European Polymer Journal, 1970, Vol. 6, pp. 569–583. Pergamon Press. Printed in England.

DEGRADATION OF POLYMER MIXTURES—III

POLY(VINYL CHLORIDE)/POLY(METHYL METHACRYLATE) MIXTURES, STUDIED BY THERMAL VOLATILIZATION ANALYSIS AND OTHER TECHNIQUES. THE NATURE OF THE REACTION PRODUCTS AND THE MECHANISM OF INTERACTION OF THE POLYMERS

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(*Received* 24 *May* 1969)

Abstract—Mixtures of PVC and PMMA yield only hydrogen chloride and methyl methacrylate as major products of degradation. Minor products include carbon dioxide, methyl chloride and benzene. The changes which occur in the PMMA in the course of the degradation were studied by extracting this polymer with toluene from the partly-degraded blend. It was found that chain scission had occurred, that anhydride structures had been formed, and that the polymer showed differences in degradation behaviour compared with the original PMMA sample. All these features, and the previously reported interaction effects in the blends, can be satisfactorily explained in terms of two processes, occurring simultaneously during the degradation of the blend. The first is attack on PMMA by chlorine radicals produced during the dehydrochlorination of the PVC; the second is the reaction between methacrylate ester groups and the hydrogen chloride. The effect on the subsequent degradation behaviour of PMMA of heating the polymer in the presence of hydrogen chloride has also been examined.

INTRODUCTION

THE PRECEDING paper in this series(1) discussed a number of aspects of the interaction between poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) which occurs during the degradation of mixtures of the two polymers. Under linear temperature programmed heating conditions, it was found that, in the early stages of decomposition, mixed films of PVC and PMMA liberate a much increased amount of MMA monomer. In the later stages of breakdown of the mixture, less MMA is produced than for the unmixed samples, and the rate maximum moves to higher temperatures. The production of hydrogen chloride from mixed films is appreciably delayed. Most of the observed features could be explained if chlorine radicals from PVC attack PMMA and induce depolymerization.

The purpose of the present work was to obtain additional evidence to permit a detailed mechanism for the interaction to be written, and to account for the apparent stabilization of that part of the PMMA sample which does not depolymerize in the lower temperature range.

A detailed examination of the degradation products by several techniques has been made; the changes produced in the PMMA during degradation have been studied using i.r. spectroscopy, mol. wt. measurements, and thermal volatilization analysis (TVA).

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ANALYSIS OF VOLATILE DEGRADATION PRODUCTS

Infra-red gas cell analysis

(a) *Products from temperature-programmed experiment.* One-hundred milligrams of PMMA anionic and 100 mg of PVC Breon 113(1) were heated, as a mixed film, in the TVA apparatus(1) at 5° per min to 500°. The residual solvent in the film had previously been removed by heating the film under vacuum at 5° per min up to 200°. The products from this degradation were trapped out at liquid nitrogen temperature, transferred to an i.r. gas cell, and the spectrum obtained. This is shown in Fig. 1.

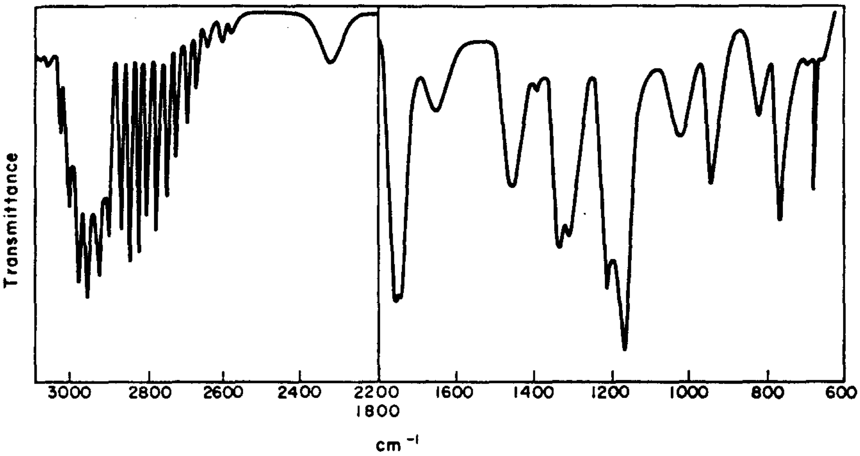


FIG. 1. Infra-red spectrum of the products of degradation to 500° of a PVC Breon 113/PMMA anionic mixed film (100 mg of each polymer, open degradation system with −196° trap, Perkin-Elmer model 257 spectrometer and 10 cm gas cell).

The characteristic band spectrum of hydrogen chloride is evident in the region 3050–2600 cm^{-1}; strong absorptions at 1750, 1180 and 1210 cm^{-1} can be attributed to methyl methacrylate; peaks at 2320 and 670 cm^{-1} are characteristic of carbon dioxide.

(b) *Products from isothermal degradation.* The i.r. spectrum of products from the pyrolysis at 210° for 4 hr of a similar mixed film was found to be qualitatively similar to that described above, except that carbon dioxide was absent and the peaks were of lower intensity.

With the exception of carbon dioxide, the products identified by i.r. analysis are the same as the products evolved by the unmixed polymers. Since the increased volatilization at low temperatures in mixed films was found to be due to the production of material which is volatile at ambient temperature but condensable at −100°, the substance evolved must be methyl methacrylate.

