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THERMAL DEGRADATION OF COPOLYMERS FROM VINYL ACETATE AND VINYL ALCOHOL

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The thermal degradation of poly(vinyl acetate) (PVA), poly(vinyl alcohol) (PVAL), vinyl acetate-vinyl alcohol (VAVAL), vinyl acetate-vinyl-3,5-dinitrobenzoate (VAVDNB) and vinyl alcohol-3,5-dinitrobenzoate (VALVDNB) copolymers have been studied using differential thermal analysis (DTA) and thermogravimetry (TG) under isothermal and dynamic conditions in nitrogen. Thermal analysis indicates that PVA and PVAL are thermally more stable than VAVAL copolymers, being PVAL the most stable polymer. The presence of small amounts of vinyl-3,5-dinitrobenzoate (VDNB) in PVA or PVAL produces a marked decrease in the thermal stability of both homopolymers, being VALVDNB copolymers the less stable materials. The apparent activation energy of the degradative process was determined by the Kissinger and Flynn–Wall methods which agree well.

Keywords: *activation energy, poly(vinyl acetate), poly(vinyl alcohol), thermal degradation, vinyl acetate-vinyl alcohol copolymers, vinyl acetate-vinyl-3,5-dinitrobenzoate copolymers, vinyl alcohol-vinyl-3,5-dinitrobenzoate copolymers*

Introduction

The thermal degradation of poly(vinyl acetate) (PVA) and poly(vinyl alcohol) (PVAL) has been the subject of several publications [1–14].

It is known that both polymers degrade by elimination of low molecular mass compounds, with formation of conjugated polyene sequences along the polymer backbone, and main chain scission [1, 8, 9].

PVA decomposes into acetic acid and polyacetylene [1–4, 7–9]. The mechanism of loss of acetic acid is based on ester pyrolysis, which takes place through a cross-linking mechanism [15]. The deacetylation of PVA takes place progressively, and the cross-linking reaction occurs in the very early stages of the degradation [3, 4].

Thermal degradation of PVAL at low temperatures results in the evolution of water, produced by the elimination of hydroxyl side groups [6–8], and yields predominantly macromolecules with a polyene structure [6–9]. At higher temperatures the polyene structure is destroyed, carbon and hydrocarbons are produced.

The present study is devoted to comparison of the thermal degradation of PVA, PVAL, vinyl acetate-vinyl alcohol (VAVAL) copolymers, vinyl acetate-vinyl-3,5-dinitrobenzoate (VAVDNB) and vinyl alcohol-vinyl-3,5-dinitrobenzoate (VALVDNB) copolymers using TG and DTA, the kinetic parameters are evaluated on the basis of isothermal and dynamic degradation data. FTIR spectroscopy has been used qualitatively to study the structure of the residue produced and elucidate the thermal degradation mechanism.

Experimental

Materials

PVA (mass average molecular mass 90,000 g mol^{-1}) and PVAL (mass average molecular mass 108.000 g mol^{-1}, degree of hydrolyzation 99.7 mol%) were supplied by Polysciences. Vinyl acetate-vinyl alcohol (VAVAL) copolymers were prepared by methoxide-catalysed transesterification of PVA, as described elsewhere [16]. Vinyl acetate-vinyl-3,5-dinitrobenzoate (VAVDNB) and vinyl alcohol-vinyl-3,5-dinitrobenzoate (VALVDNB) copolymers were prepared by homogeneous esterification of VAVAL copolymers and PVAL respectively using 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (Fluka) as solvent. Experimental details of this synthesis are described elsewhere [16]. Details of the copolymers used in this work are given in Table 1.

Methods

Thermal analysis

The thermal degradation of homopolymers and copolymers was studied by thermogravimetric analysis (TG), derivative thermogravimetric analysis (DTG) and differential thermal analysis (DTA) using a Polymer-Laboratories STA-1000 system. All the analysis were carried out with 10–12 mg of samples on platinum pans in nitrogen (28 mL min^{-1})

Thermogravimetric analysis under dynamic conditions was carried out in the range 2–20 K min^{-1} re-

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Table 1 Peak temperatures in DTA curves for PVA, PVAL, VAVAL, VAVDNB and VALDNB (heating rate 20 K min^{-1})

