Thermal Degradation of Blends of PVC with Other Polymers

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ABSTRACT

The thermal degradation behavior of blends of poly(vinyl chloride) with polyacrylonitrile, poly(n-butyl methacrylate), polyacrylamide, poly(N-butyl methacrylamide) and poly(methyl acrylate) is discussed, and the results for these blends and five other binary polyblends containing PVC previously studied are compared. The various types of interactions which can occur in these heterogeneous systems are considered, and the mechanisms of degradation are compared with those of each polymer when degraded alone. The most important interactive effects result when a small reactive species produced in the degradation of one of the two polymers in the blend diffuses into the domains of the other polymer in the two-phase system and reacts with that polymer.

INTRODUCTION

The degradation behavior of many polymers is now well understood, although in the case of PVC, the mechanism is still in some dispute.

The thermal behavior of a variety of copolymers has also now been investigated in detail. Despite the fact that blends of polymers are becoming increasingly important in practical applications, there has been until recently very little information published on the mechanism of degradation of one polymer in the presence of another.

A series of publications from our laboratories has dealt with the degradation behavior of the following binary polyblends: poly(methyl methacrylate) (PMMA)-polystyrene (PS) [1], poly(vinyl chloride) (PVC)-PMMA [2, 3], polychloroprene-PMMA [4], PVC-poly(vinyl acetate) (PVA) [5], PVC-chlorinated rubber [6], PVC-PS [7], PVC-poly-α-methylstyrene (PAMS) [8], PVA-PS [9], PVA-PMMA [10], and PMMA-polypropylene [11]. Other workers have studied the degradation of PS in the presence of PAMS [12] and polyoxyethylene glycol [13], respectively, and polypropylene in the presence of vinyl polymers [14].

Polymer blends prepared by casting of a film from a solution containing both polymers, grinding together of finely powdered polymers, coprecipitation of the polymers from solution, or mastication of the two polymers, all exist in general as heterophase systems which differ in the degree of dispersion of one phase in the other. There are few instances reported of homogeneous blends of polymers. Thus the type of interaction process which could be expected in the degradation of a blend of two polymers would be either a reaction at a phase boundary, involving polymer molecules or long-chain radicals, or a reaction involving small molecular or radical species (formed in one phase, which subsequently diffuse into the other phase) and polymer molecules. This type of behavior is indeed characteristic of most of the systems which have been investigated.

The purpose of the present communication is to report on the degradation behavior of several further systems involving PVC as one component, viz., PVC-polyacrylonitrile (PAN), PVC-poly(n-butyl methacrylate) (PBMA), PVC-poly(methyl acrylate) (PMA), PVC-poly(n-butyl methacrylamide) (PBMAM), and PVC-poly(acrylamide) (PAM), and then to discuss more generally the accumulated data on the ten different PVC polyblends, in which PVC is present in a wide variety of polymeric environments.

EXPERIMENTAL

The PVC sample used in all the experiments (with the exception of some of the work reported in which a radioactive polymer was employed [6]) was an additive-free industrial sample, Breon 113 (BP Chemicals International Ltd.).

PAN was prepared by bulk polymerization of the purified monomer in the absence of air by use of 0.05% (w/v) azoisobutyronitrile (AIBN)

initiator at 40°C ($\overline{M}_n$ = 10^6). PMA was prepared by photopolymeriza-
tion of a 20% solution of the monomer in n-propyl acetate in the
absence of air with the use of 0.1% (w/v) AIBN at 35°C ($\overline{M}_n$ 7 × 10^5).
PBMA was a sample kindly provided by Prof. A. Guyot of CNRS,
Villeurbanne, France; it had been prepared by bulk polymerization
of the purified monomer at 56°C with 0.5% benzoyl peroxide as initia-
tor. PBMAM was prepared from monomer synthesized by reaction
of n-butylamine with methacrylyl chloride in aqueous solution [15, 16].
Polymerization was carried out in bulk at 50°C in the absence of air
with 0.1% AIBN initiator. PAM was a sample prepared by Dr. R.
McGuchan using an aqueous solution of the monomer and persulfate/
bisulfite initiator. PVC, PMA, PBMA, PBMAM, and PAM were puri-
fied by reprecipitation from suitable solvents and thoroughly dried
under vacuum. PAN was washed thoroughly with methanol before
drying under vacuum.