Mass spectrometric analysis

The products from the temperature-programmed degradation to 500° at 5° min of a mixed film of equal weights of PVC Breon 113 and PMMA FR 1(1) were subjected to mass spectrometric analysis. Again, residual solvent had been removed from the film by preheating at 5°/min up to 200° under vacuum. The degradation products were collected and examined as two fractions,

(a) products condensed by a trap at $-100°$,
(b) products volatile at $-100°$ but condensed at liquid nitrogen temperature.

The spectra of the two fractions are shown schematically in Fig. 2. For fraction (a), the signals at M/e values of 100, 69 and 41 can be attributed to methyl methacrylate, the first being the parent and the others arising from the following fragments:

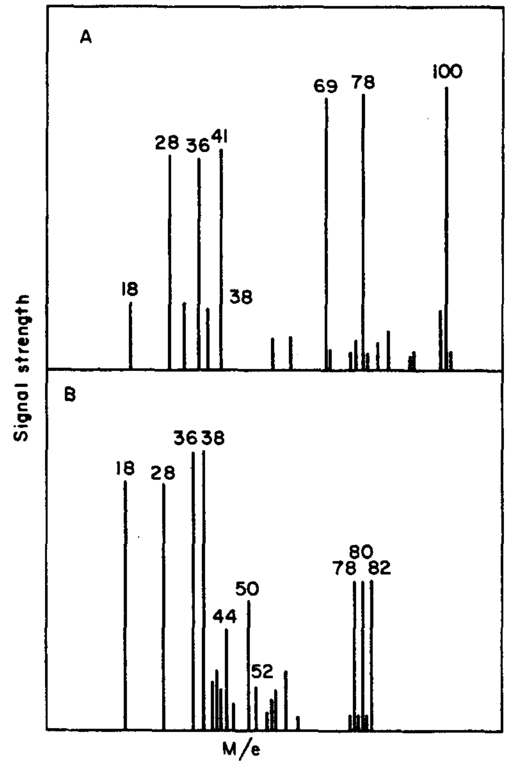
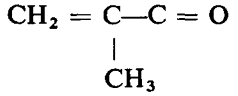
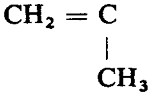


Fig. 2. Mass spectra of products of degradation of a PVC Breon 113/PMMA FR 1 mixed film, (A) products condensed at $-100°$, (B) products non-condensable at $-100°$ but condensed at $-196°$. (Degradation conditions as in caption to Fig. 1, AEI MS 12 spectrometer, operated at 20 eV.)


$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-C=O$$

(69)


$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}$$

(41)

Peaks at M/e 36 and 38 are due to $H^{35}Cl$ and $H^{37}Cl$, respectively. The signal at M/e 78 can be attributed to benzene, resulting from the breakdown at higher temperatures of the carbonaceous residue from the PVC dehydrochlorination. For fraction (b) consisting of the more volatile products, it is clear that methyl methacrylate is absent, having been fully condensed in the −100° trap. The main product in this fraction is hydrogen chloride, indicated by the strong signals at M/e 36 and 38. The peaks at M/e 50 and 52 are probably due to methyl chloride ($CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$), and that at M/e 44 to carbon dioxide, which was also detected in the products by i.r. spectroscopy.

The presence of methyl chloride in fraction (b) is in agreement with the results of Zutty and Welch,(2) who also observed that small amounts of this compound were formed in the pyrolysis of PVC/PMMA blends. In studies of copolymers of vinyl chloride and methyl methacrylate, which liberate methyl chloride as a major product of degradation,(3) it was found that this substance is not condensed by a trap at −100°. This fact, and the absence of methyl chloride in fraction (a), precludes the possibility that the increased volatilization at low temperatures in mixed films of the polymers is due to the formation of methyl chloride.

These mass spectrometric studies therefore confirm the conclusion, from TVA and i.r. evidence, that methyl methacrylate is the material produced during the increased volatilization in the initial stages of degradation of the mixed films.

Analysis of products by gas–liquid chromatography

The products of degradation from (a) PMMA anionic, and (b) a PMMA/PVC Breon 113 blend containing equal weights of the two polymers in the film, were studied by gas–liquid chromatography. In each case, the sample was heated at 5°/min to a sample temperature of 330° (i.e. just after the first TVA peak in the mixed films(1)). The products were trapped at liquid nitrogen temperature. G.l.c. separations were carried out on a 1 per cent SE 30 column, with nitrogen as carrier gas, and using a flame ionization detector. The chromatographic column was programmed at 10°/min, the program being started immediately after sample injection. Only the products which were liquid at room temperature were investigated.

Apart from small amounts of the solvent used in film preparation, the g.l.c. results indicated only methyl methacrylate as a product in case (a) and only methyl methacrylate and hydrogen chloride as products from the mixed film, case (b).

Again, therefore, it must be concluded that it is methyl methacrylate which is produced at abnormally low temperatures from PMMA breakdown in the blend, initiated in some way by the PVC degrading in this temperature region.

TABLE 1. PRODUCTS OF DEGRADATION FROM PVC/PMMA MIXED FILMS

Product	Notes
Hydrogen chloride	Major product
Methyl methacrylate	Major product
Carbon dioxide	Minor product, from degradation at higher temperatures only
Methyl chloride	Minor product
Benzene	Minor product

The products of degradation of PVC/PMMA mixed films indicated by these analytical techniques are summarized in Table 1. In addition to these products, small amounts of material not condensed by the liquid nitrogen trap in the open system were indicated by a Pirani gauge placed on the pump side of this trap.