Polymer	VAL/ mol%	Exotherm I T/K			Endotherm I T/K			Endotherm II T/K
		initial	peak	final	initial	peak	final	initial
PVA[a]	0	–	–	–	563	612	656 665^f	>683
VAVAL6[b]	6	–	–	–	557	601	648 654^f	>703
VAVAL25[b]	25	–	–	–	564	608	645 650^f	>701
VAVAL44[b]	44	–	–	–	567	607	643 650^f	>694
VAVAL67[b]	67	–	–	–	547	600	651 662^f	>700
VAVAL83[b]	83	–	–	–	545	604	657 663^f	>703
VAVAL92[b]	92	–	–	–	555	608	690	>693
PVAL[a]	100	–	–	–	594	642	700	>703
VAVDNB6[c]	6 (VDNB)	554	596	613	623	642	678	>678
VALVDNB2[d]	98	528	563 579^e	–	–	627	676	>703

VAL: vinyl alcohol; VDNB: vinyl-3,5-dinitrobenzoate; [a]polysciences; [b]transesterification of PVA; [c]esterification of VAVAL; [d]esterification of PVAL; [e]shoulder; [f]hump

cording the percentage of mass loss and the rate of mass loss as a function of temperature. The following characteristics were determined from the thermogravimetric curves: the initial thermal decomposition temperature (T_i), the temperature decomposition for different mass losses (T_D), the temperature of maximum rate of the first reaction step (T^1_{max}), the temperature of maximum rate of the second reaction step (T^2_{max}), and the mass loss for the first and the second reaction step (W^1, W^2).

In isothermal thermogravimetric analysis the sample was heated at 40 K min^{-1} until the experimental temperature was reached, taking as zero time the moment at which the temperature of the system was stabilized.

Differential thermal analysis was carried out using a heating rate of 20 K min^{-1}.

Fourier transform infrared spectroscopy

ATR-FTIR spectroscopy was done using a Nicolet Magna 560 spectrometer equipped with an ATR device with zinc selenide (ZnSe) crystal. The spectra were taken as an average of 50 scans at 8 cm^{-1} resolution.

Results and discussion

Thermal analysis by DTA

DTA curves of PVA, PVAL and VAVAL copolymer are shown in Fig. 1, while Fig. 2 shows DTA curves of PVA and VAVDNB, and Fig. 3 shows those curves of PVAL and VALVDNB. The peak temperatures for the various thermal effects are given in Table 1.

The DTA curve of PVA shows two endotherms, the first one in the temperature range 563–673 K with its peak minimum at 612 K and a hump at 665 K, and the second one appears at a temperature higher than 683 K. The endotherm at lower temperature corresponds to the evolution of acetic acid [1–3], and the endotherm at the higher temperature involves the breakdown of polymer backbone [4, 9].

The DTA curve of PVAL shows one endotherm with its peak minimum at 513 K that corresponds to the melting temperature of PVAL, a second endotherm appears between 593 and 703 K, with its peak minimum at 642 K, and a third one at a temperature higher than 703 K. The second endotherm is mainly due to the elimination of side groups [9, 12] and the one at higher temperatures is due to the breakdown of the polymer backbone [9, 12].

