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Contents

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Abstract

Polyisoprene and polychloroprene have been cross-linked either in solution or in solid state using free radical initiators. In the comparable experimental conditions higher cross-linking density was observed in the solid state process. Independent of the cross-linking method, polychloroprene tended to give a higher gel content and cross-link density than does polyisoprene. Infrared characterization of the cross-linked materials showed *cis*-trans isomerization occurred in the polyisoprene initiated by benzoyl peroxide, whereas no isomerization was found in the samples initiated by dicumyl peroxide. Polyisoprene does not cross-link by heating in a thermal analyzer, whereas polychloroprene easily undergoes cross-linking in such conditions. Infrared spectroscopy showed that in the case of polyisoprene, rearrangements occur upon heating which lead to the formation of terminal double bonds, while polychloroprene loses hydrogen chlorine which leads to a conjugated structure. There is apparently some enhancement of the thermal and thermal oxidative stability of polyisoprene because of the cross-linking. Cross-linked polychloroprene is less thermally stable than the virgin polymer. Cross-

linking promotes polymers charring in the main step of weight loss in air, which leads to enhanced transitory char.

1. Introduction

In previous work from these laboratories, we have examined the relationship between cross-linking and the thermal stability of several polymers. Polyamide-6 has been cross-linked using γ-radiation either alone or in the presence of additives and cross-linking does not appear to enhance the thermal stability of polyamide-6 in any way.[1] In investigations of polybutadiene and butadiene-containing copolymers, it has been observed that butadiene spontaneously cross-links as it is heated in thermogravimetric analysis and that prior cross-linking does not enhance its thermal stability.[2,3] The only case where we have observed that cross-linking enhances the thermal stability was that of cross-linked polystyrenes.[4] In this case as the quantity of divinylbenzene giving cross-links was increased, the onset temperature of the degradation was moved to higher temperatures. This has been attributed to the fact that the cross-links are aromatic and led to the realization that the types of cross-links are at least as important as the number of cross-links. This has been further confirmed in some cross-linked methacrylates in which we have found that when an aromatic dimethacrylate, bisphenol A dimethacrylate, was used as the cross-linker, thermal stability was enhanced while for other, aliphatic, cross-linkers, cross-linking did not enhance thermal stability.[4]

Our interest in butadiene-containing polymers has led to an investigation of the thermal degradation of polyisoprene, (PIP), and polychloroprene (PCP). Previous work on the thermal degradation of PIP has shown that at about 350°C it isomerizes from a material with internal double bonds (1,4 units) to one which contains mainly external double bonds (3,4 or 1,2 units).[5,6] A mechanism involving an initial radical cleavage followed by isomerization of these radicals to the non-main chain double bond has been suggested. The degradation of PCP begins as early as 200°C with the loss of HCl but the main degradation occurs between 300 and 450°C.[7,8,9] The lower thermal stability of PCP is likely to be due to the possibility of chain-stripping as a pathway for the degradation.

In this paper we continue to explore the connection between cross-linking and thermal stability through an examination of polyisoprene (PIP) and polychloroprene (PCP).

2. Experimental

2.1. Materials

Most chemicals and solvents in this study were supplied by Aldrich Chemical Company, including benzoyl peroxide (BPO), dicumyl peroxide (DCP), and chloroform. The polymers used in this study were polyisoprene (MW: 800,000, *cis*) and polychloroprene (MW: 20,000, 10% *cis*, 85% *trans*). Silver nitrate was purchased from Fisher Scientific Company.

2.2. Initiator-enhanced thermal cross-linking

A 5.0 g sample of polymer was dissolved in 50 ml chloroform together with 20 mmol benzoyl peroxide, BPO, or dicumyl peroxide, DCP, in a 100 ml round bottom flask. After complete dissolution, the flask was stirred for 5 min. This solution was then poured onto a Teflon plate and the solvent was allowed to evaporate at room temperature for a minimum of 2 days. A 1.0 g sample of this mixture of polymer and initiator was sealed under vacuum in an ampoule. The sample was then placed in an oil-bath, which had

been preheated to a temperature in the range of 70–75°C or 120°C, for 3 to 24 h. At the conclusion of the reaction, the ampoule was opened and the sample was removed and analyzed.