STRUCTURAL CHANGES OCCURRING IN THE PMMA DURING DEGRADATION

Molecular weight changes

100 mg samples of PMMA anionic were heated at 5°/min to a sample temperature of 330°, and then rapidly cooled. The residue was dissolved in A.R. grade toluene, and the concentration of the solution was estimated by evaporating to dryness a known weight and determining the weight of polymer present. The mol. wt. of the degraded polymer was then determined using a 'Mechrolab' Model 501 Osmometer, fitted with a Sylvania 300 grade cellophane membrane.

The same weight of PMMA was then heated under similar conditions as a mixed film with an equal weight of PVC Breon 113. The residue, which was dark brown in colour, was removed from the degradation tube and extracted with toluene, under continuous shaking, over a period of 48 hr. At no time were the toluene extracts heated. PVC is almost completely insoluble in toluene, and since the PVC sample used had previously been extracted with toluene,(1) it could reasonably be assumed that the polymer removed from the degraded blend by toluene extraction consisted almost completely of PMMA. The concentration of the solution, and the mol. wt. of the PMMA, were determined as before.

The results of this investigation, and those for a similar study of PMMA FR 1/PVC Breon 113 blends are shown in Tables 2 and 3 respectively. It is clear that in the presence of thermally degrading PVC, PMMA samples undergo a fall in mol. wt., rapid compared with that for the pure polymer.

Table 2. The effect on the mol. wt. ($\bar{M}_n$) of PMMA anionic for samples heated to 330° at 5°/min, alone and as a mixed film with an equal weight of PVC Breon 113 (PMMA original M_n = 206,000)

Expt.	M_n after heating alone	M_n after heating with PVC
1	133,000	45,000
2	130,000	43,000
3		54,000

Table 3. The effect on the mol. wt. ($\bar{M}_n$) of PMMA FR 1 for samples heated to 330° at 5°/min, alone and as a mixed film with an equal weight of PVC Breon 113 (PMMA original $\bar{M}_n$ = 1,580,000)

Expt.	$\bar{M}_n$ after heating alone	$\bar{M}_n$ after heating with PVC
1	1,405,000	253,000
2	1,265,000	324,000
3	1,210,000	337,000

Experiments were also conducted similarly under isothermal conditions, at 190°, the mol. wt. of the PMMA which had been extracted by toluene from mixed samples being again compared with that of pure PMMA, in this case heated for the same length of time. The results (Table 4) indicate that, even under such mild conditions, PMMA suffers a more rapid mol. wt. drop in the mixed system.

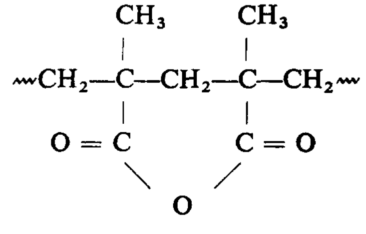
Table 4. The effect of isothermal heating at 190° on the mol. wt. (M_n) of PMMA anionic, alone and as a mixed film with an equal weight of PVC Breon 113

Time of heating (hr)	$\bar{M}_n$ after heating alone	$\bar{M}_n$ after heating with PVC
0	206,000	206,000
1	216,000	190,000
2	224,000	177,000
4	186,000	163,000

Infra-red analysis

Infra-red spectra were obtained of PMMA films, and PMMA/PVC mixed films before and after degradation. In the case of the mixed films, however, the peaks were too broad to permit detection of any changes occurring in the residue. This was probably due to scattering of the incident light beam, caused by the opacity of the mixed film.

The toluene extract from a mixed film heated to 330° at 5°/min was poured into A.R. grade methanol to precipitate the polymer. This was then dried under vacuum, and an i.r. spectrum was obtained from a powder sample incorporated in a potassium bromide disc. In Fig. 3, the regions of the spectrum in which changes occur are compared (spectrum c) with the corresponding regions in the spectra of PMMA which had been heated alone to the same temperature (spectrum a), and of poly(methacrylic acid) which had been heated at 250° for 90 min (spectrum b). Under these conditions, poly(methacrylic acid) is converted to anhydro-poly(methacrylic acid) which has the following anhydride ring structures,⁽⁴⁾



The bands which develop in the PVC-degraded sample at 1800 and 1020 cm^{-1} can be seen to be at frequencies similar to bands found in anhydro-poly(methacrylic acid), providing strong indication that the above type of anhydride rings may be present in PMMA which has been degraded in the presence of PVC.

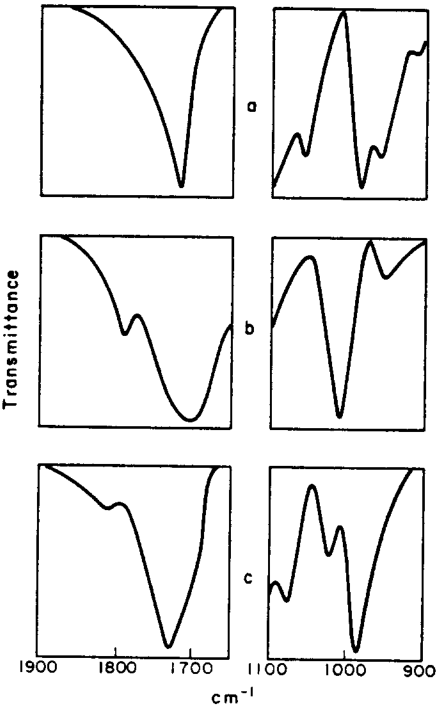


FIG. 3. Regions of interest in the i.r. spectra of powdered polymer samples in the form of KBr discs, of (a) PMMA anionic, heated to 330° at 5°/min, (b) Poly(methacrylic acid) heated at 250° for 90 min, (c) PMMA extracted with toluene from a PMMA anionic/PVC Breon 113 film heated to 330° at 5°/min.