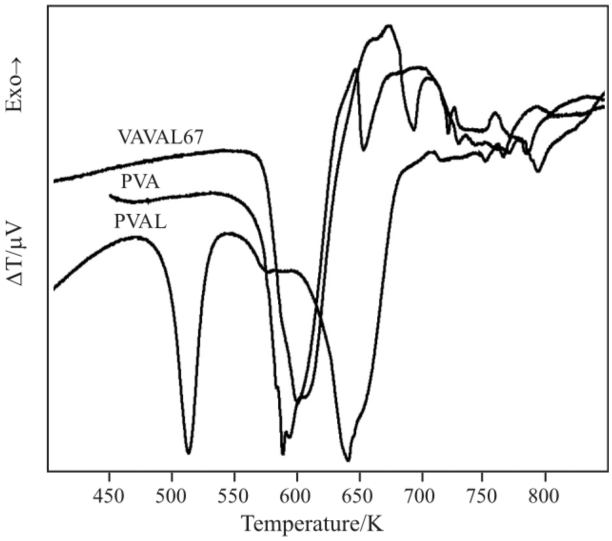

Fig. 1 DTA curves of PVA, PVAL and VAVAL copolymer. Heating rate 20 K min^{-1}

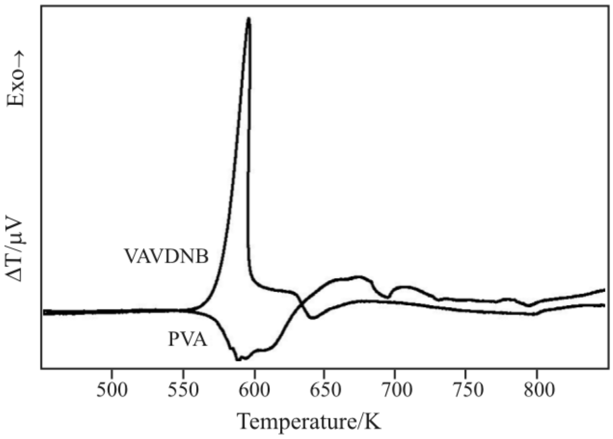

Fig. 2 DTA curves of PVA and VAVDNB6 copolymer. Heating rate 10 K min^{-1}

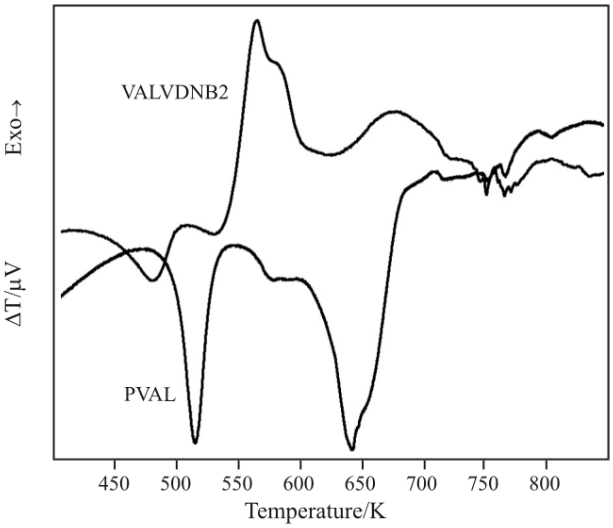

Fig. 3 DTA curves of PVAL and VALVDNB2 copolymer. Heating rate 10 K min^{-1}

DTA traces of VAVAL copolymers show two endotherms, the peak minimum of first one appears between 600–608 K, with a hump between 650–663 K and the second one appears at a temperature higher than 698 K. The endotherm at lower temperature corresponds to the evolution of acetic acid and water, and the endotherm at higher temperatures involves the breakdown of polymer backbone.

In the case of VAVDNB copolymer with 6 mol% vinyl-3,5-dinitrobenzoate (VDNB), DTA curve shows an exotherm with a maximum at 596 K, an endotherm with the maximum at 642 K, and another endotherm that takes place at a temperature higher than 673 K. On the other hand, DTA curve of VALVDNB copolymer containing 2 mol% VDNB shows one endotherm with its peak minimum at 477 K that corresponds to the melting temperature, an exotherm with a maximum at 563 K, showing a shoulder at 579 K, an endotherm with its maximum at 627 K and another endotherm that takes place at a temperature higher than 703 K.

The copolymers containing the dinitrobenzoate unit show the lower thermal stability, while PVAL shows the highest thermal stability.

Thermal analysis by dynamic TG and DTG

Thermogravimetric and differential thermogravimetric curves for PVA, PVAL, VAVAL, VAVDNB and VALVDNB copolymers, obtained at 20 K min^{-1} in nitrogen, are given in Figs 4–7. The TG curves in Fig. 4 and DTG curves in Fig. 5 show that PVA and PVAL degrade in two stages, in the first stage acetic acid or water is eliminated from PVA or PVAL respectively, while in the second one the breakdown of

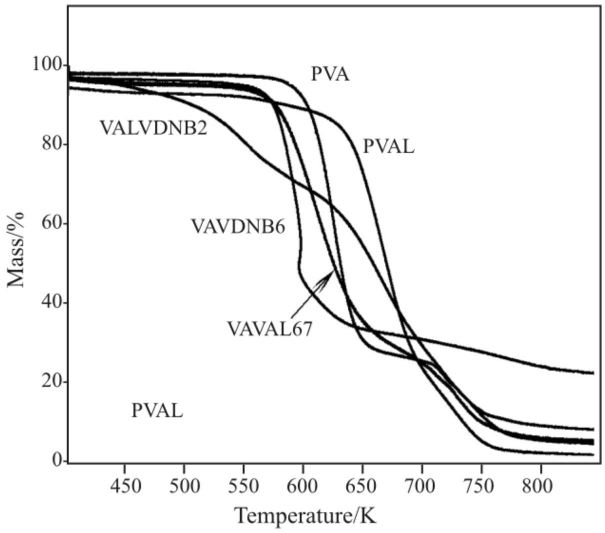

Fig. 4 TG curves of PVA, PVAL, VAVAL, VAVDNB and VALVDNB copolymers. Heating rate 20 K min^{-1}

