	DTA	TGA-a T _o (air)	TGA-b ave T _o N ₂ (lit) ^e	TGA T _o =b-a= [N ₂ -air] ^f	% ^g
		average							
		OIT (O ₂) ^a	peak time (min) (O ₂) ^b						
1 Acetal homopolymer	31	58	59	0.27	293	255	357	102	28
2 Acetal copolymer	32	26	30	1.4	333	283	378	95	25
3 Polyethylene – high density	25	32	43	49	420	297	459	162	35
4 Acrylonitrile–butadiene–styrene terpolymer – high impact	7	6.3	10	0.62	408	377	413	36	8.7
5 Polystyrene – high impact	3	6.1	6.7	0.48	388	378	423	45	11
6 Polypropylene – mica filled	46	7.5	9.2	56	391	382	425	43	10
7 Synthetic elastomer–styrene block copolymer	35	4.4	4.6	2.9	300	270	321	51	16
8 Nylon 66 – glass filled	47	3.6	4.1	0.54	436	396	414	18	4.3
9 Polyvinyl chloride – rigid	30	1.1	2.4	0.36	284	284	295	11	3.7

^a Average of two tests at 175°C and 500 psig oxygen.

^b Average of two tests at 175°C and 500 psig oxygen.

^c OIT values cited in literature in Ref. [6].

^d Average of two tests at 175°C and 500 psig oxygen.

^e Average values cited in Ref. [5].

^f Relative T_o temperature of the polymer in nitrogen vs. air.

^g Percentage change nitrogen vs. air.

Sample: LOW DENSITY POLYETHYLENE (RUN2) DSC File: RIGA.002
 Size: 3.3400 mg Operator: RMC/ATR
 Method: ISOTHERMAL @ 175 ASTM Run Date: 1-Oct-96 02:44
 Comment: 500 PSI O2, 50 CC/MIN, RT TO 175C @40C/MIN ISO 175C, SEIKO PAN

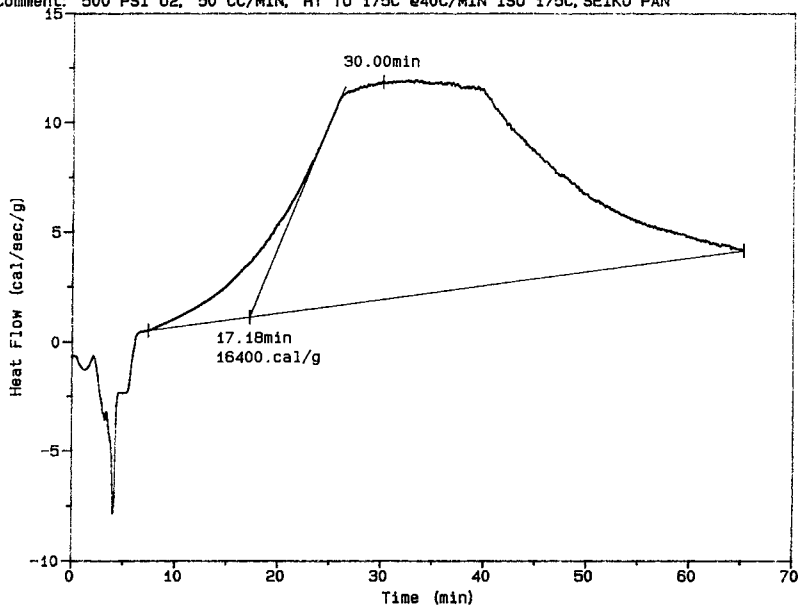


Fig. 2. PDSC of low-density polyethylene, LDPE, SPE ResinKit # 24.

Sample: EVA #34 (RUN1) DSC File: RIGA.006
 Size: 2.8700 mg Operator: RMC/ATR
 Method: ISOTHERMAL @ 175 ASTM Run Date: 2-Oct-96 07:18
 Comment: 500 PSI O2, 50 CC/MIN, RT TO 175C @40C/MIN ISO 175C, SEIKO PAN