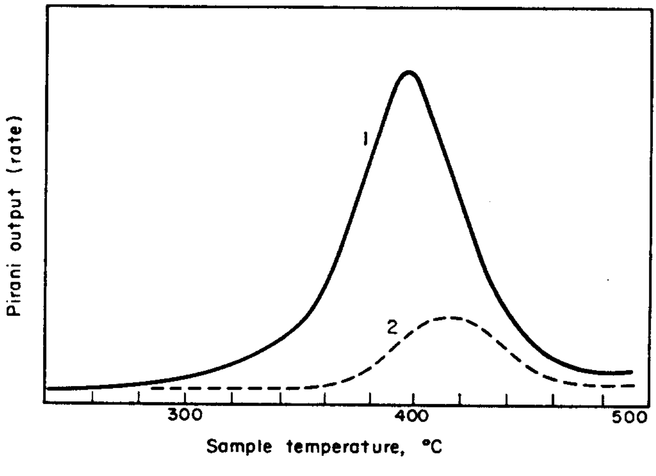


FIG. 4. Differential condensation TVA curves for a PMMA sample extracted with toluene from a PMMA anionic/PVC Breon 113 mixed film heated to 330° at 5°/min. Curve 1: products volatile under vacuum at ambient temperature, curve 2: products volatile at −100°. (Heating rate 10°/min.)

TVA investigation of polymer extracted with toluene

A small volume of the toluene extract from the residue of degradation to 330° of a PVC Breon 113/PMMA anionic film was allowed to evaporate to dryness in the degradation tube, and a TVA curve was then obtained (see Fig. 4). The observed behaviour of this PMMA sample may be compared with that of the original material shown in Fig. 3 of Ref. 1. The T_{max} value (temperature of the rate maximum) shows a displacement to higher temperatures, indicating greater stability in the sample which was partly degraded in the mixture. Other differences in behaviour for this material are the appearance of significant amounts of products not condensed at −100° (curve 2 of Fig. 4) and the production of a small amount of black residue. Neither of these are observed in the case of the original polymer, but both are characteristic of poly(methacrylic acid). The TVA behaviour of poly(methacrylic acid) has been reported previously.(5)

The toluene-soluble portion of the residue from an isothermal degradation at 190° of a mixed film of PVC Breon 113/PMMA anionic was also examined by TVA. The differential condensation TVA curves shown in Fig. 5 indicate that the main degradation peak is again displaced to higher temperatures, and products non-condensable at −100° are produced around 400°, as in the temperature-programmed degradation, but there is in this case an additional peak in the early stages of decomposition, with a maximum at 298°. Since this peak is associated with the production of a negligible amount of material non-condensable at −100°, it is confirmed that toluene extraction does not remove PVC from the polymer blend. The T_{max} of this initial peak occurs in the temperature region in which PMMA samples prepared by free radical means, having comparable mol. wt. and with unsaturated ends due to disproportionation during the termination stage of polymerization, show a similar peak.(6) The possible significance of this feature will be further discussed subsequently.

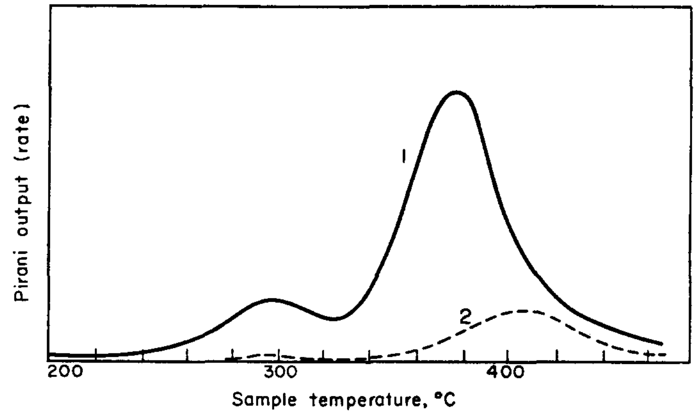


FIG. 5. Differential condensation TVA curves for a PMMA sample extracted with toluene from a PMMA anionic/PVC Breon 113 mixed film heated at 190° for 1 hr. Curves 1 and 2 as in caption to Fig. 4. (Heating rate 10°/min.)

It is evident, however, from this study of the PMMA which has been extracted from the partially-degraded blend, that the displacement of the second degradation peak in the TVA curve for the mixed film is almost certainly due to structural changes which occur in the PMMA during the PVC dehydrochlorination process.

Information on the structural changes induced in PMMA by heating as a blend with PVC may conveniently be summarized at this point.

(a) The i.r. spectrum shows anhydride structures.
(b) The mol. wt. falls.
(c) The polymer leaves a black residue when degraded.
(d) TVA shows a shift of main degradation peak to higher temperatures.
(e) Some non-condensable products are now obtained around 400°.
(f) Polymer from isothermal degradation at 190° shows an additional small peak in the TVA curve, at 298°.

