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An XPS investigation of thermal degradation and charring of cross-linked polyisoprene and polychloroprene

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Abstract

Our interest in butadiene-containing polymers had led to an investigation of the thermal degradation of polyisoprene, PIP, and polychloroprene, PCP. The connection between cross-linking and thermal stability through an examination of PIP and PCP has been reported. Like the course of thermogravimetric analysis (TGA) the cross-linking and charring of polymers subjected to heat can also be experimentally observed as function of temperatures by the pseudo-in-situ XPS (X-ray Photoelectron Spectroscopy). Data acquisition of C1s spectra as

function of temperature permits us to explore: (1) the extent of cross-linking and/or carbon accumulation of systems of PCP and PIP with/without initiators, BPO and DCP, via the analysis of the relative intensity versus temperature; and (2) the onset of charring by determining the limiting transition temperature (LT_{GRL}) of the graphite-like structure and particularly the plasmon loss (ΔE_L).

Keywords

1. Introduction

There has been previous work from these laboratories on the relationship between cross-linking and carbon accumulation (charring) of non-cross-linked and cross-linked polymers. This has included work on polyamide-6 [1] and butadiene-containing polymers [2]. Quite recently work has appeared on polyisoprene (PIP) and polychloroprene (PCP) both of which undergo cross-linking by a thermal process as well as an initiator-enhanced thermal cross-linking [3]. There are a number of issues concerning the measure of both processes that must be addressed and X-ray photoelectron spectroscopy, XPS, provides a very useful technique to address these questions. In addition to answering these questions, an intent of this work is to show the value of an XPS investigation in better understanding the process of char formation.

2. Experimental

For XPS experiments a thin film, with a thickness in the order of microns, must be prepared. Dilute polymeric solutions were obtained by the dissolution of polymer in chloroform, followed by pouring these solutions onto aluminum foil, which had been treated with sulfuric acid, then thoroughly washing with distilled water, followed by organic solvents. The required thin films were obtained by permitting the solvent to evaporate.

The preparation of the samples for initiator-enhanced thermal cross-linking was accomplished by dissolving the polymer, together with 2 mmol benzoyl peroxide (BPO) or dicumyl peroxide (DCP) in 25 ml chloroform in a 100 ml round bottom flask. The resulting solution was then treated as above for the preparation of the virgin polymer samples. The solvent was allowed to evaporate at room temperature for 24 h. Each thin film of the polymer and initiator combination was sealed under vacuum in an ampoule. The samples were then placed in an oil bath at 70°C (for BPO-containing samples) or 120°C (for DCP-containing samples) for 3–24 h. At the conclusion of the reaction, the ampoules were opened and the samples were removed and analyzed.

3. Results and discussion

3.1. Thermal degradation and charring of un-crosslinked PCP and PIP

In previous work [4], [5], [6], [7], [8], it has been shown that the cross-linking and charring of polymers subjected to heat can be experimentally observed as a function of temperature by the pseudo-in-situ XPS (X-ray photoelectron spectroscopy). This is similar to the experiment that can be performed by thermogravimetry (TGA), but is more sensitive.

3.1.1. PCP

The data for PCP is shown in Table 1, Table 2 and Fig. 1, Fig. 2, Fig. 3. The important parameters derived from this work to characterize cross-linking and char formation included the relative intensity of carbon, the plasmon loss peak (ΔE_L) in the C1s spectra and the atomic concentration of chlorine in the C12p spectra. All parameters, as shown in Table 1 from left to right, can be defined as follows: C1s (the 2nd column) is the binding energy of the main peak in C1s spectra; CPS and intensity % (the 3rd column) represents the counts per second of C1s photoelectrons and the relative intensity referencing to the CPS at room temperature, plasmon loss peak (ΔE_L)

(the fifth column) in C1s spectrum is the difference between values in the 4th and 2nd columns; and shake-up (satellite) peak (the last column) denotes π–π* transition originating from benzene moieties.

Table 1. XPS data for C1s of PCP thin film on Al foil

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	C1s Plasmon (eV)	C1s ΔE_L (eV)	C1s shake-up (eV)
25	285.9	48800	0.0	308.8	22.9	292.9
100	285.9	49020	0.5	308.7	22.8	292.7
150	286.3	49160	0.7	308.9	22.6	292.9
200	286.3	49460	1.4	309.0	22.7	292.9
250	286.2	50120	2.7	309.0	22.8	292.7
280	286.0	52550	7.7	309.2	23.2	n.d.[a]
310	285.7	54210	11.1	309.2	23.5	n.d.
330	285.6	55580	13.9	309.3	23.7	n.d.
350	285.3	56200	15.2	309.3	24.0	n.d.
360	285.1	57710	18.3	309.2	24.1	n.d.
370	284.9	59310	21.5	311.2	26.3	n.d.
380	284.9	59520	22.0	311.3	26.4	n.d.
400	284.9	59640	22.2	311.2	26.3	n.d.
420	284.9	59720	22.4	311.2	26.3	n.d.
450	284.9	56690	16.2	311.4	26.5	n.d.
500	284.9	56630	16.1	311.5	26.6	n.d.

a n.d.: not detectable.

Table 2. XPS data for C12p and C1s of PCP thin film on Al foil

Temperature (°C)	C12p CPS	r.i. (%)[a]	C1s C□C/C□Cl[b]
25	20068	100	3/1
100	19862	98.97	–
150	79331	96.33	–
200	17852	88.96	3.5/1
250	12555	62.56	–
280	8062	40.17	9/1
310	3741	18.64	–
330	1352	6.74	58/1
350	254	1.27	–
360	212	1.06	–
370	104	0.52	99.9/1
380	n.d.	n.d.	–
400	n.d.	n.d.	–
420	n.d.	n.d.	–
450	n.d.	n.d.	–
500	n.d.	n.d.	–