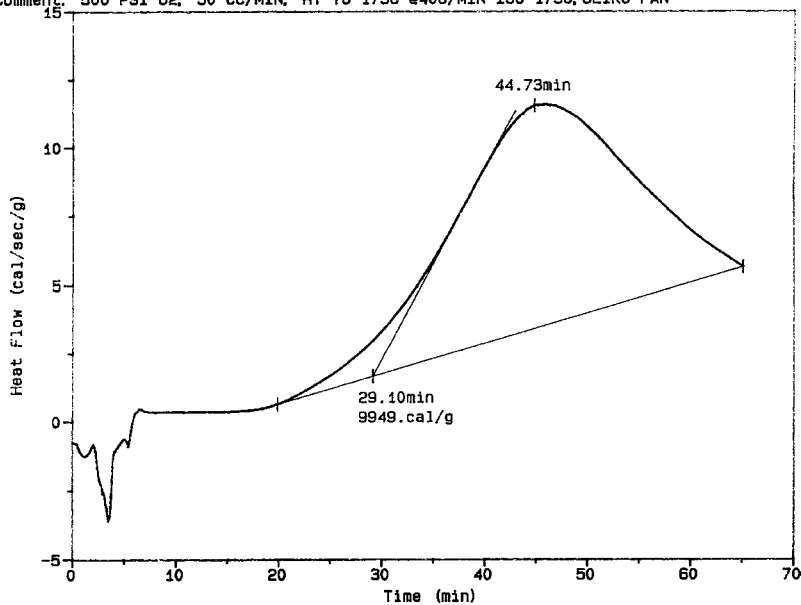


Fig. 3. PDSC of ethylene vinyl acetate copolymer, EVA, SPE ResinKit # 34.

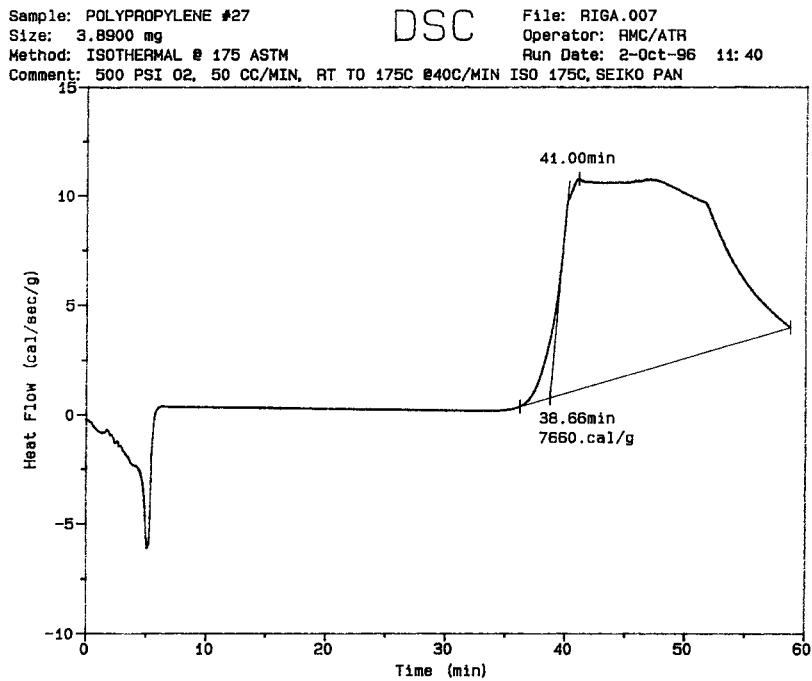


Fig. 4. PDSC of polypropylene, PP, ResinKit # 27.