2.3. Cross-linking in solution

A 0.5 g sample of polymer was dissolved in 20 ml chloroform in a 50 ml round bottom flask and then 0.5 ml of a 0.2 M acetone solution of BPO was added. The sample was heated in an oil bath at 70°C for 3 to 24 h. At the conclusion of the reaction, methanol was added to the contents of the flask to precipitate the polymer. The sample was recovered and thoroughly dried at room temperature and then gel content, swelling ratio and thermal stability were measured.

2.4. Characterization of cross-linking

In this work the cross-linking behavior was characterized by gel content and swelling ratio[10,11] which were measured as previously described.[12] Gel content was determined by the heating a sample of known mass in a solvent for 24 h. The recovered insoluble sample is then thoroughly dried at elevated temperatures under vacuum and the mass of insoluble polymer is determined. The ratio of insoluble polymer to starting sample gives the fraction, which has undergone gelation. Swelling ratio is determined by a similar process, after the heating period the insoluble sample is permitted to air dry for a few minutes and then its mass is obtained. The ratio of solvent swollen sample to that of the starting sample is defined as the swelling ratio and is a measure of the cross-link density.

2.5. Instrumentation

Infrared spectra were obtained by transmission on a Mattson Galaxy Fourier Transform Infrared Spectrometer at 4 cm^{-1} resolution. Thermogravimetric analysis (TGA) was carried out using a Mettler model 3000 thermoanalyzer at a heating rate of 10°C per min under either air or argon. TGA/FTIR data was obtained using a Cahn TG-131 interfaced to a Mattson Galaxy Infrared Spectrometer under inert atmosphere at a scan rate of 20°C per min. Elemental analysis was performed by Midwest Microlabs.

Solid state NMR spectroscopy was carried out using a Bruker MSL spectrometer operating at a frequency of 25 MHz for carbon. All experiments were carried out using cross polarization (CP) and magic angle spinning (MAS) at a frequency of 5 kHz. Spinning sidebands accounted for 6% of the total aromatic carbon. A recycle delay of 2 s was used for all experiments. The CP-MAS contact time was varied in order to determine the optimal contact time; this was found to be 1.5 ms and this was used for all experiments. CP-MAS dipolar dephasing experiments were also carried out using dephasing times of 1 and 45 μs to differentiate between protonated and non-protonated carbons.

2.6. Analysis for evolved chlorine

Chlorine, as hydrogen chloride, is evolved from PCP upon heating. A sample was placed in a tube through which nitrogen was flowed and this was heated at 360°C for 10 min in a sand bath. The evolved gases were directed by the flow of nitrogen into an aqueous solution of silver nitrate; the precipitated silver chloride was repeatedly washed with water, dried at 100°C overnight and then determined gravimetrically.

3. Results and discussion

3.1. Cross-linking

3.1.1. Initiator-enhanced thermal cross-linking

It has been shown in previous work[3] of the cross-linking of polybutadiene and its copolymers that the initiator-enhanced thermal process is the most effective process to achieve high cross-linking. This process is also an effective means to cross-link PIP and PCP, since the cross-linking occurs facilely for both PCP and PIP but the cross-linking behavior of the two polymers is different. This can be seen from the gel contents and swelling ratios which are given in Table 1.

Table 1. Gel contents (GC) and swelling ratios (SR) for polyisoprene and polychloroprene which have been cross-linked by an initiator-enhanced thermal process

Time h	PIP		PCP	
	GC (%)	SR (%)	GC (%)	SR (%)
BPO initiation at 70°C				
0	0	∞	0	∞
1	–	–	–	–
3	16	8300	89	800
6	65	6300	91	800
12	91	2400	–	–
24	93	2400	89	800
30	n.m.[a]	n. m.	89	800
DCP initiation at 120°C				
0	0	∞	0	∞
1	n.m.	n.m.	n.m.	n.m.
2	n.m.	n.m.	96	1300
3	92	1000	n.m.	n.m.
5	n.m.	n.m.	95	1000
6	92	700	n.m.	n.m.
12	91	600	91	900
24	91	500	95	800

[a] n.m., not measured.