aPercentage of chlorine remained in the solids.
bC□C/C□Cl represents the ratio of carbon atoms linked to carbon over that of carbons linked to chlorine.
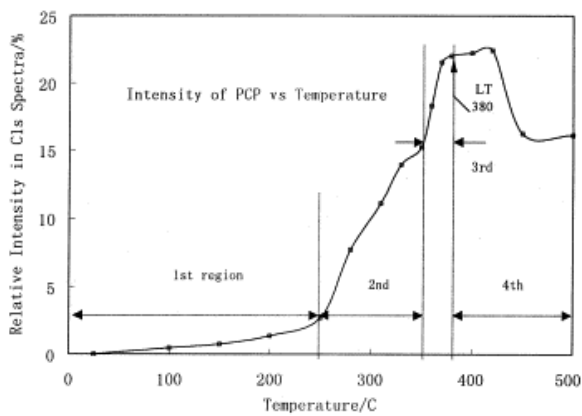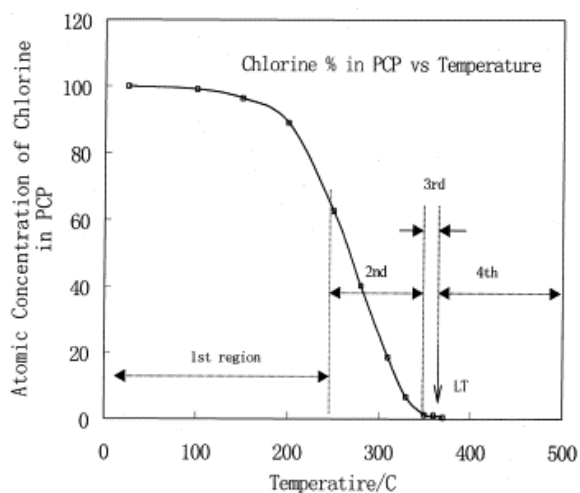
Fig. 1. Relative intensity (%) of PCP vs temperature.

Fig. 2. Atomic concentration of chlorine in PCP as a function of temperature.
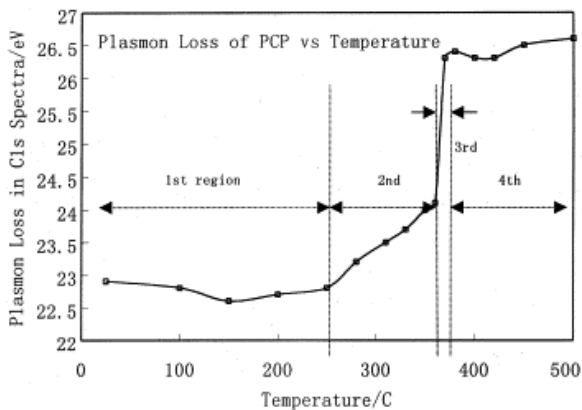
Fig. 3. Plasmon loss (ΔE_L) in C1s spectra of PCP vs temperature.

In Fig. 1, four distinctly different temperaure regions can be described: 1st region (ambient — 250°C), 2nd region (250–350°C), 3rd region (350–380°C) and 4th region (>380°C). The absence of a negative peak in the first region indicates the absence of adventitious contamination of this sample, very often met in modern surface analytical techniques, such as XPS, AES (Auger electron spectroscopy), ISS (ion scattering spectroscopy), and SIMS (secondary ion mass spectroscopy), etc. Such contamination is usually observed and its absence must be explained; it may be ascribed to the presence of hydrophobic chlorine atoms in PCP [8]. A large increase in the

relative intensity within the 2nd region, which continues but, with a change in slope, during the 3rd region, is in fairly good agreement with the available information on gel content and swelling ratio [3], and this shows that the extent of cross-linking and the cross-link density increases as the temperature increases. Above 420°C the relative intensity begins to decrease, perhaps due to pyrolysis and/or evaporation of the char.

The concentration of chlorine atoms in PCP decreases as the temperature increases and falls to zero at 380°C, which lies at the border between the 3rd and 4th region (Fig. 2). The thermal degradation of PCP takes place in two stages, i.e. elimination of hydrogen chloride, followed by degradation of the backbone [9]. The evolution of HCl is observed at as early as 100°C, because of the much higher sensitivity of the XPS technique in the surface layers compared to TGA in the bulk. The ratio of C□C/C□Cl, as indicated in Table 2, is the relative amount of carbon attached to another carbon relative to that attached to chlorine; this increases with temperature, indicating the loss of HCl, and finally reaches the value of this ratio, 99.9/1 at 370°C. Table 3 provides a comparison between XPS and the conventional techniques [10].

Table 3. Comparison of the temperature T_x at fixed chlorine loss % in PCP by different techniques

T_x and technique	T_x (°C)	
Chlorine loss (%)	XPS	Isothermal thermolysis [8]
On-set ($T_{1.0}$)	100	150–200
77 (T_{77})	300	380
At the end (ca. 90% loss)	380	420

The Limiting Transition Temperature of Graphite-like Structure, LT_{GRL} is used to characterize the charring of polymers [11]. For chlorine containing polymers, for example, PVC and systems of PVC/transition metals, the LT_{GRL} were taken as the temperatures at which the chlorine atoms just completely vanish, corresponding to the maxima in the plots of relative intensity in C1s spectra vs temperature [12], [13], [14], [15]; in other words, charring defined by LT_{GRL} occurs just subsequent to the complete loss of chlorine atoms. In Fig. 1 the LT_{GRL} of PCP was determined to be 380°C as indicated by the arrow, which was caught up with the deep increase in ΔE_L within the narrow region (Fig. 3).

Here, the plasmon loss (ΔE_L) in C1s spectra can also be divided into four regions, similar to that observed for the C1s spectra, i.e. 1st region (ambient — 250°C), 2nd (250–360°C), 3rd (360–380°C) and 4th (>380°C). Following the 2nd region of moderate cross-linking, a dramatic increase in ΔE_L from 24.1 to 26.4 eV and relative intensity in 3rd region in Fig. 1 (360–380°C), shows the presence of a graphite-like structure, even though the relative intensity in the C1s spectra dropped significantly in the 4th region in Fig. 1. In addition, the gradual disappearance of the shake-up peaks (π–π^* transition, see Table 1) is likely an alternative indication of the local benzene ring vanishing at temperatures above 280°C. It may be stated that the relative intensity in the C1s spectra, the LT_{GRL} and the plasmon loss (ΔE_L) are distinct factors that are indispensable for understanding the charring process.