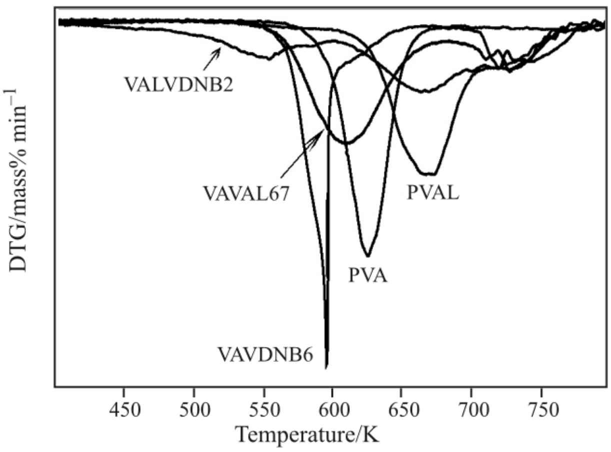

Fig. 5 DTG curves of PVA, PVAL, VAVAL, VAVDNB and VALVDNB copolymers. Heating rate 20 K min^{-1}

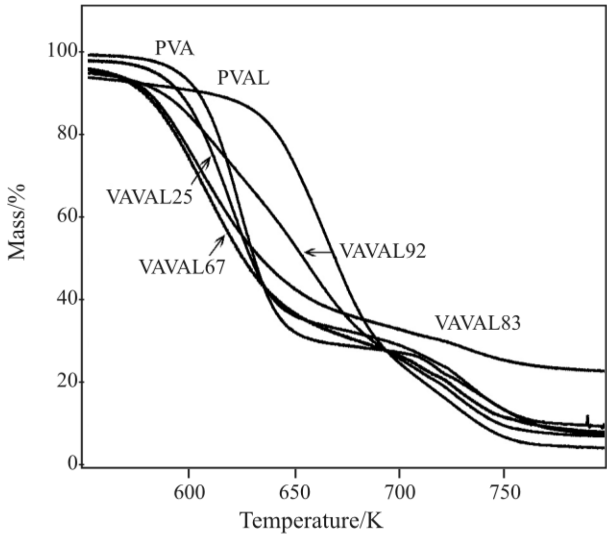

Fig. 6 TG curves of PVA, PVAL and VAVAL copolymers. Heating rate 20 K min^{-1}

the polymer backbone takes place [9]. Thermal degradation of PVA starts about 553 K and continues up to 693 K with 70% mass loss, whereas the decomposition process of PVAL starts at 593 K and continues up to 718 K with 72% mass loss.

The decomposition of VAVAL copolymers takes place in two distinct steps (Figs 6 and 7). The temperature range of each step depends on the copolymer composition of the copolymer sample. The mass loss of each step also depends on the composition.

The decomposition process of VAVDNB copolymers shows one step that starts at 548 K, whereas VALVDNB copolymers decompose in two steps, starting at 503 K (Figs 4 and 5). When the VDNB content of the copolymers is 15 mol% or higher, a fast mass loss takes place and during this step an increase in the sample temperature was observed as shown in Fig. 8.

From the characteristics of thermal degradation summarized in Table 2, it can be seen that the presence of hydroxyl groups in PVA has effect on thermal stability, the thermal decomposition of all VAVAL samples, obtained by base-catalysed transesterification with blockier sequence distributions [16], starts at a temperature lower than that of

Table 2 Thermal analytical data for PVA, PVAL, VAVAL, VAVDNB and VALVDNB copolymers (heating rate 20 K min^{-1})

Polymer	VAL/mol%	T_i^1/K	T_{max}^1/K	W^1/%	T_i^2/K	T_{max}^2/K	W^2/%	Residue/%	Char/%
PVA	0	558	625	70	697	–	20	8.3	6.8
VAVAL6	6	557	625	68	685	–	13	6.7	5.6
VAVAL25	25	561	621	64	683	–	22	10.5	9.0
VAVAL44	44	557	621	62	689	–	21	12.0	9.0
VAVAL67	67	523	609	66	685	–	22	8.3	7.5
VAVAL83	83	521	608	62	693	–	11	23.2	22.0
VAVAL92	92	541	656	71	709	–	16	7.7	7.0
			618^a			–			
PVAL	100	593	668	72	717	–	14	5.0	4.0
VAVDNB6	6 (VDNB)	548	596	65	–	–	–	28.5	24.0
VAVDNB15	15 (VDNB)	547	–	–	–	–	–	–	25.1
VAVDNB30	30 (VDNB)	528	–	–	–	–	–	–	24.5
VAVDNB54	54 (VDNB)	523	–	–	–	–	–	–	24.8
VALVDNB2	98	503	553	21	665	665	58	13.4	10.3
VALVDNB17	83	513	–	–	–	–	–	–	30.0