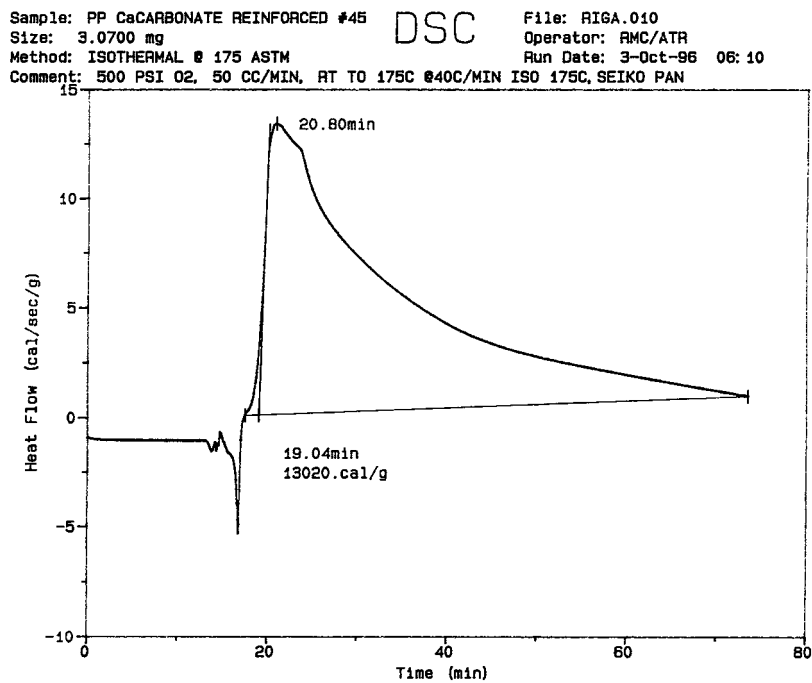


Fig. 5. PDSC of polypropylene with calcium carbonate, ResinKit # 45.

Sample: PP MICA REINFORCED #46
 Size: 3.2100 mg
 Method: ISOTHERMAL @ 175 ASTM
 Comment: 500 PSI O2, 50 CC/MIN, RT TO 175C @40C/MIN ISO 175C, SEIKO PAN

DSC

File: RIGA.012
 Operator: RMC/ATR
 Run Date: 4-Oct-96 08:56

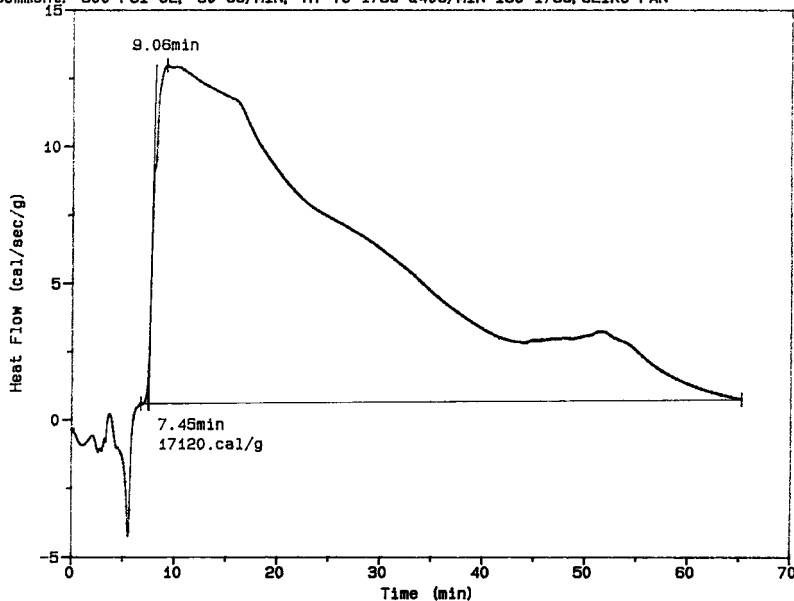


Fig. 6. PDSC of polypropylene with mica, ResinKit # 46.