3.1.2. PIP

Essential data for PIP are shown in Fig. 4, Fig. 5 and the data is tabulated in Table 4. A much lower relative intensity for PIP, than PCP, in C1s spectra, along with the presence of a negative region, ascribed to contamination [8], is noted. The relative intensity does not exceed 10% at a temperature below 380°C. The fact that plasmon loss (ΔE_L) remains constant at about 22.0 eV below 380°C indicates that there is little or no change in the extent of conjugation within the polymeric matrix. One can, therefore, conclude that very little cross-linking occurs until a temperature of 380°C is reached.
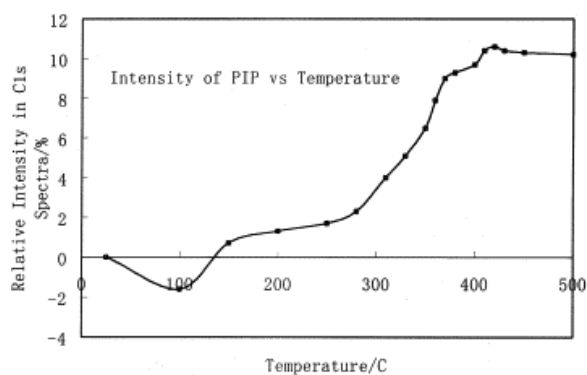
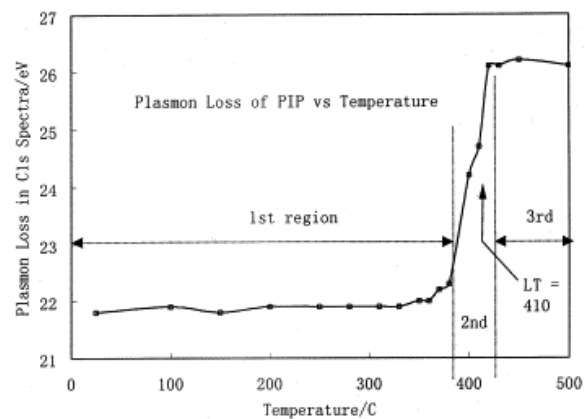Fig. 4. Relative intensity (%) of PIP vs temperature.

Fig. 5. Plasmon loss (ΔE_L) of PIP vs temperature.

Table 4. XPS data for PIP thin film on Al foil

Temperature	C1s	C1s		Plasmon	ΔE_L	Shake-up
(°C)	(eV)	CPS	Intensity (%)	(eV) in C1s	(eV) in C1s	(eV)
25	285.6	56820	0.0	307.4	21.8	292.2
100	285.6	55890	−1.6	307.5	21.9	292.2
150	285.6	57240	0.7	307.4	21.8	292.3
200	285.6	57570	1.3	307.5	21.9	292.3
250	285.7	57810	1.7	307.6	21.9	292.2
280	285.7	58120	2.3	307.6	21.9	292.1
310	285.7	59080	4.0	307.6	21.9	292.2
330	285.7	59720	5.1	307.6	21.9	292.2
350	285.7	60520	6.5	307.7	22.0	292.3
360	285.7	61290	7.9	307.7	22.0	292.2
370	285.7	61910	9.0	307.9	22.2	292.0
380	285.6	62120	9.3	307.9	22.3	292.0
400	285.3	62330	9.7	309.5	24.2	292.0
410	285.3	62740	10.4	310.0	24.7	n.d.[a]
420	285.3	62820	10.6	311.4	26.1	n.d.
430	285.3	62320	10.4	311.4	26.1	n.d.
450	285.3	62660	10.3	311.5	26.2	n.d.
500	285.3	62590	10.2	311.4	26.1	n.d.

an.d.: not detectable.

This agrees well with the literature assertion [3] that PIP does not easily cross-link during the course of thermogravimetric analysis. The very large increase in ΔE_L from 22.0 to 26.0 eV, between 380–420°C reveals the

emergence of the graphite-like structure which is defined by $LT_{GRL}=410°C$. In the 2nd region, an increase in intensity of the Cls peak arises but, it is weak in comparison to that observed for PCP. The plasmon loss of 26.1 eV at 420°C confirms the appearance of aromatics.

The data shown in Fig. 6, Fig. 7 clearly show that the substitution of a hydrogen for a chlorine has a very important role in the cross-linking process and, ultimately, in fire retardancy of the polymer.
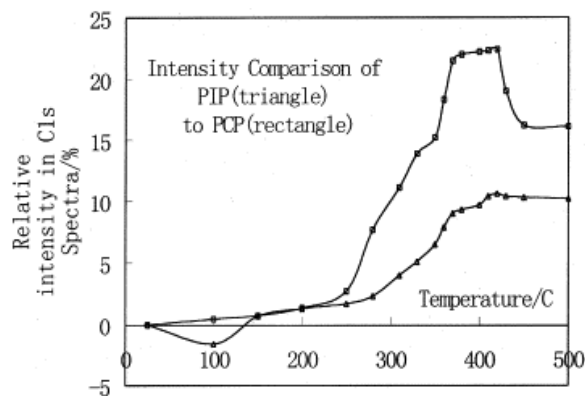

Fig. 6. Comparison of relative intensity between PIP and PCP.
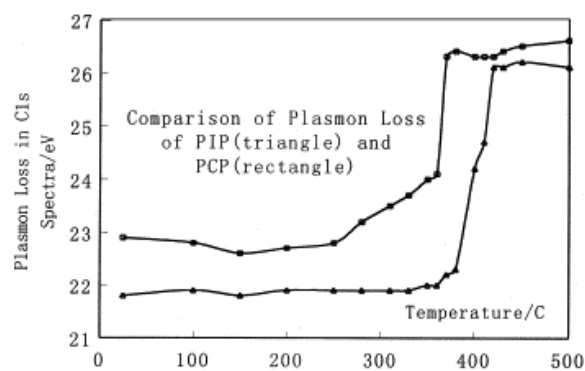
Fig. 7. Comparison of plasmon loss between PIP and PCP.