In the presence of BPO, PIP cross-links much less efficiently than PCP. On the other hand in the presence of DCP, PIP apparently shows higher cross-linking density. This might be related to the difficulty of isomerization of PIP at 70°C, whereas it isomerizes easier at 120°C.

3.1.2. Cross-linking in solution

For this process both polymers have been cross-linked by refluxing a chloroform solution of the polymer in the presence of benzoyl peroxide, BPO. The gel content and swelling ratio are listed in Table 2.

Table 2. Gel contents (GC) and swelling ratios (SR) for PIP and PCP cross-linked in chloroform with benzoyl peroxide

Reaction time (h)	Polyisoprene		Polychloroprene	
	% GC	% SR	% GC	% SR
0	0	∞	0	∞
3	88	12 000	n.m.	n.m.
6	82	11 000	n.m.	n.m.
8	n.m.	n.m.	84	4000
12	72	10 300	n.m.	n.m.
24	71	9000	86	3200

This is a much less effective process to obtain cross-linking as shown by the much higher swelling ratios compared to those in Table 1. The cross-linking behavior of the two polymers is quite different in this process. The extent of gel formation is comparable but the cross-link densities are quite different with PCP having significantly higher cross-link densities, in agreement with the initiator-enhanced thermal cross-linking.

3.1.3. Infrared spectra of cross-linked samples

Cis-PIP shows absorptions at 3036, 2728 and 835 cm^{-1} which undergo changes upon thermally induced cross-linking of the polymer. The bands at 3036 cm^{-1} and 835 cm^{-1}, attributable to the olefinic C–H stretching and C–H out-of-plane deformation of >C=CH-, largely vanish upon cross-linking by BPO but are still strong when DCP is used to initiate the cross-linking. Another change in infrared spectra of BPO initiated PIP samples is the weakness of band at 1665 cm^{-1}, attributable to cis-double bonds, and the development of a new band at 1651cm^{-1}. This last band is sharp and much stronger than the band at 1665 cm^{-1}, and implies that trans-double bonds are formed while the disappearance of the bands at 3036 and 835 cm^{-1} is also indicative of the loss of cis-double bonds. It appears that BPO initiation leads to the formation of trans-double bonds at the expense of cis-double bonds while DCP leaves the cis-double bonds unchanged.

There are three allylic positions which may be attacked by initiator radicals, two are on the main chain while the other is the pendant methyl group. In the work of Minoura[13] using squalene as a model compound, it was found that all the three positions may be attacked; this has been confirmed in unpublished work from the Marquette laboratory on anionic initiation of PIP.[14] The observation that

many external, i.e. vinyl, double bonds are developed in the samples cross-linked by BPO while only a few are formed in DCP initiated cross-linking may indicate that the two initiators interact at different positions. Radicals created in the main chain can more easily cross-link and *cis–trans* isomerization provides addition flexibility to the polymeric chains which allows higher cross-linking densities.

There is a smaller difference in the infrared spectrum of cross-linked PCP and unreacted PCP. The olefinic C–H stretching vibration, 3022 cm^{-1}, and the carbon–carbon double bond stretching frequency, 1658 cm^{-1}, are both observed in the unreacted polymer and in a sample which has been heated to 350°C. The C=C stretching vibration disappears upon heating at 450°C and a new band at 1638 cm^{-1} appears.

3.2. Thermal degradation of the virgin polymers

3.2.1. Polyisoprene
In the previous work from these laboratories [2,3] it has been noted that cross-linking of polybutadiene has little effect on its thermal stability; this is apparently related to the observation that polybutadiene spontaneously cross-links in a thermogravimetric analyzer. The results of this study indicate that PIP behaves quite differently and is not easily cross-linked during the course of thermogravimetric analysis. In the temperature range of 250 to 450°C, the residue is a sticky liquid which is soluble in chloroform, indicated that no gel is formed and no cross-linking occurs.