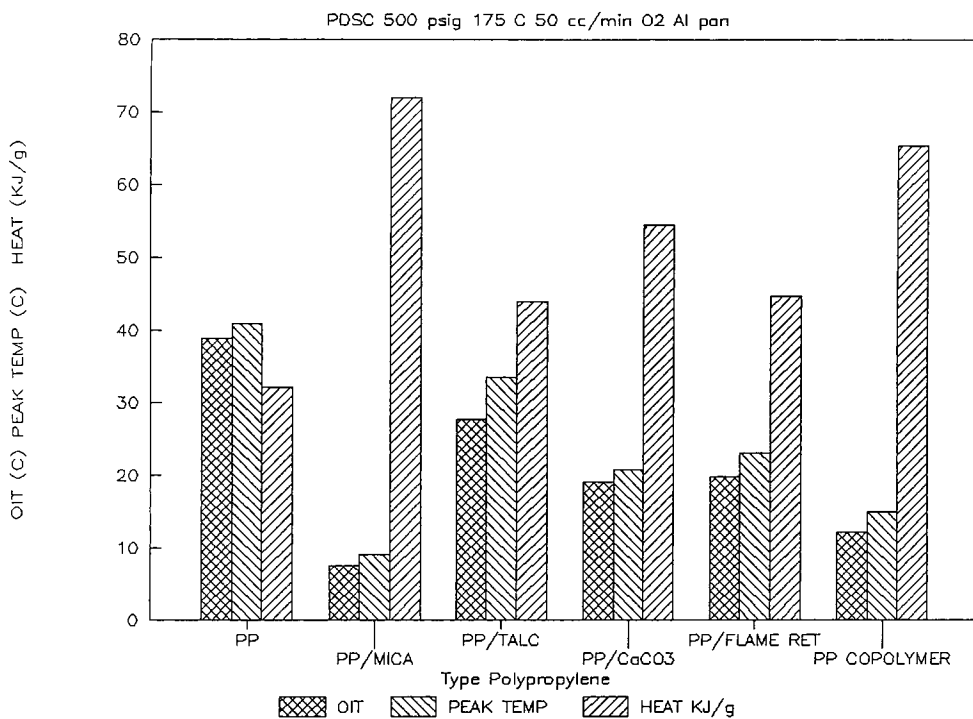


Fig. 7. Polypropylene oxidation induction time, OIT, peak temperature and heat of combustion by PDSC.

Table 4

Polyolefin oxidation induction time and heat of combustion (PDSC @ 500 psig; isothermal @ 175°C; 50 cc/min; Al pan)

			OIT	T_p	Heat of Combustion	
					cal/g	J/g
Polyethylene						
1	EVA ^a	34	29.1	44.7	9950	41600
2	LDPE ^b	24	17.2	30.1	16400	68600
3	MDPE ^c	49	28.7	39.5	13600	56900
4	HDPE ^d	25	30.3	42.6	15300	64000
	Average		26.3	39.2	13800	57800
	SD		6.1	6.6	2820	11800
	%SD		23.3	16.8	20.4	20.4
Polypropylene						
5	PP ^e	27	38.9	41.0	7660	32100
6	PP/MICA ^f	46	7.5	9.1	17200	72000
7	PP/TALC ^g	44	27.7	33.5	10500	43900
8	PP/CaCO ₃ ^h	45	19.1	20.8	13000	54400
9	PP/FR ⁱ	38	19.9	23.1	10700	44800
10	PP COP ^j	26	12.1	14.9	15600	65300
	Average		20.9	23.7	12400	52100
	SD		11.2	11.8	3540	14800
	%SD		53.7	49.8	28.5	28.4

^a Ethylene-vinyl acetate copolymer.^b Low-density polyethylene.^c Medium-density polyethylene.^d High-density polyethylene.^e Polypropylene homopolymer.^f Polypropylene+mica filler.^g Polypropylene+talc filler.^h Polypropylene+calcium carbonate filler.ⁱ Polypropylene+fire retardant.^j Copolymer of polypropylene + polyethylene.

oxygen (air) (compare the TGA onset temperatures (T_0) in nitrogen (TGA-b) and air (TGA-a). There was a greater percentage change (%) in TGA onset temperatures for the crystalline polymers than the non-crystalline polymers (see Table 3, 1–3 vs. 4–9).

There was a linear relationship between the OOT (DTA) and OIT (PDSC) for eight polyolefins, with a coefficient of variation of 0.91 [6]. However, in this study there was no apparent relationship between the OOT and OIT for the engineering plastics evaluated, Table 3. A universal oxidation test was desired, but not achieved. The diverse types of polymers studied, the numerous mechanistic paths to degradation, thermal and oxidative, prevented achieving this lofty goal.

The oxidative properties of additional polyethylene and polypropylene samples were examined by determining their heat of combustion (kJ/g) under pressure (by PDSC). The results are summarized in Table 4 and

Fig. 7. The OIT for each polymer set varied widely, but the average heats of combustion were consistently high. The average heat of combustion for the four polyethylene samples studied was 57.8 and 52.1 kJ/g for the six polypropylene samples. The remaining polymers studied had heats of combustion of <3 kJ/g, Table 3. These results suggest the use of polyethylene and polypropylene, either as scrap or recycled plastic products, as a fuel. Handa reports that polyolefins (polyethylene) can be used as a fuel source [16].