Apparently for both PCP and PIP, but particularly important for PCP, a large increase in the plasmon loss occurs within a very small temperature range, as seen in Fig. 7. Cross-linking and char formation for PCP proceed at an extremely high rate within a quite narrow temperature interval, 10°C, and this must be related to the presence of the chlorine atom and the double bond. The PCP curve lies above the PIP curve and this indicates the important role that chlorine plays in cross-linking and char formation.

3.2. Thermal degradation and charring of cross-linked PCP and PIP

3.2.1. PCP/BPO
TGA data for both PIP and PCP are shown in Table 5 while Table 6, Table 7, Table 8, Table 9 provide the XPS data for PCP which has been cross-linked with BPO for times ranging from 3 to 24 h. The main data can directly be depicted in Fig. 8, Fig. 9. The time of the cross-linking reaction apparently induces changes in the patterns in the plots of relative intensity vs temperature. On one hand a much stronger relative intensity, in contrast with original PCP, is seen in cross-linked samples at 70°C and times shorter than 6 h. On the other hand a much weaker relative intensity relative to original PCP is seen in cross-linked samples at 70°C and times longer than say, 12 h.

Table 5. TGA/DTG data of chemically cross-linked PIP and PCP

Polymers	$T_{10\%}$ (°C)	Peak₁ (°C)	(%/min)	Peak₂ (°C)	(%/min)	$R_{500°C}$ (%)
PIP	345.2	371.2	22.3	–		0
PIP/BPO	340.4	372.1	17.2	–		1.7
PCP	307.2	367.8	9.4	434.1	8.7	17.1
PCP/BPO	266.3	354.1	5.6	445.4	6.0	26.5

Table 6. XPS data on PCP/BPO at 70°C for 3 h

Temperature (°C)	C1s C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	285.9	38610	0.0	309.6	23.7
100	285.8	38800	0.5	309.6	23.8
150	286.5	38910	0.8	309.8	23.3
200	286.0	39200	1.5	309.8	23.8
250	285.7	41370	7.1	309.8	24.1
280	285.5	41850	8.4	309.9	24.4
310	285.2	45250	17.2	309.9	24.7
340	284.9	45490	17.8	311.4	26.5
370	284.7	46030	19.2	311.6	26.9
400	284.7	46060	19.3	311.6	26.9
430	284.8	46110	19.4	311.7	26.9
460	284.9	46440	20.3	311.5	26.6
500	284.9	46620	20.7	311.7	26.8

Table 7. XPS data on PCP/BPO at 70°C for 6 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	285.9	37060	0.0	309.5	23.6
100	285.9	37330	0.7	309.4	23.5
150	286.3	37500	1.2	309.5	23.2
200	285.9	38370	3.5	309.5	23.6
250	285.6	41260	11.3	309.7	24.1
280	285.4	41700	12.5	309.7	24.3
310	285.0	42710	15.2	309.7	24.7
340	284.8	45270	22.1	311.1	26.3
370	284.6	45600	23.0	311.5	26.9
400	284.6	45850	23.7	311.5	26.9
430	284.6	46100	24.4	311.6	27.0
460	284.7	47080	27.0	311.7	27.0
500	284.9	47390	27.9	311.7	26.8

Table 8. XPS data on PCP/BPO at 70°C for 12 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	285.8	40980	0.0	309.6	23.8
100	285.8	41040	0.2	309.5	23.7

150	285.7	41740	1.9	309.7	24.0
200	285.6	42040	2.6	309.7	24.1
250	285.5	42110	2.8	309.6	24.1
280	285.4	42820	4.5	309.7	24.3
310	285.1	42920	4.7	310.0	24.9
340	284.9	46250	12.9	311.1	26.2
370	284.7	46670	13.9	311.2	26.5
400	284.7	46800	14.2	311.3	26.6
430	284.8	46930	14.5	311.3	26.5
460	285.0	47070	14.9	311.2	26.2
500	284.9	47170	15.1	311.3	26.4

Table 9. XPS data on PCP/BPO at 70°C for 24 h

| Temperature	C1s	C1s		Plasmon	ΔE_L
(°C)	(eV)	CPS	Intensity (%)	(eV)	(eV)
25	285.8	40560	0.0	310.2	24.4
100	285.7	40620	0.1	310.2	24.5
150	285.7	40770	0.5	310.1	24.4
200	285.7	40820	0.6	310.3	24.6
250	285.5	41800	3.1	310.2	24.7
280	285.3	42010	3.6	310.3	25.0
310	285.2	42240	4.2	310.2	25.0
340	284.9	44500	9.7	310.2	25.3
370	284.7	45720	12.7	311.2	26.5
400	284.6	45790	12.9	311.3	26.7
430	284.7	45840	13.0	311.6	26.9
460	284.9	45897	13.2	311.6	26.7
500	285.0	45970	13.3	311.4	26.4
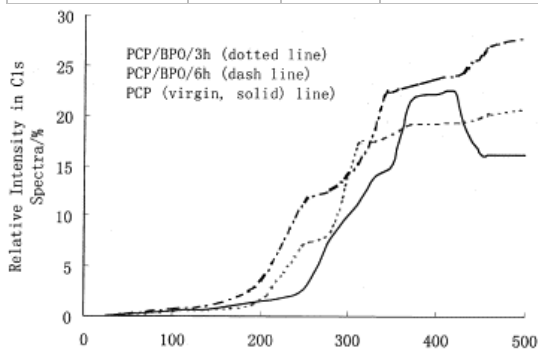
Fig. 8. Relative intensity of PCP/BPO heated in an oil bath at 70°C for 3 (dotted line) and 6 h (dash line).
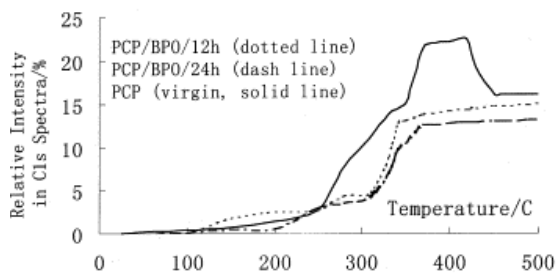

Fig. 9. Relative intensity of PCP/BPO heated in an oil bath at 70°C for 12 (dotted line) and 24 h (dash line).