Previous workers have stated that *cis*-polyisoprene will undergo isomerization in a thermogravimetric analyzer but, this isomerization is negligible below 300°C. During the thermolysis partial consumption of *cis* isoprenic double bonds [−C(CH$_3$)=CH–IR absorption at 835 cm^{-1}] and formation of exomethylene units (RR'C=CH$_2$, 885 cm^{-1}) and some vinyl group (−CH=CH$_2$, 909 cm^{-1}) were observed.[5,6] When the thermal degradation is extended to 75% mass loss, the residue has a chemical structure which is essentially that of cyclized rubber.[5]

In this work, only minor changes in the infrared spectra were observed below 300°C for the residue obtained from TGA, but the changes between 350° and 450°C are obvious. The bands at 3036 and 837 cm^{-1} are missing and the bands at 1661 and 2960 cm^{-1} are weaker. The weakness of band at 2960 cm^{-1}is evidence for the loss of methyl groups which may be partially converted to RR'C☐CH$_2$, and the absence of the band at 3036 cm^{-1} and the weakness of band at 1661 cm^{-1} are evidence for the loss of the double bonds during the course of thermolysis.

3.2.2. Polychloroprene
Different from polyisoprene but similar to polybutadiene [2,3], PCP undergoes a facile cross-linking upon thermolysis. The cross-linking is confirmed by gel content and swelling ratio, shown in Table 3.

Table 3. Gel content, swelling ratio and mass loss of PCP at different temperatures in TGA with heating rate at 10°c/min in an Inert atmosphere

Temperature (°C)	Mass loss (%)	Swelling ratio (%)	Gel content (%)
150	0	∞	Trace
200	0.1	5900	79
250	1.6	2000	86

350	28.6	900	97
450	54.8	100	

One sees that PCP becomes insoluble in chloroform upon thermolysis in a TGA. The gel content shows that the extent of cross-linking increases as the temperature increases while the swelling ratio decreases, indicating a higher cross-link density. At 450°C, the residue becomes brittle and it is difficult to recover the entire sample so the gel content cannot be accurately measured.

According to the literature,[7] the thermal degradation of PCP takes place in two stages: elimination of hydrogen chloride followed by decomposition of the backbone polymer. The first stage ends at about 420°C both in air and in argon and it is reported that about 90% of the available chlorine is lost as hydrogen chloride and the percentage of chlorine which is lost depends upon the temperature, at 380°C about 77% is reported to be lost.

The loss of chlorine obtained in this work is around 75% when the sample is heated isothermally at 360°C for 10 min; when the thermolysis time is extended to 30 min, the amount of chlorine which is evolved does not show a significant change (77%). This corresponds to the mass loss of 31%, lower than the total mass loss, which is about 44% as measured by TGA. Thus in the first stage of the degradation both chlorine loss as well as other degradation processes might occur. PCP contains about 40% chlorine by mass, if chlorine is completely evolved in the form of hydrogen chloride, the corresponding mass loss should be around 41%. The mass loss at different temperatures is listed in Table 4 for a 30 min isothermal pyrolysis.

Table 4. Mass loss, swelling ratio, and gel content for PCP isothermally thermolyzed at various temperatures for 30 min

Temperature (°C)	Mass loss (%)	Swelling ratio (%)	Gel content (%)
200	1.6	1800	88
250	6.2	1100	95
300	13.4	900	97
325	30.2	800	95
350(10 min)	36.3	–	–
350	44.4	600	98
350 (60 min)	46.4	500	98

According to the literature, polyenes are formed during the course of thermolysis but the polyene chain is not as long as that obtained from poly(vinyl chloride), (PVC).[7,8] The color changes from light yellow to dark brown and this may be indicative of the formation of conjugation. A comparison of the infrared spectrum of PCP before and after pyrolysis gives further evidence for the polyene structure. The band at 1658 cm^{-1} which occurs in the virgin PCP is unchanged upon thermolysis at 350°C but disappears upon heating to 450°C. At a pyrolysis time of 30 min, a new band appears in the carbon–carbon double bond region at 1638 cm^{-1} while a band in the C–H out-of-plane bending region at 806 cm^{-1} disappears. These changes may be indicative of the evidence for the formation of polyene.