In an attempt to account for the various oxidation mechanisms, glass-filled Nylon 66 and reinforced polypropylene were studied in an air oven at 300°C as a function of time by the Fourier transform infrared spectroscopy, FTIR, Figs. 8–11. The thermal-oxidation degradation was different for these polymers. The oxidation of polyolefin was delineated, as expected,

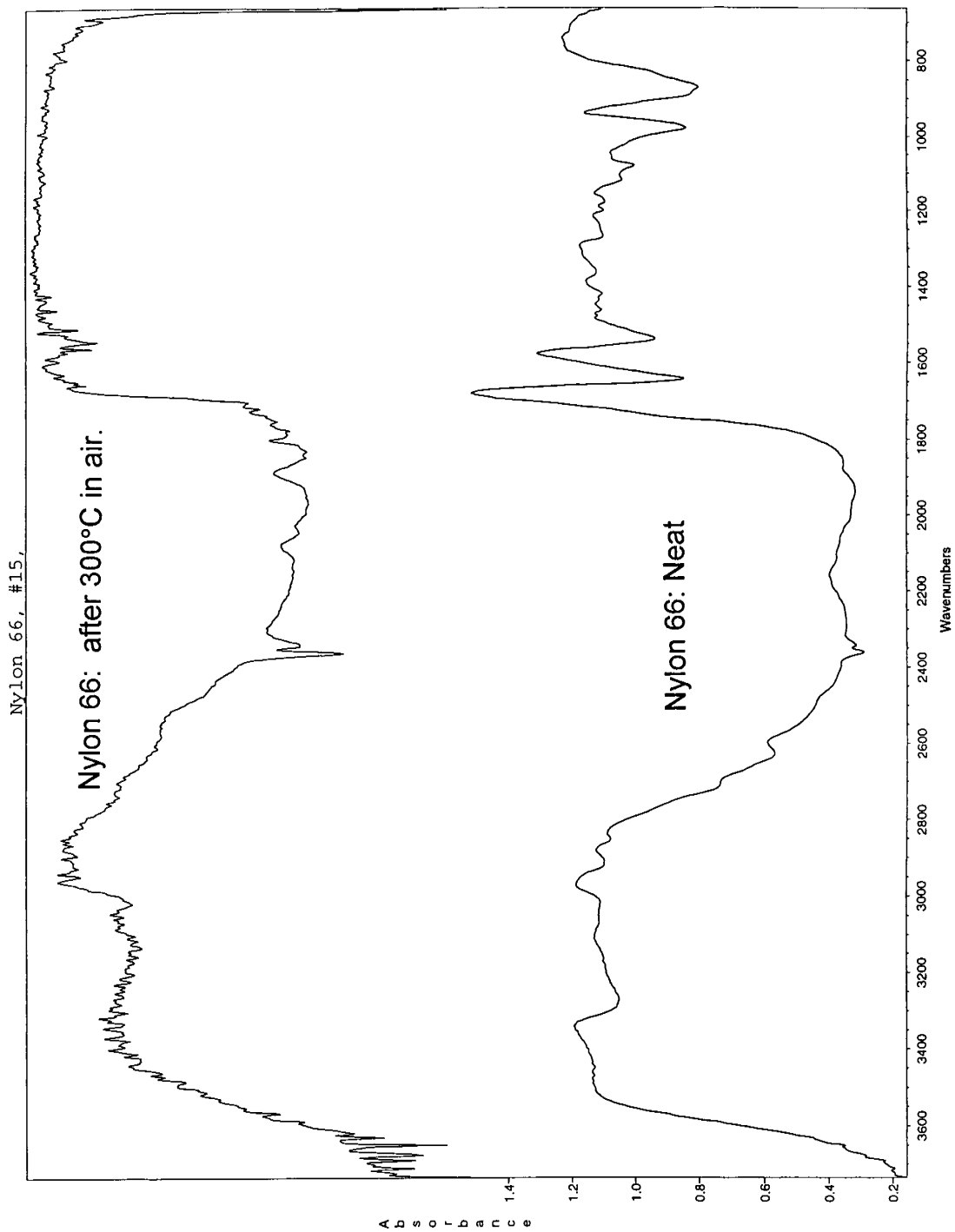


Fig. 8. FTIR spectra of Nylon 66: neat, and after 300°C in air.