3.2.2. XPS data on percentage of chlorine in PCP vs temperature

The XPS data which relates the amount of chlorine remaining to temperature is collected in Table 10. The loss of chlorine in both cross-linked and virgin polymer begins at about 200°C but the cross-linked systems lose chlorine much more readily. At 370°C the cross-linked polymers retain more chlorine than does the virgin material. This is presumably due to the rigidity of the cross-linked system preventing the facile loss of chlorine.

Table 10. Percentage of chlorine remaining in PCP vs temperature[a]

Temperature	PCP Virgin		PCP/BPO/ 3 h		PCP/BPO/ 6 h		PCP/BPO/ 12 h		PCP/BPO/ 24 h	
(°C)	CPS	Intensity (%)	CPS	Intensity (%)	CPS	Intensity (%)	CPS	Intensity (%)	CPS	Intensity (%)
25	20070	100.0	7060	100.0	6670	100.0	6630	100.0	4630	100.0
100	19860	99.0	7060	100.0	6630	99.4	6570	99.1	4610	99.6
200	17850	89.0	4130	58.5	3850	57.8	4500	67.8	3100	66.9
310	3740	18.6	880	12.5	2150	32.2	800	12.1	680	14.7
370	100	0.5	220	3.1	200	3.1	190	2.9	210	4.5

aRelative intensity (%) in C12p spectra as function of temperature for PCP.

3.2.3. PIP/BPO

Table 11, Table 12, Table 13, Table 14 give the XPS data for systems of PIP modified with BPO at 70°C for time period 3–24 h. A summation of all of the above data is provided in Fig. 10, Fig. 11. There is a strong change in the relative intensity as a function of reaction time, indicating the strong dependence of cross-linking on this parameter. Cross-linking does not occur with virgin PIP to any significant extent upon heating but, in the samples containing BPO, there is a very significant amount of cross-linking with a short reaction time. This will be discussed later in the text.

Table 11. XPS data on PIP/BPO at 70°C for 3 h

Temperature	C1s	C1s		Plasmon	ΔE_L
(°C)	(eV)	CPS	Intensity (%)	(eV)	(eV)
25	286.5	13790	0.0	308.6	21.1
100	286.3	14710	6.7	308.6	22.3
150	286.3	15740	14.1	308.7	22.4
200	286.2	16120	16.9	308.7	22.5
250	286.2	16090	16.7	308.8	22.6
280	286.2	16180	17.3	308.8	22.6
310	286.1	19500	41.4	308.8	22.7
340	285.9	19610	42.2	308.7	22.8
370	285.6	21280	54.3	308.9	23.6
400	285.3	23130	67.7	310.3	25.0
430	285.1	23360	69.4	310.4	25.3
460	285.2	23450	70.0	310.5	25.3
500	285.5	23520	70.5	311.0	25.5

Table 12. XPS data on PIP/BPO at 70°C for 6 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	286.3	14560	0.0	308.7	22.4
100	286.1	14880	6.7	308.7	22.6
150	286.1	15760	14.1	308.8	22.7
200	286.1	16410	16.9	308.8	22.7
250	286.1	15090	16.7	308.8	22.7
280	286.0	17300	17.3	308.9	22.9
310	286.0	19630	41.4	308.8	22.8
340	285.8	20130	42.2	308.8	23.0
370	285.6	20610	54.3	308.8	23.2
400	285.4	21390	46.9	309.9	24.5
430	285.0	22190	52.4	310.0	25.0
460	284.8	23220	59.4	310.4	25.6
500	285.3	23570	61.8	311.4	26.1

Table 13. XPS data on PIP/BPO at 70°C for 12 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	285.6	40860	0.0	308.0	22.4
100	285.5	41360	1.2	308.1	22.6
150	285.5	41420	1.4	308.1	22.6
200	285.5	41610	1.8	307.9	22.4
250	285.5	41920	2.6	308.0	22.5
280	285.4	42050	2.9	308.1	22.7
310	285.4	42310	3.6	308.1	22.7
340	285.3	42410	3.8	308.1	22.8
370	285.1	42840	4.9	308.1	23.0
400	284.7	47260	15.7	309.0	24.3
430	284.5	48307	18.2	309.8	25.3
460	284.7	49670	21.6	310.1	25.4
500	284.9	49870	22.1	310.1	25.2

Table 14. XPS data on PIP/BPO at 70°C for 24 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	285.3	28210	0.0	308.0	22.7
100	285.3	28440	0.5	308.0	22.7
150	285.2	28900	2.4	308.1	22.9
200	285.2	28970	2.7	308.1	22.9
250	285.3	29050	3.0	308.0	22.7
280	285.3	29050	3.0	308.0	22.7
310	285.3	29170	3.0	308.2	22.9
340	285.3	29190	3.1	308.3	23.0
370	285.3	29420	4.3	308.9	23.6
400	285.1	32070	13.7	309.0	23.9
430	284.9	32120	13.8	309.1	24.2

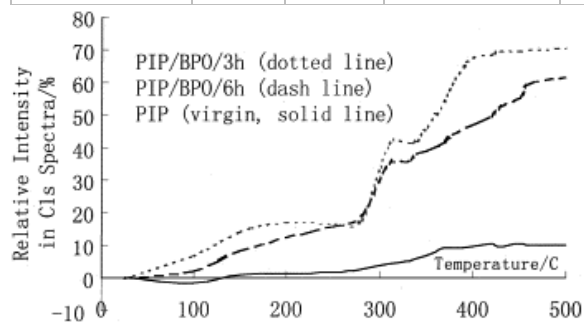| 460 | | 284.9 | 32120 | 13.9 | | 309.1 | 24.2 |
| 500 | | 285.0 | 31900 | 13.1 | | 309.2 | 24.2 |

Fig. 10. Relative intensity of PIP/BPO heated in an oil bath at 70°C for 3 (dotted line) and 6 h (dash line).
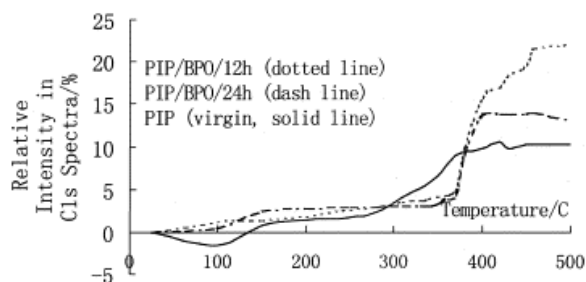

Fig. 11. Relative intensity of PIP/BPO heated in an oil bath at 70°C for 12 (dotted line) and 24 h (dash line).