In order to better characterize the chars which are produced upon heating, solid-state ^{13}C NMR experiments were performed. The spectrum of polychloroprene consists of four resonances, 135.6 (C–Cl), 124.7 (C–H) (unsaturated), 39.0 (CH$_2$–C–Cl), and 27.5 (CH$_2$–CH). When the sample is heated at 350°C

for 5 min, the peaks are in essentially the same positions but a significant amount of broadening of the peaks has occurred because of cross-linking and restriction of the chain motions.[15] There is no change in the spectrum with a longer heating time. Dipolar dephasing experiments permit the identification of protonated and non-protonated resonances. The dipolar dephasing spectra with a delay time of 1 and 45 μs are shown in Fig. 1. With a delay time of 1 μs both protonated and non-protonated carbons are observed while at 45 μs only non-protonated carbons and methyl groups are observed. The majority of the sp^3 carbon is protonated; the spectra at a delay time of 45 μs shows that there is a small amount of methyl present in the chars. When the sample is heated at 450°C for 5 mins, the sample contains 3.5% more sp^2 carbon, indicative of more cross-linking. Table 5 shows the composition of the samples as a function of heating time. The chlorine constant of the heated samples is quite constant at about one chlorine atom per 100 carbon atoms. Each sample contains about 30% sp^2 carbon and only 1% of these will be bound to chlorine.
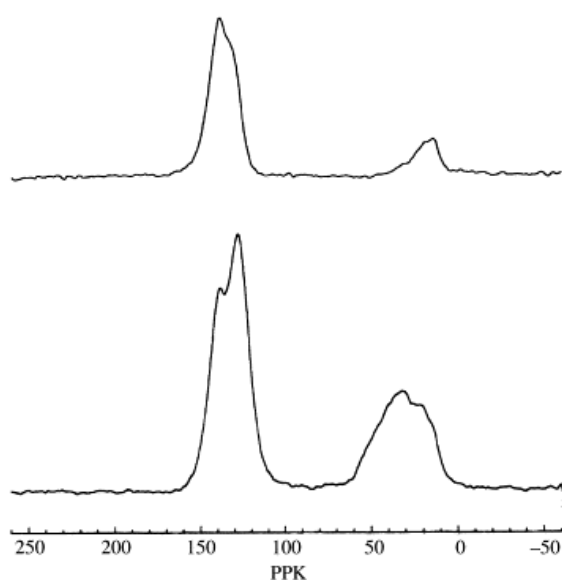

Fig. 1. Dipolar dephasing spectra of polychloroprene heated for 5 min at 450°C: lower, 1 μs delay time: upper, 45 μs delay time.

Table 5. Distribution of carbon, mol%, from CP-MAS dipolar dephasing experiments

	Virgin PCP (%)	5 min @ 350°C (%)	10 min @ 350°C (%)	20 min @ 350°C (%)	5 min @ 450°C (%)
Total sp^3 carbon	50	39	39	39	36
sp^2 protonated	25	30	30	29	32
sp^2 non-protonated	25	31	30	31	32
Total sp^2 carbon	50	61	60	61	64

The virgin PCP, before any reaction, contains equal amounts of both sp^2 and sp^3 carbons, after heating at 350°C, about 10% of the sp^3 carbons are converted into sp^2 carbons. In order to decide which bond may break first, one can refer to bond energies. There is, unfortunately, a large amount of ambiguity in the literature. Benson[16] gives the allylic C–H bond energy as 87 kcal/mol and the vinyl C–Cl bond as 91

kcal/mol. Carey and Sundberg[17] give the allylic C–H bond strength as 85 kcal/mol while Fessenden and Fessenden[18] give the vinyl C–Cl bond energy as 84 kcal/mol. These values indicate some confusion so it is not possible to decide which bond is first broken based on this information. One can envision a process in which a chlorine atom is lost, generating a radical site along the polymer chain. The hydrogen atom on the adjacent carbon is then lost, followed by a γ-hydrogen shift to give a conjugated system. It is also possible that the C–H bond is initially broken or that there is some competition between C–H and C–Cl bond cleavage. The reaction in which the C–Cl bond is broken first is illustrated below as Scheme 1
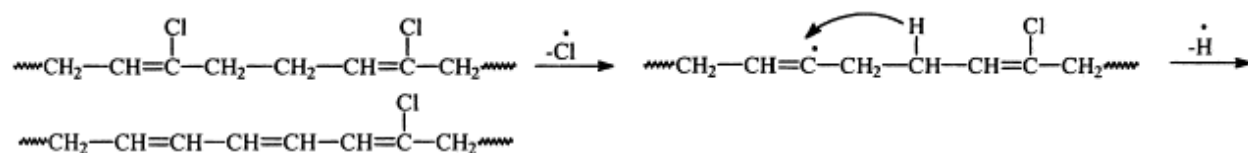
Scheme 1. Formation of conjugated double bonds in polychloroprene.