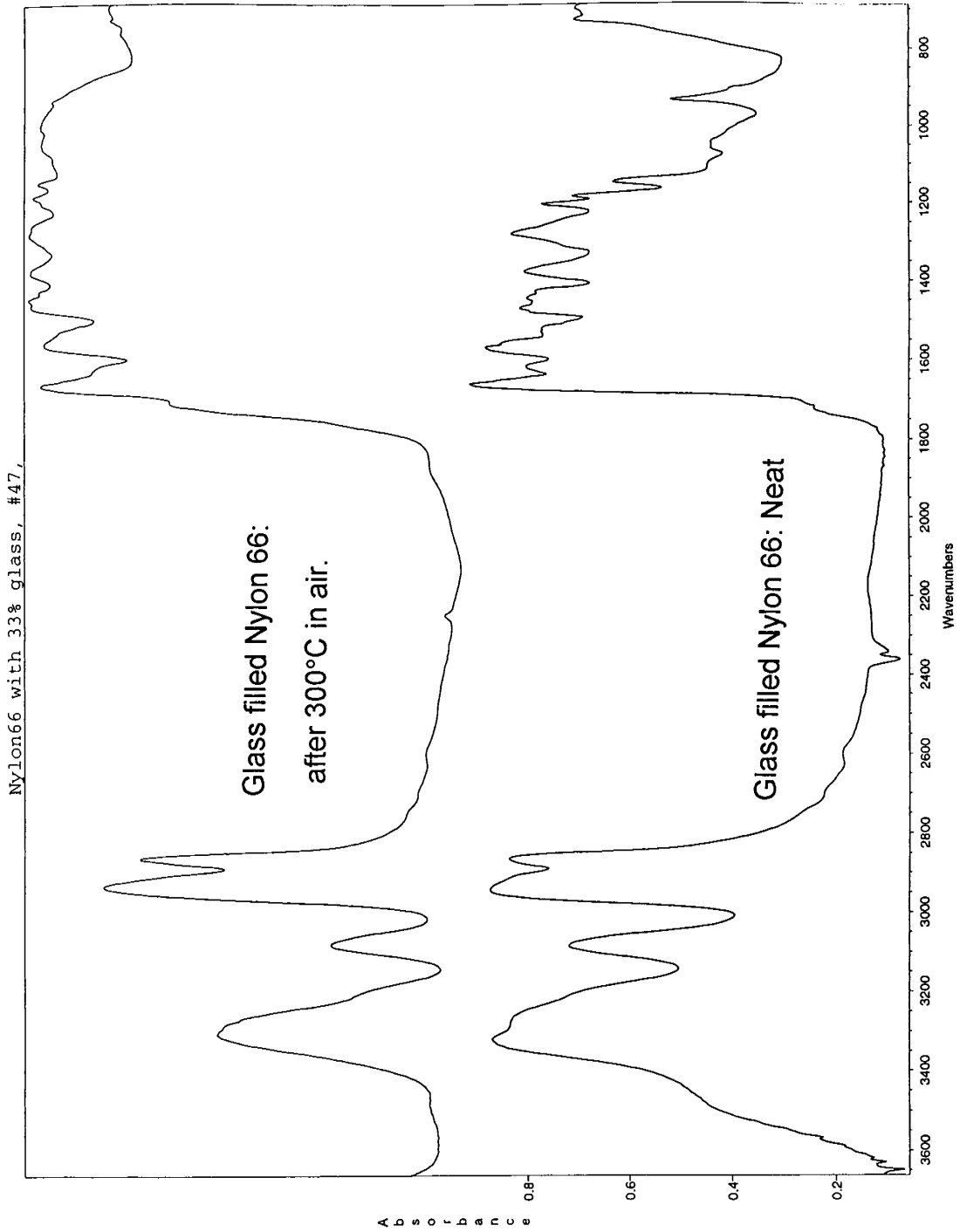


Fig. 9. FTIR spectra of glass-filled Nylon 66: neat, and after 300°C in air.