INTERPRETATION AND DISCUSSION

Any explanation of the interaction between PVC and PMMA during degradation as a blend has to account for the various features previously reported in Part II,(1) for the products of degradation which are found (Table 1), and for the structural changes which are observed to result in the PMMA during degradation, listed above.

It is not possible to account for every aspect in terms of a single type of interaction, but it will be shown that the simultaneous occurrence of two interaction processes, for each of which there is substantial evidence, can provide an adequate explanation.

Increased monomer production from PMMA at low temperatures, and chain scission

These features, occurring in the temperature range for PVC dehydrochlorination, are probably related phenomena. The most likely explanation is that PMMA is subjected to a radical attack, by a hydrogen abstraction process, leading to subsequent chain scission and depropagation:

$$\begin{array}{llcll}
(1) & \mathrm{PVC} & \rightarrow & \mathrm{R}^{\cdot} & \\
(2) & \mathrm{R}^{\cdot} + \mathrm{M}_n & \rightarrow & \mathrm{RH} + \mathrm{P}_n^{\cdot} & \text{Hydrogen abstraction} \\
(3) & \mathrm{P}_n^{\cdot} & \rightarrow & \mathrm{P}_j^{\cdot} + \mathrm{M}_{n-j} & \text{Chain scission} \\
(4) & \mathrm{P}_j^{\cdot} & \rightarrow & \mathrm{P}_{j-1}^{\cdot} + \mathrm{M}_1 & \text{Depropagation}
\end{array}$$

where the P species are radicals and the M species are stable molecules.

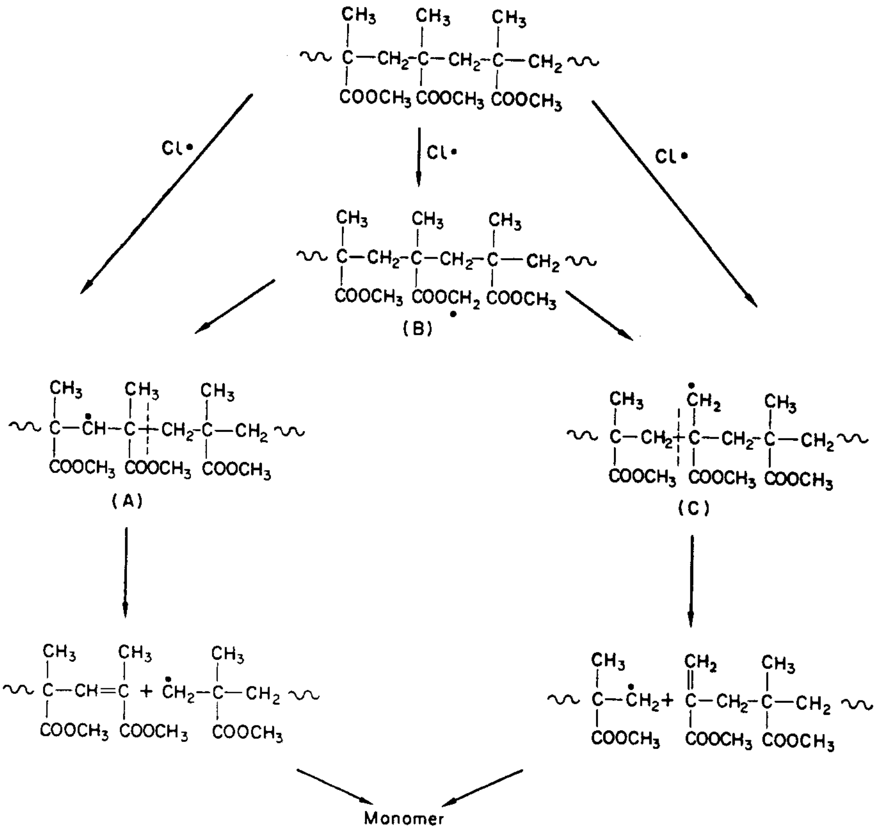
The fall in mol. wt. results from step (3), while step (4) leads to monomer production.

If PVC degrades by a radical mechanism, as is implied in the above reaction scheme, then two types of radicals might be capable of participating in step (2), viz. chlorine atoms, or macromolecular radicals:

$$\mathrm{Cl}^{\cdot} \text{ or } \sim\!\mathrm{CH}=\mathrm{CH}\text{—}\dot{\mathrm{C}}\mathrm{H}\text{—}\mathrm{CH}_2\text{—}\mathrm{CHCl}\!\sim$$

As previously discussed,(1) any radical species formed during the decomposition of PVC must, in order to react with a PMMA chain, be capable of migrating across a phase boundary, since for the compositions used in these experiments, the mixed films are heterogeneous. Since the motion of the PVC polymer radical is severely restricted, it appears much more likely that the attacking species is the chlorine atom. Furthermore, the residue from dehydrochlorination of PVC, which has been shown to contain polymer radicals,(7–9) has been found to have no effect on PMMA during degradation.(1)

A possible reaction scheme for the attack of chlorine radicals on PMMA is shown below. It is impossible to state with certainty which hydrogen atoms in the PMMA chain would be most susceptible to radical attack. The evidence from chlorination experiments(10, 11) is that each of the hydrogens in the chain can be replaced by chlorine. Moreover, it has been observed that the mol. wt. of PMMA falls during chlorination.