VAL: vinyl alcohol, VDNB: vinyl-3,5-dinitrobenzoate, ^{a}shoulder, T_i^1: initial thermal decomposition temperature of the first reaction step, T_{max}^1: temperature of maximum rate of the first reaction step, W^1: mass loss for the first reaction step, T_i^2: initial thermal decomposition temperature of the second reaction step, T_{max}^2: temperature of maximum rate of the second reaction step, W^2: mass loss for the second reaction step

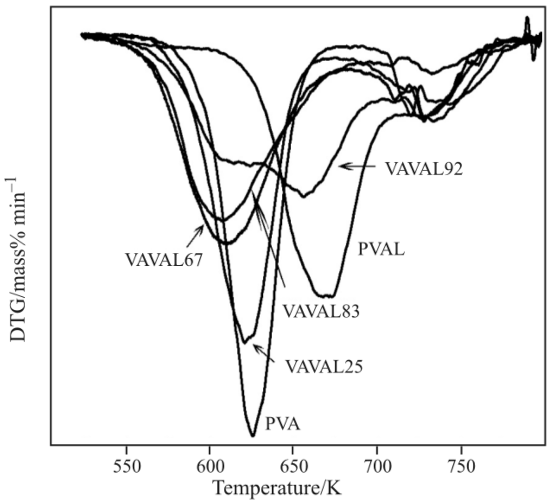

Fig. 7 DTG curves of PVA, PVAL and VAVAL copolymers. Heating rate 20 K min^{-1}

PVA. The initial degradation temperature of VAVDNB copolymers decreases with increasing proportions of VDNB. On the other hand, the initial degradation temperature of PVA is higher than that of all VAVAL and VAVDNB copolymers, whereas PVAL has the highest initial degradation temperature. The results indicate that for PVA, PVAL and VAVAL copolymers the residue at the end of the cycle is less than 10%, while the residue of the copolymers containing VDNB units is higher than 24% for VAVDNB copolymers, and increases with increasing proportions of VDNB for VALVDNB copolymers.

As shown in Table 3, the incorporation of a small amount of VDNB in PVA or PVAL (2–6 mol%) produces a marked decrease in the T_D (at mass loss between 10–60%) value of the copolymers as compared to those values of PVA or PVAL, being remarkably higher that effect on the thermal stability of PVAL. T_D (at mass loss between 10–50%) values for VAVAL copolymers with 6–83 mol% VAL are between those for the two homopolymers. The thermal stability of PVAL is reduced by the presence of a small content of VA units. All these results indicate that the stability of PVA and PVAL decrease with the incorporation of VAL or VDNB units in the polymer chain. Therefore, it is deduced that the more stable material is PVAL followed by PVA and VAVAL copolymers, and the less stable are those copolymers containing VDNB units.

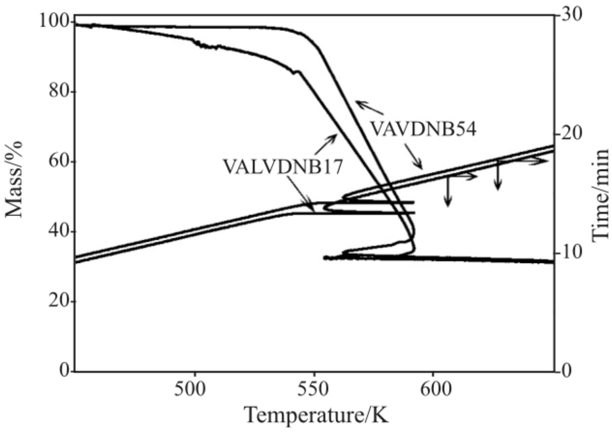

Fig. 8 TG and the simple temperature curves of VAVDNB54 and VALVDNB17. Heating rate 20 K min^{-1}

Calculation of kinetic parameters in dynamic experiments

Thermogravimetry is a method widely used for determination of kinetics of degradation of polymers [17, 18]. A reaction rate may be defined as the derivative of conversion. For thermogravimetric measurements, conversion may be defined as:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \tag{1}$$

where m_0, m and m_f are the initial, actual, and final mass of the sample, respectively. The rate of conver-

Table 3 Temperature of decomposition at different mass losses of PVA, PVAL and VAVAL (heating rate 20 K min^{-1})