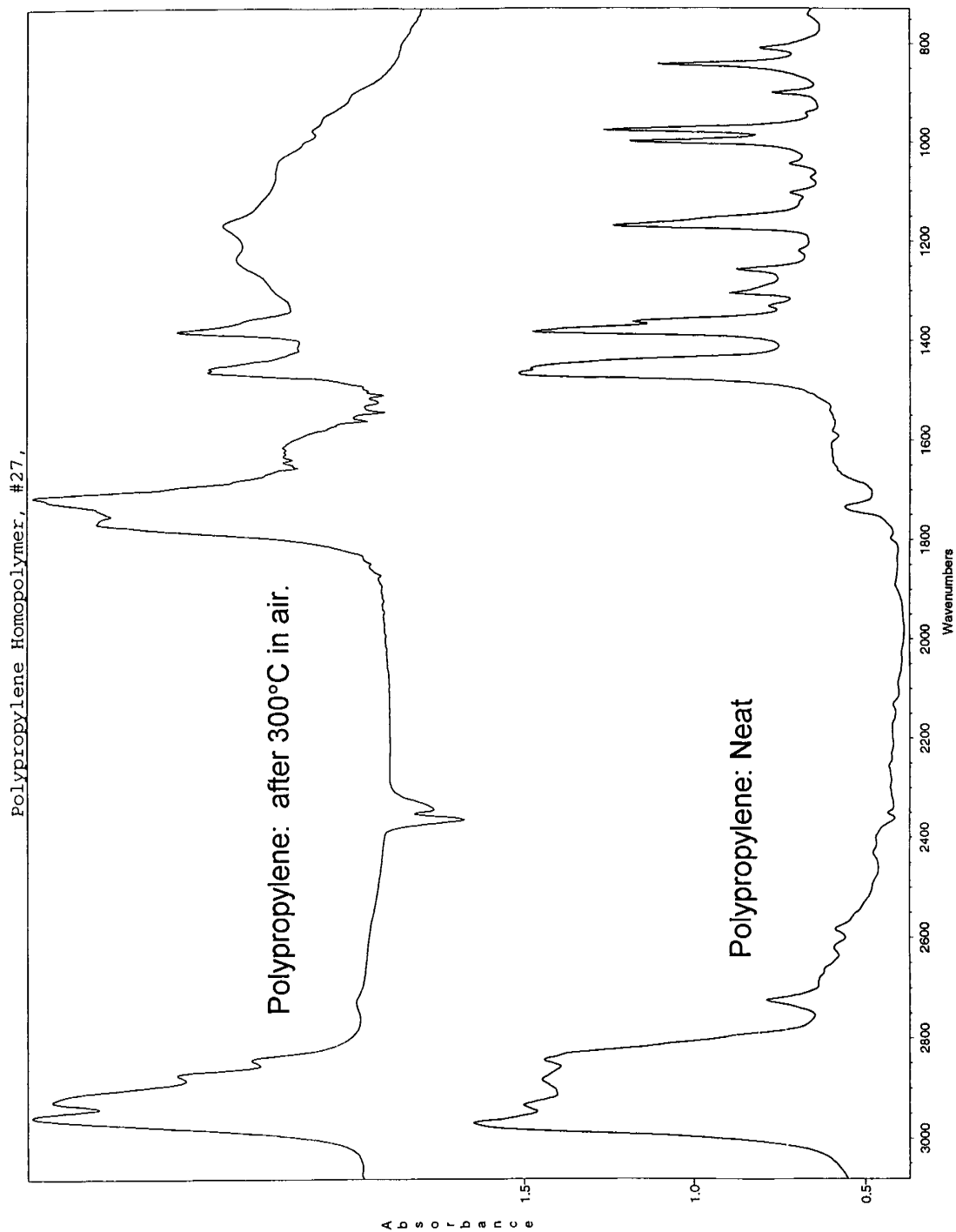


Fig. 10. FTIR spectra of polypropylene: neat; and after 300°C in air.