Cross-linking from this conjugated system can now occur by an intramolecular cyclization. The ratio of non-protonated aromatic carbons in the chars is 1:1 and this indicates an average of trisubstitued aromatic rings. There is no information currently available to indicate the pathway by which the reaction proceeds from polyene to cyclized product.

3.3. Thermal decomposition of the cross-linked polymers

3.3.1. Polyisoprene

The thermal stability of both virgin and cross-linked samples was characterized by thermogravimetric analysis; we have previously interpreted thermal stability in terms of the onset temperature of the degradation, usually measured as the temperature at which 10% degradation occurs. An alternative measure of thermal stability is the fraction of char which is obtained at elevated temperatures. This data is recorded in Table 6 and the TGA curves in argon and in air for PIP which has been heated at 120°C in the presence of DCP are shown in Fig. 2, Fig. 3, respectively. If one looks only at the table, it is clear that the onset of degradation occurs earlier in cross-linked PIP than in the virgin polymer. In argon for all of the procedures which have been used to cross-link PIP, the onset of the degradation is clearly at lower temperatures, probably due to the formation of some low molecular weight fragments in the cross-linking process. On the other hand, an examination of the TGA curves gives different information. The mid-point of the degradation curve is about the same, or a little higher, for the cross-linked materials as for the virgin polymer. This indicates that after the loss of low molecular weight fragments there is some slight enhancement in thermal stability. When the TGA is performed under an air atmosphere, the midpoint of the degradation is shifted about 20°C to higher temperatures. The shape of the curve in either argon or air is little changed from that of virgin polymer.

Table 6. TGA results for cross-linked polyisoprene samples

PIP/DCP	Argon atmosphere				Air atmosphere			
Time (h)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	$Char_{450°C}$(%)	$Char_{600°C}$(%)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	$Char_{450°C}$(%)	$Char_{600(°C)}$(%)
−	279	321	6.9	2.0	253	300	12.2	−
3	173	250	2.9	−	174	240	9.9	0.1
6	198	287	3.9	2.0	189	269	10.7	0.1
12	224	323	4.5	1.6	206	309	10.2	0.2
24	250	336	1.3	−	313	341	13.6	4.1

PIP/BPO (CHCl$_3$)	Argon atmosphere				Air atmosphere			
Time (h)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	$Char_{450°C}$(%)	$Char_{600°C}$(%)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	$Char_{450°C}$(%)	$Char_{600°C}$(%)
−	279	321	6.9	2.0	253	300	12.2	−
3	276	312	4.4	2.3	242	282	12.1	0.1
6	281	324	2.6	0.1	250	302	11.7	1.3
12	255	299	4.4	−	268	321	14.4	0.1
24	277	314	5.4	−	258	304	17.9	0.3

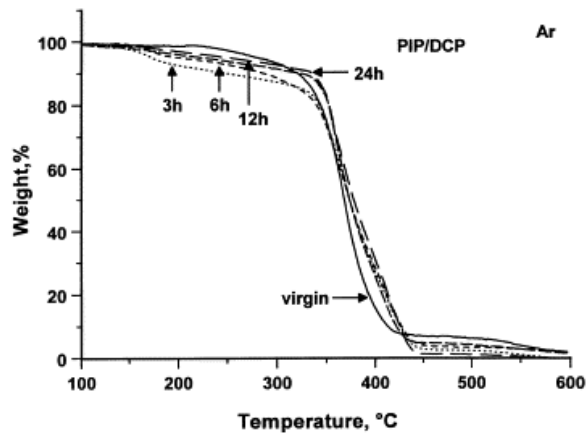| PIP/BPO	Argon atmosphere				Air atmosphere				
Time (h)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	$Char_{450°C}$(%)	$Char_{600°C}$(%)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	$Char_{400°C}$(%)	$Char_{450°C}$(%)	$Char_{600°C}$(%)
−	279	321	6.9	2.0	253	300	19.5	12.2	−
3	227	298	2.7	0.1	205	270	25.2	13.4	0.1
6	244	298	2.5	0.1	230	289	23.9	12.0	0.1
24	222	283	2.5	0.1	213	279	25.4	13.9	0.1
48	230	296	2.6	0.6	221	275	26.5	14.6	0.2