Polymer	VAL/ mol%	T_D/K at mass loss of							
		10%	20%	30%	40%	50%	60%	70%	80%
PVA	0	606	615	622	627	633	640	668	733
VAVAL6	6	604	614	620	626	632	640	678	730
VAVAL25	25	597	609	617	624	631	643	699	735
VAVAL44	44	594	607	616	625	634	652	704	734
VAVAL67	67	580	595	606	616	628	644	685	727
VAVAL83	83	582	597	609	621	636	662	727	–
VAVAL92	92	587	608	625	641	655	669	689	721
PVAL	100	611	644	655	664	672	681	693	715
VALVDNB2	2 (VDNB)	519	559	609	643	662	681	704	732
VAVDNB6	6 (VDNB)	576	586	592	597	596	622	752	–

VAL: vinyl alcohol, VDNB: vinyl-3,5-dinitrobenzoate, T_D: temperature decomposition sion in a dynamic TG experiment at constant heating rate can be expressed as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=B\frac{\mathrm{d}\alpha}{\mathrm{d}T}=k(T)f(\alpha) \tag{2}$$

where B is the heating rate, B=dT/dt, $k(T)$ is the rate constant, and $f(\alpha)$ is the conversional functional relationship.

For polymer degradation, it is assumed that the rate of conversion is proportional of the concentration of nondegraded material:

$$f(\alpha)=(1-\alpha)^{\mathrm{n}} \tag{3}$$

where n is the apparent reaction order.

Arrhenius expression, which describes the temperature dependence of the rate constant, $k(T)$, may be expressed as:

$$k(T)=A\exp\left(-\frac{E}{RT}\right) \tag{4}$$

where E is the apparent activation energy, A is the pre-exponential factor, R is the gas constant and T the absolute temperature.

Combining Eq. (1) through Eq. (4), the following relation may be derived:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=B\frac{\mathrm{d}\alpha}{\mathrm{d}T}=A(1-\alpha)^{\mathrm{n}}\exp\left(-\frac{E}{RT}\right) \tag{5}$$

The differential Eq. (5), is usually manipulated until a straight line can be obtained and the kinetic parameters are predicted from the slope and ordinate values.

In the present study to different non-isothermal methods, the Kissinger [19] and Flynn–Wall [20] methods, are used for the computation of the kinetic parameters. Kissinger uses the temperature at which the rate of mass loss is at maximum (T_{m}) from which the kinetic parameters are obtained, and assumes that these parameters are independent of B. Since the maximum rate occurs when d(dα/dt)/dt is zero, differentiation of Eq. (5) with respect to time and setting the resulting expression equal to zero gives:

$$\frac{BE}{RT_{\mathrm{m}}^{2}}=An(1-\alpha)_{\mathrm{m}}^{\mathrm{n}-1}\exp\left(-\frac{E}{RT_{\mathrm{m}}}\right) \tag{6}$$

Kissinger also assumes that the product $n(1-\alpha)_{\mathrm{m}}^{\mathrm{n}-1}$ is not only independent of B, but is equal or very near to the unity. Substituting this value in Eq. (6) and differentiating, neglecting small quantities, then the following expression is obtained:

$$\frac{\mathrm{d}\left(\ln\frac{B}{T_{\mathrm{m}}^{2}}\right)}{\mathrm{d}\left(\frac{1}{T_{\mathrm{m}}}\right)}=-\frac{E}{R} \tag{7}$$

Therefore a plot of $\ln(B/T_{\mathrm{m}}^{2})$ *vs.* $1/T_{\mathrm{m}}$ gives the apparent activation energy for each degradation step.

Flynn and Wall expressed the Eq. (5) as:

$$-\frac{\mathrm{d}\log B}{\mathrm{d}\frac{1}{T_{\alpha}}}=0.457\frac{E}{R} \tag{8}$$

where T_{α} is the temperature for an isoconversion level. The apparent activation energy E can be obtained from the slope of isoconversional plots of log$B$ *vs.* $1/T_{\alpha}$. This method provides activation energies as

Table 4 Values of apparent activation energies and their confidence intervals (at a level of confidence of 95%) for the various stages of thermal degradation of PVA, PVAL, VAVAL, VAVDNB and VALVDNB copolymers under dynamic conditions

Polymer	VAL/mol%	α/%	F–W[a]		K[a]	
			E/ kJ mol^{-1}	Confidence interval for E	E/ kJ mol^{-1}	log$A$/ min^{-1}
PVA	0	5–70	164	162–166	166	15.05
VAVAL6	6	5–65	166	165–164	158	14.36
VAVAL25	25	5–50	155	153–157	148	16.37
VAVAL44	44	5–60	146	145–147	135	12.45
VAVAL67	67	5–65	146	143–149	141	13.22
VAVAL83	83	5–55	171	167–175	155	14.49
VAVAL92	92	10–70	140	136–144	115	10.13
PVAL	100	5–70	151	148–154	133	11.42
VAVDNB6	6 (VDNB)	5–50	140	138–142	139	13.32
VALVDNB2	2 (VDNB)	5–20	144	141–147	137	14.14
		25–80			144	12.37