Most of the experiments were carried out on blends containing
equal weights of the two polymers.

The principal methods of assessing the occurrence of interaction
effects during degradation of the blends were thermogravimetry (TG)
and thermal volatilization analysis (TVA) [17]. TG experiments were
performed on a Du Pont model 950 thermobalance under dynamic
nitrogen flow (75 ml/min). The boat-shaped platinum sample holder
measured 10 mm × 5 mm × 2.5 mm deep, and the temperature-
measuring thermocouple was placed 1 mm from the sample holder.
Weight losses for the two polymers and for the blend prepared by
grinding together the mixed powders were obtained under programmed
heating conditions (10°C/min), and a weight loss curve for the two
polymers together was constructed on the assumption that each poly-
mer behaves independently of the other. This curve was then com-
pared with the experimental behavior of the blend. For the TVA
experiments, in which pressure of volatile products in a continuously
evacuated system was recorded as a function of temperature (heating
rate 10°C/min), a twin-limbed reaction tube was employed [2], and
experimental results were compared for the situations (a) with one
polymer in each limb, but degraded simultaneously, and (b) with both
polymers present as a blend in both limbs. These situations will be
referred to subsequently as "unmixed" and "mixed." Differential
thermal analysis (DTA) was also employed in some cases, by use of
a Du Pont model 900 thermoanalyzer.

Where a common solvent was available for the two polymers,
blends for the TVA experiments were prepared as films cast from a
common solution. Freshly distilled cyclohexanone was used for the
PVC-PBMA and PVC-PMA systems. The remaining blends were
made by grinding together the powdered polymers.

Each of the thermal analysis methods was found to be extremely

sensitive to changes in degradation behavior due to blending. In addition, product analysis was carried out by evolved gas analysis for acid products, gas-liquid chromatography, and infrared spectroscopy of volatile degradation products.

RESULTS AND DISCUSSION

Summary of Previous Work

The behavior found in 1:1 by weight blends of PVC with chlorinated rubber, PVA, PS, PAMS and PMMA, respectively, is summarized in Table 1, together with brief details of the interpretation given.

PVC-PAN System

Programmed heating of PVC leads first to dehydrochlorination; at higher temperatures the conjugated polyene structure initially formed breaks up into chain fragments and small amounts of low molecular weight materials. Under the same conditions, PAN first undergoes oligomerization of the nitrile groups in a highly exothermic reaction leading also to some chain scission. Small amounts of ammonia and hydrogen cyanide are evolved. Further chain scission occurs as the temperature is raised still higher [18].

These features are reflected in the TVA curves for the two polymers presented in Fig. 1. PVC shows a double peak for dehydrochlorination when powder or thick film samples are used, as a result of autocatalysis by escaping hydrogen chloride [2]; the final low rate maximum is associated with the main chain scission reaction. The unusually sharp peak in the TVA trace for PAN results from the highly exothermic reaction (NH_3, HCN) which probably causes the polymer for a short time to have a temperature higher than that of the sample tube. The exothermicity is discussed further below in connection with DTA measurements.

Figure 2 shows the TVA curves obtained by decomposition of equal weights of the two polymers (a) simultaneously, but separately ("unmixed"), and (b) as mixed powders, using the twin-limbed tube technique previously employed [2]. The rate maxima associated with both PVC and PAN decomposition are evident in both cases. This is particularly surprising, since degradation of the two homopolymers suggests considerable overlap in their main volatilization reactions (cf. Fig. 1). It is clear that when both polymers are degraded together (whether mixed or not), the PAN exotherm is shifted to higher temperatures by as much as 60°C.