3.2.4. Comparison between PCP and PIP chemically cross-linked by BPO

There is a significant difference in the extent of cross-linking between PCP and PIP; this is shown in Fig. 12, Fig. 13, Fig. 14, Fig. 15. For reaction times of 3 and 6 h, the retention of carbon is much greater for PIP than for PCP, indicating that the cross-linked PIP samples with BPO can more easily lose other elements than does PCP. At longer reaction times, there is more similarity between PIP and PCP.
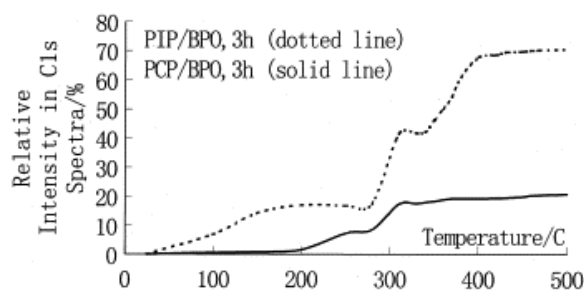

Fig. 12. Relative intensity of PIP/BPO (dotted line) and PCP/BPO (solid line) heated in an oil bath at 70°C for 3 h.
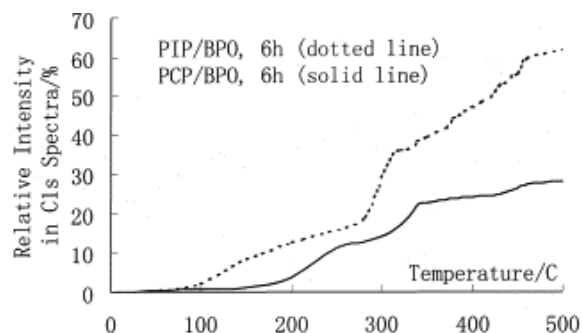

Fig. 13. Relative intensity of PIP/BPO (dotted line) and PCP/BPO (solid line) heated in an oil bath at 70°C for 6 h.
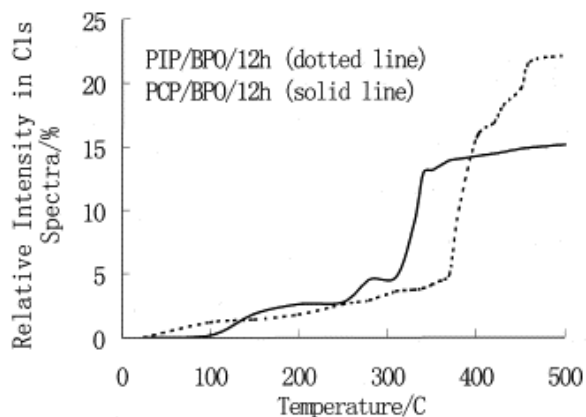
Fig. 14. Relative intensity of PIP/BPO (dotted line) and PCP/BPO (solid line) heated in an oil bath at 70°C for 12 h.
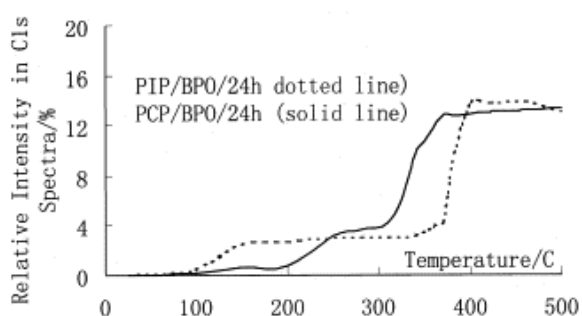
Fig. 15. Relative intensity of PIP/BPO/24 h (dotted line) and PCP/BPO/24 h (solid line).

3.2.5. XPS data for PCP/PIP chemically cross-linked with DCP

The differences between PCP and PIP as a function of reaction time are shown in Fig. 16, Fig. 17; the tabular data for PCP modified with DCP is shown in Table 15, Table 16, Table 17, Table 18 while the data for the PIP system is in Table 19, Table 20, Table 21, Table 22.

Fig. 16. Relative intensity of PCP/DCP heated in an oil bath at 120°C for 3, 6, 12, 24 h separately.

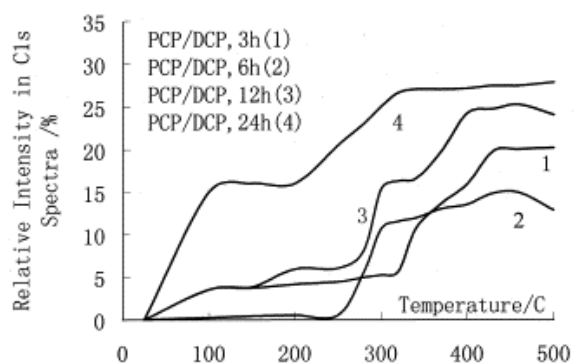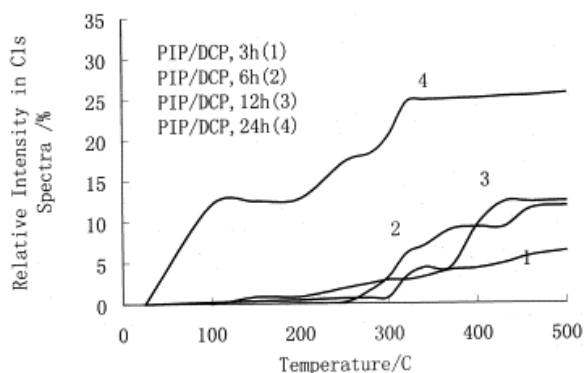Fig. 17. Relative intensity of PIP/DCP heated in an oil bath at 120°C for 3, 6, 12, 24 h separately.