VAL: vinyl alcohol, VDNB: vinyl-3,5-dinitrobenzoate; [a]F–W: Flynn–Wall's method; K: Kissinger´s method a function of conversion without any assumption about the reaction order. If the determined activation energy is the same for the various values of α, the existence of a single-step reaction can be concluded with certainty. On the contrary, a change in E with increasing degree of conversion is an indication of a complex reaction mechanism.

The kinetic parameters were calculated from the TG and DTG curves, using the Eqs (7) and (8). The Kissinger method allows calculation of activation energy from one point (maximum on DTG curve) at several heating rates. The method of Flynn–Wall requires several curves at different heating rates. E was calculated from the slope of the plots of Eq. (8) ($\log B$ *vs.* $1/T_\alpha$) at various degrees of conversion to test the constancy with respect to conversion.

The values of E determined by the above mentioned methods together with their confidence intervals (at a level of confidence of 95%) are given in Table 4, for PVA, PVAL, VAVDNB and VALVDNB copolymers. This parameter has been evaluated using the method of least squares for all the methods. The preexponential factor has been calculated at the maximum of reaction rate by Eq. (6) for each step of degradation, assuming that $n(1-\alpha)_m^{n-1}$ is equal or very near to the unity.

The activation energy of the first stage of PVA may be assumed to be 165 kJ mol^{-1}. That value obtained for the activation energy is similar to those reported by Holland and Hay [4], Barrales-Rienda *et al.* [5]. The activation energy of the first stage of degradation of PVAL is between 133–154 kJ mol^{-1}. For VAVAL copolymers the activation energy of the first stage is between 115–175 kJ mol^{-1}, decreasing as VAL content increases. The activation energy of degradation of VAVDNB copolymer (6 mol% VDNB) is 140 kJ mol^{-1}, while that of the first stage of VALVDNB (2 mol% VDNB) is between 137–147 kJ mol^{-1}.

For the copolymers containing VDNB units, when the copolymer composition is 15 mol% VDNB or higher a fast mass loss took place, and during this step it was observed that the sample temperature exceeded that dictated by the temperature programme. For these copolymers it was impossible to determine the kinetic parameters from TG and DTG curves. A similar behaviour was observed in the pyrolysis of other polymers containing nitroaromatic side groups [21–23].

Isothermal degradation

The thermogravimetric behaviour of PVA, PVAL, VAVAL, VAVDNB and VALVDNB copolymers under isothermal conditions was studied in the temperature interval 483–578 K.

Table 5 Initial rates, dα/d*t*, and activation energies obtained from the initial reaction rates in isothermal experiments

Polymer	VAL/ mol%	T/K	dα/dt 10^3/min^{-1}	E/ kJ mol^{-1}
PVA	–	548	2.8	200
		558	6.4	
		568	14.0	
		578	26.4	
VAVAL6	6	533	1.2	201
		543	3.4	
		553	6.9	
		563	14.0	
VAVAL44	44	523	1.2	188
		533	3.0	
		543	6.4	
		553	12.2	
VAVAL92	92	533	2.6	122
		543	4.2	
		553	7.3	
		563	10.9	
PVAL	100	543	7.3	104
		553	11.1	
		563	15.7	
		573	24.7	
VAVDNB6	6 (VDNB)	518	2.6	207
		528	6.6	
		538	18.7	
		548	37.9	
VALVDNB2	2 (VDNB)	483	4.1	64
		493	6.1	
		503	8.0	
		513	10.3	

VAL: vinyl alcohol, VDNB: vinyl-3,5-dinitrobenzoate

The initial rates of degradation, expressed as the fraction, α, of the sample decomposed per minute, are presented in Table 5. The apparent activation energies for the beginning of the reaction evaluated from the Arrhenius plot are reported in Table 5.

Infrared spectra of residual products

The degraded VAVDNB and VALVDNB samples were studied at different stages by infrared spectrometry.

Both samples at low extents of degradation (10% mass loss) yielded a brown residue insoluble in normal solvents for undegraded polymers. At extents of degradation higher than 10% mass loss, a black tar was obtained.