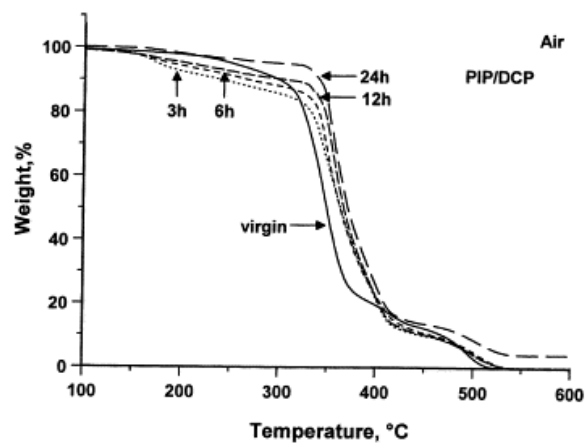Fig. 2. TGA curve in air for PIP cross-linked with DCP at 120°C.

Fig. 3. TGA curves in air for polyisoprene.

There is very little of non-volatile residue from these samples at 600°C but there is some amount of a transitory char which is formed after the main step of the weight loss. The transitory char is larger in experiments in air, however it is unstable to oxidation and vanishes at higher temperature. Only heavily cross-linked samplesshowed an enhanced tendency for char formation (Fig. 3).

3.3.2. Polychloroprene

The situation for PCP is quite different; the data is collected in Table 7 and the TGA curves for the DCP initiated cross-linking in both argon and air are shown in Fig. 4, Fig. 5, respectively. The behavior of PCP is quite similar to that of polybutadiene.[12] As the polymer is heated in the TGA experiment, cross-linking spontaneously occurs and the cross-link density is higher for the sample heated in the TGA experiment than is obtained in any of the cross-linking processes used in these experiments. The data in the table shows that in argon the preliminary cross-linked samples show a smaller residue at a given temperature than does the virgin material.

Table 7. TGA data for cross-linked polychloroprene

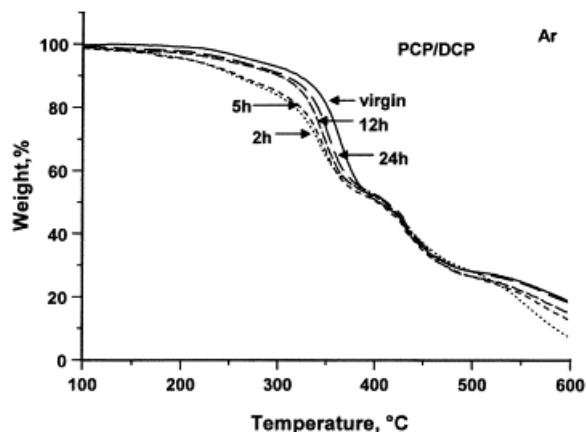| PCP/BPO (CHCl$_3$)	Argon atmosphere					Air atmosphere				
Time (h)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	Char$_{400°C}$(%)	Char$_{500°C}$(%)	Char$_{600°C}$(%)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	Char$_{400°C}$(%)	Char$_{450°C}$(%)	Char$_{475°C}$(%)
–	275	321	51.0	28.1	19.0	242	300	49.8	34.7	30.7
8	158	212	44.3	23.0	14.2	154	209	44.6	31.8	27.4
24	159	228	49.2	27.2	19.5	154	218	50.2	34.7	26.9
PCP/DCP	Argon atmosphere					Air atmosphere				
Time (h)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	Char$_{400°C}$(%)	Char$_{500°C}$(%)	Char$_{600°C}$(%)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	Char$_{400°C}$(%)	Char$_{450°C}$(%)	Char$_{475°C}$(%)
–	275	321	51.0	28.1	19.0	242	300	49.8	34.7	30.7
2	211	256	52.3	27.9	7.7	209	253	54.4	40.1	33.6
5	210	260	50.5	26.5	13.2	229	276	54.9	38.6	31.1
12	243	301	52.0	26.6	15.3	256	306	55.0	38.4	31.8
24	254	307	52.5	28.0	18.5	266	310	53.4	38.3	32.3
PCP/BPO	Argon atmosphere					Air atmosphere				
Time (h)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	Char$_{400°C}$(%)	Char$_{500°C}$(%)	Char$_{600°C}$(%)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	Char$_{400°C}$(%)	Char$_{450°C}$(%)	Char$_{475°C}$(%)
–	275	321	51.0	28.1	19.0	242	300	49.8	34.7	30.7
3	221	272	52.6	28.5	16.7	185	238	53.9	38.7	33.1
6	221	255	47.5	24.3	15.9	215	254	52.4	37.4	31.6
22	221	260	52.6	31.1	15.1	214	255	54.1	38.3	32.2
30	238	274	53.8	30.2	22.2	209	263	54.2	38.5	32.1