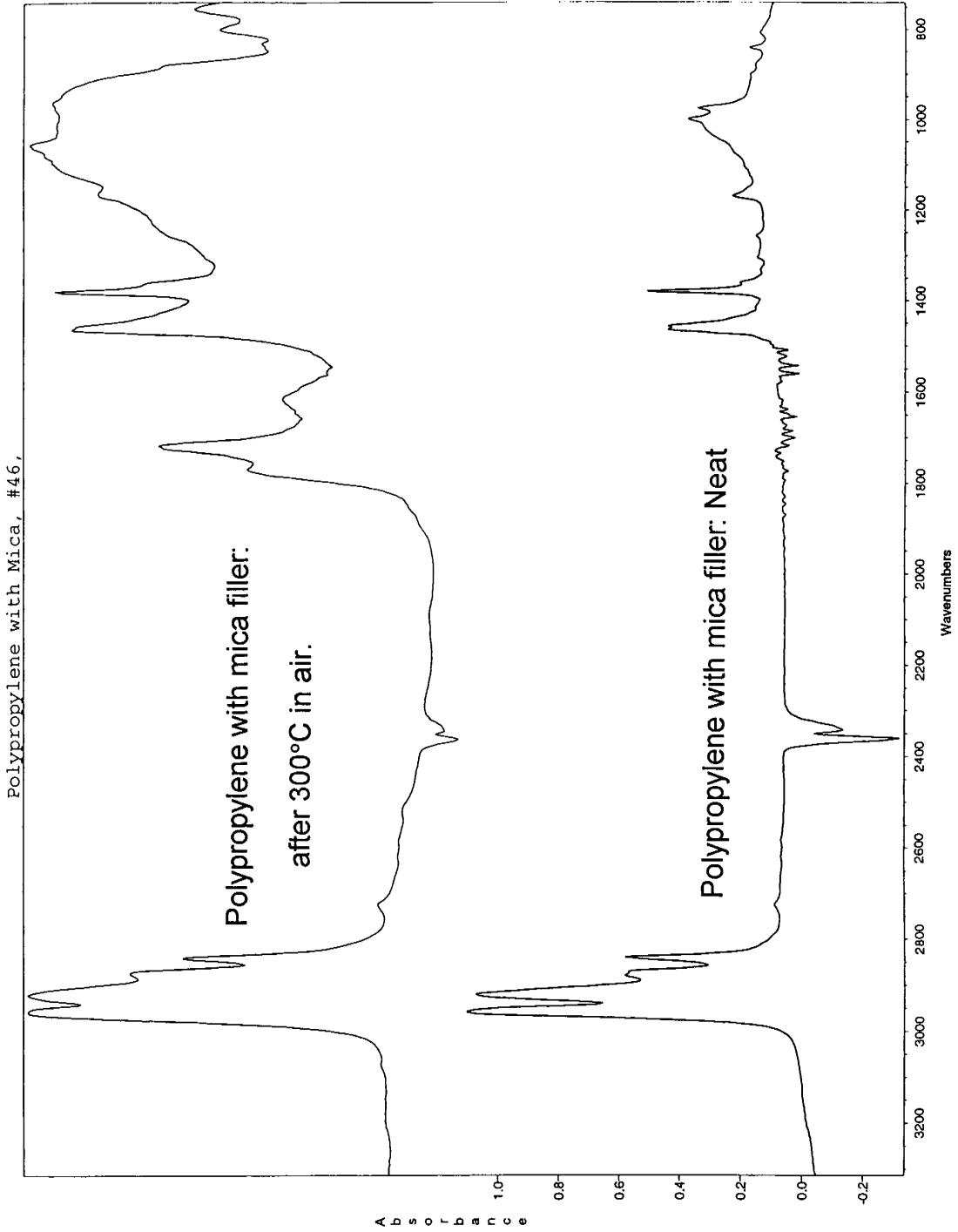


Fig. 11. FTIR spectra of polypropylene with mica filler: neat; and after 300°C in air.

by rapid carbonyl formation [12]. It appears that the nylon-polyamides thermally degrade, in air, into water, carbon dioxide and ammonia. The IR spectra of the oxidized nylon showed only minor changes in their amide functional groups and no detectable formation of carbonyl [15]. Future studies will include a comparison of the TGA-DTA and PDSC thermal and oxidative stability of the polymers cited in this research study with the isothermal air-oven oxidation monitored by FTIR spectroscopy.

4. Conclusions

The PDSC-OIT and DTA-OOT oxidation test results were in good agreement for the polyethylenes and polypropylenes. There was no apparent relationship between oxidation onset times (in oxygen) and oxidation onset temperatures (in air) for the engineering plastics and elastomers studied.

Polyphenylene sulfide, polycarbonate and polysulfone were the most stable of the polymers studied based on TGA-DTA. Polyvinyl chloride, both flexible and rigid versions, were the least oxidatively stable. The urethane elastomers were significantly more oxidatively stable than the synthetic elastomer or the thermoplastic rubber.

The polyacetals, homopolymer and copolymer, along with high-density polyethylene were the most oxidatively stable under high-pressure oxygen at 175°C (PDSC). It is interesting to note that these polymers were much more stable in nitrogen and strongly susceptible to attack by oxygen.

Polyethylene and polypropylene, waste or scrap, should be considered as a source of heat energy when combusting these polymers at high temperatures and pressures.

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