Production of radicals A and C, followed by cleavage of the carbon—carbon bond beta to the unpaired electron, produces a radical capable of depolymerizing, and an unsaturated chain end. Production of radical B, by attack on the ester hydrogen, cannot lead to evolution of monomer directly. It is proposed, however, that B, by intramolecular transfer of hydrogen, can transfer the radical activity so that A or C radicals are produced.

The mechanism can therefore account for the production of monomer, and for chain scission, but also predicts that unsaturated molecular chain ends are produced during the reaction. If so, then these structures, provided they are produced at low temperatures, should be revealed by TVA, owing to their thermal instability. The appearance of an additional peak in the TVA curve for PMMA anionic which had been extracted from a mixed film partly degraded isothermally at low temperature (Fig. 5) has already been commented upon. It may be that this peak is due to such end structures. Certainly, the T_{max} value is within the range observed for samples of PMMA of comparable mol. wt. prepared by free radical mechanism, containing this type of end structure.

Delay in the production of hydrogen chloride from mixed films

The experimental evidence for this delay in dehydrochlorination has been presented in Part II. There are several possible explanations.

In films of the thickness used in these experiments, there is some evidence for autocatalysis by hydrogen chloride, whereas thinner films behave differently (Fig. 2 of Ref. 1). Hence the mixed films may disperse the hydrogen chloride, reduce the catalytic effect, and so delay the dehydrochlorination. The fact that relatively small amounts of PMMA are capable of delaying hydrogen chloride production in isothermal experiments, and the heterogeneous nature of the mixture, suggest that this is not an adequate explanation.

A second interpretation is that hydrogen chloride reacts with PMMA in mixed films, and it is this secondary reaction which causes the delay in hydrogen chloride production. Although it will be shown that there is good evidence for reaction between PMMA and hydrogen chloride during the degradation, this again does not provide a complete explanation, since hydrogen chloride production is also delayed in the case of PVC/polyisobutene blends, and it seems most unlikely that any reaction would occur between hydrogen chloride and the second polymer in this case.

Thirdly, it may be argued that chlorine atoms which react with PMMA will not be available to attack PVC in the dehydrochlorination reaction. In other words, the second polymer may be competing with PVC for chlorine atoms, acting as a rather inefficient radical scavenger. If the chlorine atoms are chain carriers in a chain reaction for PVC breakdown, then the removal in this way of even a small number of these radicals may have a quite significant effect. If this interpretation is correct, then it would be expected that any polymer containing hydrogen atoms which are capable of abstraction by chlorine atoms, would delay the dehydrochlorination of PVC. The experiments previously reported(1) on a series of blends of PVC with other polymers, suggest that this delay is indeed a general phenomenon.

The third of these explanations is therefore considered to be the most plausible.

Displacement of the main peak in the TVA curve for PMMA

As has been noted earlier, structural changes occur in PMMA as a result of heating with PVC, and they cause the main degradation peak in the TVA curve to be displaced to higher temperatures. This is seen in the case of mixed films, mixed powders, and PMMA which has been extracted from the blend after partial degradation.

It has been shown that the mol. wt. of PMMA falls during degradation with PVC, and it is known(6) that T_{max} for the main degradation peak in PMMA occurs at higher temperatures for samples of lower mol. wt. The effect observed in the degradation of the mixtures, however, is too great to be accounted for in this way, and it must therefore be assumed that the depolymerization process is considerably retarded in these samples. Evidence has been presented for the presence of anhydride structures in PMMA extracted from partially-degraded blends. Whatever their mode of formation, if these ring structures in the chain act as blocking units in the depolymerization and drastically reduce the zip length, then a displacement of T_{max} to higher temperatures in the temperature programmed degradation would be the expected result. The formation of lactone rings in the PMMA chain during the degradation of MMA/VC copolymers has been found to produce a very similar effect.(5)

The presence of small amounts of carbon dioxide in the degradation products of mixed films, as suggested by i.r. analysis of the products, can be attributed to the thermal decomposition of anhydride units. This reaction is probably responsible for the appearance of the peak around 400° in the TVA curve for production of material non-condensable under vacuum at −100° (Figs. 4 and 5).

Confirmation that carbon dioxide is evolved during the decomposition of anhydride ring units comes from the analysis of the decomposition products of anhydro-poly(methacrylic acid). An i.r. spectrum of the products resulting from the degradation of this polymer in a closed system, initially at high vacuum, indicated a strong absorption for carbon dioxide, together with peaks suggesting the presence of carbon monoxide and methane. The latter materials are not trapped out in liquid nitrogen in a continuously pumped system, so that their absence in the analyses of products from the blends is not unexpected. An indication of the presence of such non-condensable materials was obtained in the TVA experiments, however.

THE EFFECT OF HYDROGEN CHLORIDE ON PMMA

Production of anhydride structures

The most probable cause of the formation of anhydride units in PMMA which has been degraded along with PVC is the attack on the PMMA chain by hydrogen chloride.

To test this assertion, a 100 mg sample of PMMA anionic was heated for 12 hr in a closed system in the presence of the hydrogen chloride produced by decomposing 100 mg of PVC Breon 113. The degradation temperature was 190°. As a result of this treatment, the PMMA was rendered insoluble and could not be powdered, so that it was not possible to examine the i.r. spectrum. A TVA curve was obtained, however, and this is shown in Fig. 6. It was also noted that the polymer left a black residue after degradation.