Table 15. XPS data on PCP/DCP at 120°C for 3 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	286.4	36630	0.0	309.7	23.3
100	286.4	37920	3.5	309.8	23.4
150	286.4	38000	3.7	309.8	23.4
200	286.2	38120	4.1	309.8	23.6
250	286.1	38230	4.4	309.8	23.7
280	285.9	38430	4.9	309.8	23.9
300	285.7	38540	5.2	309.9	24.2
320	285.6	38690	5.6	309.9	24.3
340	285.4	40550	10.7	310.8	25.4
370	285.1	41620	13.6	310.9	25.8
400	284.7	42450	15.9	312.2	27.5
430	284.7	43890	19.8	312.2	27.5

Table 16. XPS data on PCP/DCP at 120°C for 6 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	286.3	39140	0.0	309.5	23.2
100	286.3	39230	0.2	309.6	23.3
150	286.2	39300	0.4	309.5	23.3
200	286.1	39320	0.5	309.6	23.5
250	285.9	39330	0.5	309.7	23.8
280	285.7	41290	5.5	309.6	23.9
300	285.6	43270	10.6	309.6	24.0
320	285.4	43660	11.5	309.6	24.2
340	285.4	43800	11.9	309.6	24.2
370	285.0	44230	13.0	311.5	26.5
400	284.6	44430	13.5	311.7	27.1
430	284.8	44920	14.8	311.7	26.9
460	284.9	44980	14.9	311.7	26.8
500	284.9	44140	12.8	311.7	26.8

Table 17. XPS data on PCP/DCP at 120°C for 12 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	286.3	36070	0.0	310.3	24.0
100	286.3	37340	3.5	310.3	24.0
150	286.3	37440	3.8	310.4	24.1
200	286.1	38190	5.9	310.4	24.3
250	285.9	38230	6.0	310.4	24.5
280	285.7	38250	6.0	310.6	24.9
300	285.6	41600	15.3	310.7	25.1
320	285.4	41950	16.3	310.7	25.3
340	285.3	42040	16.6	310.7	25.4
370	285.0	43210	19.8	310.7	25.7
400	284.6	44800	24.2	312.0	27.4
430	284.6	44990	24.7	312.0	27.4
460	284.8	45150	25.2	311.8	27.0
500	285.0	44720	24.0	312.0	27.0

Table 18. XPS data on PCP/DCP at 120°C for 24 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	286.3	33930	0.0	310.8	24.5
100	286.2	38200	12.6	310.8	24.6
150	286.3	38410	13.2	310.8	24.5
200	286.2	38510	13.5	310.9	24.7
250	285.9	39620	16.8	310.9	25.0
280	285.8	40380	19.0	310.9	25.1
300	285.6	41060	21.0	310.9	25.3
320	285.4	41410	22.0	310.9	25.5
340	285.3	41510	22.3	310.9	25.6
370	285.1	42610	25.6	310.9	25.8
400	284.6	43470	28.1	311.5	26.9
430	284.6	43770	29.0	311.5	26.9
460	284.9	43900	29.4	311.9	27.0
500	284.8	43930	29.5	311.9	27.1

Table 19. XPS data on PIP/DCP at 120°C for 3 h

Temperature (°C)	C1s (eV)	C1s CPS	Intensity (%)	Plasmon (eV)	ΔE_L (eV)
25	285.6	41010	0.0	307.3	21.7
100	285.6	41020	0.0	307.4	21.8
150	285.6	41340	0.8	307.3	21.7
200	285.6	41350	0.8	307.3	21.7
250	285.5	41730	1.8	307.3	21.8
280	285.5	41990	2.4	307.4	21.9
300	285.4	42170	2.8	307.4	22.0
320	285.4	42180	2.8	307.6	22.2
340	285.3	42320	3.2	307.9	22.6

370	285.4	42640	4.0	308.3	22.9
400	285.3	42750	4.2	308.7	23.4
430	284.7	42960	4.8	309.4	24.7
460	284.5	43340	5.7	309.6	25.1
500	284.5	43600	6.3	309.6	25.1

Table 20. XPS data on PIP/DC P at 120°C for 6 h

Temperature	C1s	C1s		Plasmon	ΔE_L
(°C)	(eV)	CPS	Intensity (%)	(eV)	(eV)
25	285.7	39600	0.0	307.9	22.2
100	285.7	39570	−0.1	308.1	22.4
150	285.7	39580	−0.1	308.1	22.4
200	285.7	39590	0.0	308.1	22.4
250	285.7	39630	0.1	308.1	22.4
280	285.7	40250	1.6	308.3	22.6
300	285.6	40880	3.2	308.4	22.8
320	285.6	41980	6.0	308.4	22.8
340	285.6	42370	7.0	308.5	22.9
370	285.6	43120	8.9	308.5	22.9
400	285.5	43240	9.2	309.1	23.6
430	284.9	43240	9.2	309.2	24.3
460	284.5	44110	11.4	309.5	25.0
500	284.6	44230	11.7	310.3	25.7

Table 21. XPS data on PIP/DCP at 120°C for 12 h

Temperature	C1s	C1s		Plasmon	ΔE_L
(°C)	(eV)	CPS	Intensity (%)	(eV)	(eV)
25	285.7	39110	0.0	307.7	22.0
100	285.6	39180	0.2	307.7	22.1
150	285.6	39220	0.3	307.6	22.0
200	285.7	39280	0.4	307.7	22.0
250	285.6	39340	0.6	307.7	22.1
280	285.6	39340	0.6	307.7	22.1
300	285.7	39400	0.7	308.0	22.3
320	285.6	40360	3.2	308.1	22.5
340	285.6	40790	4.3	308.1	22.5
370	285.7	40810	4.3	309.0	23.3
400	285.6	42820	9.5	309.0	23.4
430	285.0	43870	12.2	309.1	24.1
460	284.7	43890	12.2	309.5	24.8
500	284.6	43900	12.3	309.8	25.2