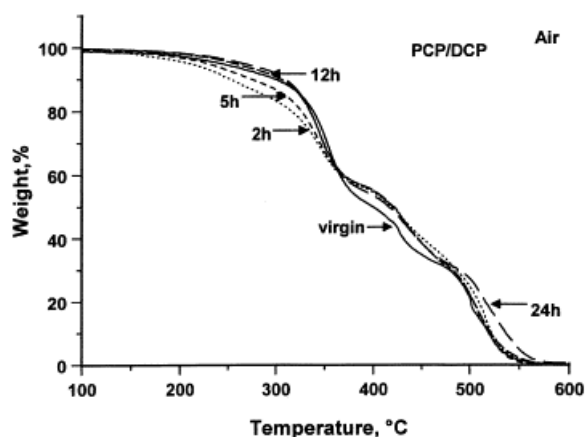Fig. 4. TGA curves for DCP cross-linked polychloroprene in argon.

Fig. 5. TGA curves for cross-linked polychloroprene in air.

In air the cross-linked samples showed higher transitory char between about 350 and 450°C. This implies the participation of oxygen in the thermolysis and a different mechanism of degradation depending upon the atmosphere. A variety of C☐O and C–O chromophores have been detected in the infrared spectra of the oxidized PCP[19,20] and this agrees with the participation of oxygen in the degradation reaction.

There is a significant difference between BPO and DCP initiation when one examines the evolution of hydrogen chloride. Virgin PCP loses between 73 and 79% of its chlorine as HCl when it is heated isothermally at 360°C for 10 mins. A sample which has been cross-linked by DCP loses 75% of its chlorine while one cross-linked with BPO loses about 40% chlorine. This can be explained by the fact that highly cross-linked polymer has less labile β-hydrogens which are used for the volatilization of HCl; these hydrogens were consumed in the cross-linking reactions.

3.3.3. TGA/FTIR Results
TGA/FTIR enables one to correlate the identity of the evolved gaseous products with the mass loss. In these experiments we have compared the temperature at which certain products are evolved in the cross-linked samples with that of the virgin polymer. For polyisoprene the evolution of isoprene has been used as a marker to understand the degradation pathway. Isoprene is evolved at the same temperature for the virgin polymer and for that cross-linked with DCP but isoprene evolution occurs

20°C higher for BPO cross-linked material. This implies a somewhat higher thermal stability for this sample. One can clearly see in the TGA data that the degradation of DCP initiated material commences earlier than does BPO initiated cross-linked polymer. Similar results are obtained for polychloroprene. The evolution of both ethylene and hydrogen chloride occur at the same temperature for the virgin polymer and for DCP cross-linked material but the evolution occurs about 20°C higher for BPO initiated cross-linking.

4. Conclusion

Polychloroprene undergoes cross-linking much easier than polyisoprene and the density of cross-links is higher. Polychloroprene can be thermally cross-linked without initiator, whereas polyisoprene does not undergo cross-linking upon heating. Cross-linking of polyisoprene simultaneously leads to some generation of the low molecular weight products. This results in apparently lower temperature of the onset of weight loss of the cross-linked polymer, but the main step of weight loss of the cross-linked polyisoprene occurs at the higher temperature. Unlike, cross-linked polychloroprene decomposes at lower temperature than the virgin polymer. Both cross-linked polyisoprene and polychloroprene produce higher transitory char after the main step of thermal oxidative decomposition.

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