The effect of this treatment on the thermal behaviour of the polymer is considerable. There is no reduction of stability at 200°–300°, but the main degradation peak is now shifted to 430°, a temperature more characteristic of anhydro-poly(methacrylic acid) than of PMMA. A substantial proportion of the degradation products are now not condensed at −100° (carbon dioxide, carbon monoxide, methane). This feature, and the formation of the black residue, are also atypical of PMMA breakdown but found in the case of degradation of poly(methacrylic acid).

There is therefore good reason to believe that the effect of heating PMMA in presence of hydrogen chloride is to cause the formation of anhydride ring structures in the polymer. Under the much less severe reaction conditions in the degradation of the blends (shorter time of heating, evacuated system), the proportion of anhydride units is probably much smaller than in this experiment, and hence a smaller shift in T_{max} and a smaller amount of the non-condensable products are observed.

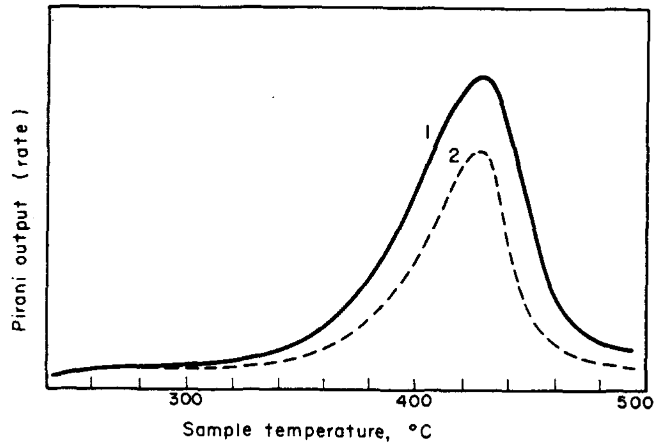


Fig. 6. Differential condensation TVA curves for a PMMA anionic sample, heated at 190° for 12 hr in a closed system with hydrogen chloride. Curves 1 and 2 as in caption to Fig. 4. (Heating rate 10°/min.)

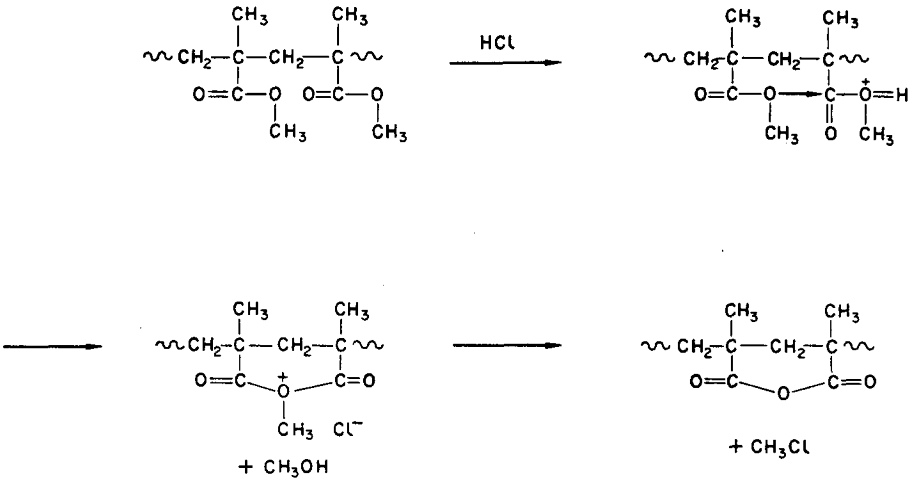
Further evidence that hydrogen chloride can react with PMMA in this manner comes from the work of Gardner and McNeill,(12) in a study of the TVA behaviour of mixed and unmixed samples of polychloroprene and PMMA. Since the principal volatile product of thermal degradation of polychloroprene is hydrogen chloride, it might be expected that the two polymers would interact in a similar fashion to the PVC/PMMA system.

The mixed polymers do interact on degradation, the main degradation peak of PMMA being displaced to higher temperatures in the presence of polychloroprene, and carbon dioxide is evolved from the blend, suggesting that hydrogen chloride from the polychloroprene has attacked the PMMA chain, again producing anhydride units, which decompose to carbon dioxide. However, in the early stages of decomposition of polychloroprene/PMMA blends, there is no increase in the rate of volatilization, compared to the unmixed samples. This is in contrast to the situation in PVC/PMMA blends, in which even small amounts of added PVC are capable of significantly reducing the stability of PMMA. This provides further proof that the reaction between hydrogen chloride and PMMA does not account for the early production of MMA monomer from the PVC/PMMA blends.

Mechanism of anhydride formation

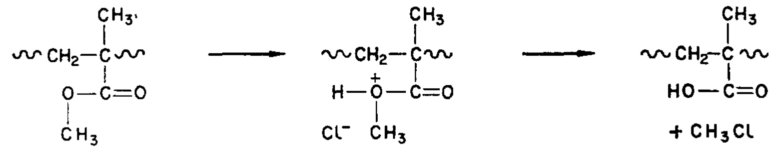
A possible mechanism for the reaction between anhydrous hydrogen chloride and PMMA to produce anhydrides directly, is shown overleaf.