Table 22. XPS data on PIP/DCP at 120°C for 24 h

Temperature	C1s	C1s		Plasmon	ΔE_L
(°C)	(eV)	CPS	Intensity (%)	(eV)	(eV)
25	285.9	34080	0.0	308.2	22.3
100	285.9	38200	12.0	308.2	22.3
150	285.9	38320	12.4	308.3	22.4

200	285.8	38420	12.7	308.3	22.5
250	285.9	39960	17.2	308.3	22.4
280	285.8	40320	18.3	308.4	22.6
300	285.7	41070	20.5	308.4	22.7
320	285.7	42430	24.5	308.5	22.8
340	285.6	42550	24.8	308.5	22.9
370	285.6	42560	24.9	309.7	24.1
400	285.5	42600	25.0	309.7	24.2
430	284.8	42680	25.2	311.0	26.2
460	284.5	42710	25.3	310.6	26.1
500	284.6	42810	25.6	310.8	26.2

The first analysis can be based upon relative intensity: A comparison of the influence of the reaction time on the maximum relative intensity, I_{max}, for cross-linked PCP and PIP is shown in Table 23. It is valuable to make a few observations. The maximum relative intensity, I_{max}, (70.5%) observed for PIP must be contrasted to the value (20.7%) observed for PCP in the presence of BPO at 3 h reaction time, even though PCP does give a higher intensity in the absence of initiators. This is not observed for DCP and this implies that the cross-linking reaction of PIP can be enhanced by the presence of BPO at times less than 12 h. At long reaction times, 24 h, this is diminished. In the presence of BPO the relative intensity is roughly constant for both PCP and PIP. The general changes in the DCP systems are opposite to those in the BPO system. The differences between PCP and PIP gradually decrease between 3 and 24 h reaction times; this is exactly consistent with the literature [2].

Table 23. Influence of reaction time t on the maximal relative intensity I_{max} for cross-linked PCP and PIP

System	PCP		PIP	
Reaction time t/h	BPO	DCP	BPO	DCP
3	20.7	20.2	70.5	6.3
6	27.9	14.9	61.8	11.7
12	15.1	25.4	22.1	12.3
24	13.2	29.5	13.9	25.6

We now turn to the plasmon loss, ΔE_L. Looking at the onset temperatures derived from Table 6, Table 7, Table 8, Table 9 (PCP/BPO), 11–14 (PIP/BPO), 15–18 (PCP/DCP) and 19–22 (PIP/DCP) and corresponding Fig. 12, Fig. 13, Fig. 14, Fig. 15, one may conclude that charring always occurs earlier for PCP than PIP, by about 60°C in case of BPO, and more than 100°C in the case of DCP. This is clearly due to the presence of chlorine atoms and double bond in polymeric matrices although the differences between PCP and PIP seem to be unimportant in relative intensity along with the progressive extension of reaction time t.

3.2.6. Comparison of thermal stability of PCP characterized by $T_{60\%}$

Chlorine loss must produce double bonds which may then undergo a cross-linking reaction. Another way to distinguish the thermal stability of PCP cross-linked with BPO or DCP involves the loss of chlorine. As an indication of cross-linking, it has been somewhat arbitrarily decided to use the temperature $T_{60\%}$ at which 60% of the chlorine has been lost, i.e. the char contains 40% of the chlorine. This data is collected in Table 24 and one can see that the $T_{60\%}$ is relatively constant for BPO up to 12 h reaction time. The $T_{60\%}$ is higher for DCP, indicating that BPO is more effective than DCP is promoting cross-linking of PCP.

Table 24. $T_{60\%}$ (°C) values derived from C12p spectra for PCP

Reaction time/h	PCP cross-linked by BPO	PCP cross-linked by DCP
3	242	285
6	240	280
12	245	260
24	260	260

4. Conclusion

There are a number of issues concerning the measure of thermal degradation and charring of polymers upon heating that must be addressed and XPS provides a very useful technique to address these questions. One can conclude as follows:

1. Parameters derived from XPS, such as the relative intensity of carbon, the plasmon loss peak (ΔE_L) in C1s spectra and the atomic concentration of chlorine in C12p spectra are the most important for the characterization of cross-linking and char formation.
2. Much lower relative intensity for original PIP than PCP was observed. The relative intensity does not exceed 10% for PIP below 380°C which is in agreement with the fact that plasmon loss (ΔE_L) remains constant (~22.0 eV) up to 380°C. In fact very little cross-linking and cross-link density appear until 380°C.
3. There exists a great increase in the plasmon loss for both PCP and PIP, particularly for PCP. This indicates that cross-linking and charring reactions for PCP proceed at an extremely high rate within the narrow interval of 10°C, possibly due to the coexistence of chlorine atoms attached to carbon and double bonds in the backbone.
4. The cross-linking reaction for PIP on heating can be extensively enhanced by BPO at least at $t<$l2 h. This effect is diminished as the time increases to 24 h. In the presence of DCP the relative intensity stays more or less constant for both PCP or PIP.
5. The relative intensity of PIP/BPO at 3 h on heating gives a surprisingly high value of ca 70%. Unlike the original PIP, which does not undergo cross-linking upon heating, cross-linking of PCP developed in almost all the samples reacted with BPO at 70°C within the time period 3 to 24 h.
6. An extremely high I_{max} (70.5%) had been observed for PIP, in contrast to PCP (20.7%), in the presence of BPO at. t=3 h, even though the original PCP does display higher intensity than PIP in the absence of initiators.
7. In the presence of DCP the relative intensity stays more or less constant whether PCP or PIP is used. Changes for the DCP system are opposite to those observed with BPO.
8. The differences between PCP and PIP gradually decrease when the reaction time increases from 3 to 24 h. This must be indicative of a significant difference between the initiators.
9. On the basis of the plasmon loss, ΔE_L, the onset temperatures indicate that charring always occurs earlier for PCP than PIP. This is clearly due to the presence of chlorine atoms and double bonds in the polymer.

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