The infrared analysis of VAVDNB (30 mol% VDNB) at different degrees of degradation leads to the following observations.

For undegraded VAVDNB, absorption bands related to aromatic C–H stretching at 3100 cm^{-1}, C–H stretching at 3000–2850 cm^{-1} (alkanes), C=O stretching at 1730 cm^{-1} (ester), and NO_2 antisymmetric and symmetric stretching at 1548 and 1343 cm^{-1}, respectively were observed. The brown residue produced at low extents of degradation (10–30% mass loss) was found to contain the same infrared bands that the undegraded copolymer (3100, 3000–2840, 1730, 1548 and 1343 cm^{-1}), the carbonyl band of the ester group is attenuated. The IR spectra of the residue after 45% mass loss contains new bands in the 3500–2500 cm^{-1} region (O–H stretching, acid), at 1700 cm^{-1} (C=O stretching, acid), at 1600 cm^{-1} due to double bonds (C=C stretching) along the carbon backbone, the bands due to NO_2 stretching at 1548 and 1343 cm^{-1} are present, while the band at 1730 cm^{-1} (ester) is absent, suggesting the total elimination of the dinitrobenzoate and acetate groups at this extent of degradation, with subsequent formation of double bonds [4]. When the mass loss has reached 70% the IR shows the intense band at 1600 cm^{-1} (C=C stretching), a shoulder at 1700 cm^{-1} (C=O stretching, acid), the bands due to NO_2 stretching at 1548 and 1343 cm^{-1} are attenuated, and new bands at 870, 810 and 750 cm^{-1} due to C–H vibrations of substituted polycondensed aromatic rings. The formation of polycondensed aromatic rings originate from unsaturated aliphatic chains, which undergo cyclisation and then aromatisation through elimination of hydrogen and condensation of aromatic rings [14].

The residue produced by degradation of VALVDNB (17 mol% VDNB), after 30% mass loss, was found to contain the same infrared bands that the undegraded polymer, alcohol O–H stretching in the region 3600–3200 cm^{-1}, aromatic C–H stretching at 3100 cm^{-1}, C–H stretching at 3000–2850 cm^{-1} (alkanes), C=O stretching at 1730 cm^{-1} (ester), and NO_2 antisymmetric and symmetric stretching at 1548 and 1343 cm^{-1}. The IR spectra of the residue after 50% mass loss contains new bands in the 3500–2500 cm^{-1} region (O–H stretching, acid), at 1700 cm^{-1} (C=O stretching, acid), at 1600 cm^{-1} due to double bonds (C=C stretching) along the carbon backbone, the bands due to NO_2 stretching at 1548 and 1343 cm^{-1} are present, while the band at 1730 cm^{-1} (ester) is absent, suggesting the total elimination of the dinitrobenzoate groups at this extent of degradation, with subsequent formation of double bonds. When the mass loss has reached 70% the IR shows the intense band at 1600 cm^{-1} (C=C stretching), a shoulder at 1700 cm^{-1} (C=O stretching, acid), the bands due to NO_2 stretching at 1548 and 1343 cm^{-1} are attenuated, and new bands at 870, 810 and 750 cm^{-1} due to C–H vibrations of substituted polycondensed aromatic rings.

Conclusions

The results have shown that VAVDNB and VALVDNB copolymers are less thermally stable compared to the corresponding homopolymers, PVA and PVAL. VAVAL copolymers are less thermally stable than PVA and PVAL. The thermal stabilities of vinyl polymers here studied are in the order PVAL>PVA>VAVAL>VAVDNB>VALVDNB.

From the results, TG and DTG analysis, it can be concluded that two degradation steps occur in the thermal degradation of PVA, PVAL and VAVAL copolymers. From DTA curves of PVA and VAVAL copolymers, we can state that in the first degradation step a superposition of two processes takes place. In PVA, first acetic acid is evolved from the acetate together with a crosslinking reaction, followed by the main chain degradation. In PVAL first water is eliminated from side groups, followed by the main chain degradation. In VAVAL copolymers together with the elimination of acetic acid and water a crosslinking reaction takes place, then the breakdown of polymer backbone occurs. In VAVDNB and VALVDNB copolymers it can be suggested that first the elimination of the acid, and acid and water in the case of VALVDNB copolymers and formation of a polydiene type structure, then the main chain scission together with further cyclisation and aromatisation of the remaining aliphatic segments with conjugated double bonds takes place. The residue and char for the copolymers containing VDNB units is remarkably higher than that of the corresponding homopolymers, suggesting that the degraded products from the copolymers containing the dinitrobenzoate units are less volatile probably due to cross-linking.

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