This suggests that for each anhydride unit formed, molecules of methyl chloride and methanol are produced. Although the presence of the former was detected by mass spectrometry, no experimental evidence was obtained for the presence of methanol, nor was it reported by Zutty and Welch(2) or Barlow, Lehrle and Robb.(13) It must be remembered, however, that the transformation of only quite a small number of methacrylate units would be required to produce the observed effects on the thermal behaviour, if the unzipping of the methacrylate chain is effectively blocked by an



anhydride ring, so that both of these materials are very minor products of reaction and the failure to identify methanol in the products may not invalidate the mechanism.

It may be the case, however, that the effect of the hydrogen chloride is to convert ester groups to carboxyl groups, with evolution of methyl chloride,



and that anhydride units are then formed by dehydration of pairs of methacrylic acid units. Thus this mechanism indicates methyl chloride and water as volatile products of the reaction, but no methanol. A choice cannot be made between these two possible schemes, without further evidence, such as might be obtained from a study of methacrylic acid/methyl methacrylate copolymers.

CONCLUSIONS

All the observed features of the interaction between PVC and PMMA during degradation of a blend may be explained in terms of two reactions occurring simultaneously.

The first reaction, attack of a chlorine atom from the degrading PVC on the PMMA chain, accounts for the observed chain scission in the PMMA, the production of MMA monomer at abnormally low temperatures, and the delay in dehydrochlorination of the PVC.

The second reaction, attack of hydrogen chloride from the PVC on the methacrylate ester group, accounts for the changes found to occur in the i.r. spectrum of PMMA, for the stabilization of that part of the polymer which does not degrade in the lower temperature range, for the appearance of methyl chloride, carbon dioxide and non-condensable products, and the fact that the PMMA leaves a carbonaceous residue.

Acknowledgement—Thanks are due (from D.N.) to the Science Research Council for the award of a Studentship, during the tenure of which this work was carried out.

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Résumé—Les mélanges de PCV et de PMAM ne donnent, comme produits principaux de dégradation, que du gaz chlorhydrique et du méthacrylate de méthyle. Les produits de moindre importance comprennent le CO_2, le chlorure de méthyle et le benzène. Les changements qui interviennent dans le PMMA au cours de la dégradation ont été étudiés en extrayant ce polymère par le toluène du mélange partiellement dégradé. On a trouvé qu'il se produit des ruptures de chaîne, que des structures anhydrides se forment et le polymère extrait présente, par rapport à l'échantillon de PMAM initial, des différences de comportement à la dégradation. Tous ces faits, ainsi que les effets d'interactions dans les mélanges précédemment décrits, peuvent être convenablement expliqués en tenant compte de deux processus, intervenant simultanément au cours de la dégradation du mélange. D'autre part une attaque du PMAM par des radicaux libres chlore produits au cours de la dé chlorhydratation du PCV; d'autre part une réaction entre les groupements esters méthacrylates et le gaz chlorhydrique. On a également examiné l'effet produit sur le comportement à la dégradation du PMAM, par un chauffage du polymère en présence de gaz chlorhydrique.

Sommario—Miscele di PVC e PMMA producono solo acido cloridrico e metacrilato di metile come prodotti principali della degradazione. I prodotti secondari includono biossido di carbonio, cloruro di metile e benzene. I mutamenti che si verificano nel PMMA nel corso della degradazione furono studiati estraendo questo polimero con toluene dalla miscela parzialmente degradata. Fu trovato che era avvenuta rottura della catena, che si era formata una struttura di anidride e che il polimero mostrava differente comportamento alla degradazione rispetto al campione originale di PMMA. Tutti questi fatti e gli effetti delle interazioni nelle miscele precedentemente riportati, possono essere soddisfacentemente spiegati in termini di due processi che si verificano simultaneamente durante la degradazione della miscela. Il primo consiste nell'attacco nel PMMA da parte di cloro radicalico prodotto durante la perdita di acido cloridrico da parte del PVC; il secondo é costituito dalla reazione fra gruppi esteri metacrilato e acido cloridrico. E' stato anche esamianto l'effetto del riscaldamento del polimero in presenza di acido cloridrico sulla successiva degradazione del PMMA.

Zusammenfassung—Mischungen von PVC und PMMA liefern beim Abbau als Hauptprodukte Chlorwasserstoff und Methylmethacrylat. Nebenprodukte sind Kohlendioxid, Methylchlorid und Benzol. Die an PMMA im Verlaufe des Abbaus stattfindenden Veränderungen wurden untersucht durch Extraktion dieses Polymeren aus der teilweise abgebauten Mischung mit Toluol. Es wurde festgestellt, daß Kettenspaltung eingetreten war, daß sich Anhydridstrukturern gebildet hatten und daß das Polymere im Vergleich zum ursprünglichen PMMA Unterschiede im Abbauverhalten zeigte. Alle diese Merkmale, sowie die Wechselwirkungseffekte in den Mischungen, über die vorher berichtet wurde, können befriedigend erklärt werden durch zwei Prozesse, die gleichzeitig während des Abbaus der Mischung ablaufen. Der erste ist ein Angriff auf PMMA durch Chlorradikale, die bei der Chlorwasserstoffabspaltung aus PVC gebildet werden; der zweite ist die Reaktion zwischen Methacrylatestergruppen und dem Chlorwasserstoff. Es wurde außerdem geprüft, welchen Einfluß eine Erhitzung des PMMA bei Gegenwart von Chlorwasserstoff auf das darauffolgende Abbauverhalten des Polymeren hat.