TABLE 1. Degradation Behavior of Some PVC Blends

System	Behavior of blend compared to unmixed polymers	Interpretation	Ref.
PVC-chlorinated rubber	HCl is sole volatile product up to 350°C. Blend is much less stable. Increased HCl yield is provided by the PVC.	HCl from chlorinated rubber (less stable than PVC) catalyzes PVC dehydrochlorination. Cl· radicals may also be involved.	[6]
PVC-PVA	Acetic acid production greatly increased. HCl production also increased but not as much.	HCl catalyzes the deacetylation process in PVA. Acetic acid also catalyzes dehydrochlorination of PVC but does not become available in appreciable amount for this purpose until much higher temperatures.	[5]
PVC-PS	HCl production slightly retarded. PS considerably stabilized towards volatilization but molecular weight falls, without associated volatilization, below 350°C, at a faster rate than for PS alone	PS stabilizes PVC by acting as a "radical sink," providing tertiary H atom sites for ready H-abstraction by Cl· radicals. Resulting PS macro-radical undergoes scission but not volatilization below 350°C. Polyene structure of PVC formed by HCl loss stabilizes PS in higher temperature range by reacting with polystyryl radicals.	[7]
PVC-PMMA	MMA monomer evolved initi-ally at lower temperatures, but subsequent breakdown of PMMA occurs at higher	Chlorine radicals from PVC dehydrochlorination reaction enter the PMMA phase and initiate depolymerization. PMMA competes	[2], [3]

(continued)

TABLE 1 (continued)

| System	Behavior of blend compared to unmixed polymers	Interpretation	Ref.
PVC-PMMA	temperature. HCl evolution slightly retarded.	with PVC for reaction with Cl· radicals. HCl interacts with ester groups in PMMA to give anhydride rings in the polymer chain which then block depropagation at higher temperatures.	
PVC-PAMS	AMS monomer evolved at lower temperatures. HCl evolution retarded.	Cl· radicals from PVC dehydrochlorination reaction enter PAMS phase and initiate depolymerization. PAMS competes with PVC for reaction with chlorine radicals.	[8]
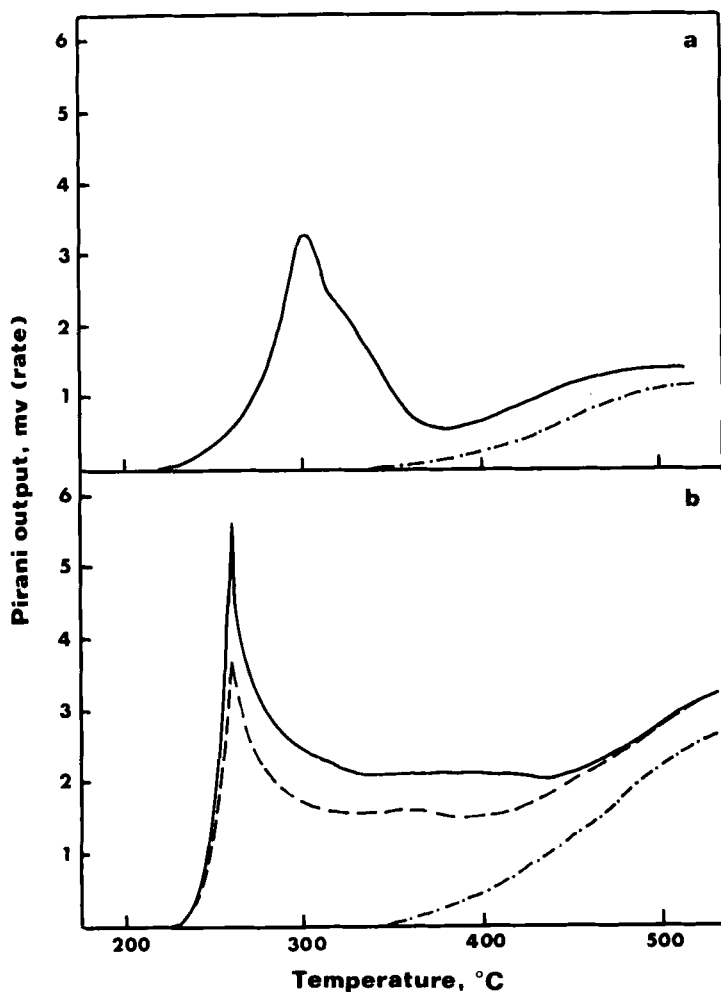
FIG. 1. TVA curves for (a) PVC and (b) PAN powders. Sample size, 50 mg; heating rate, 10°C/min.

Destabilization of the PVC in the mixed system is shown by the lower peak maximum temperature (295°C compared with 305°C) and the increased peak height, relative to the unmixed system. The temperature at which dehydrochlorination begins, however, remains the same. The considerable destabilization of the PVC is revealed even more strikingly when the behavior of the unmixed and mixed polymers is compared (Fig. 3) under isothermal heating conditions at 285°C.
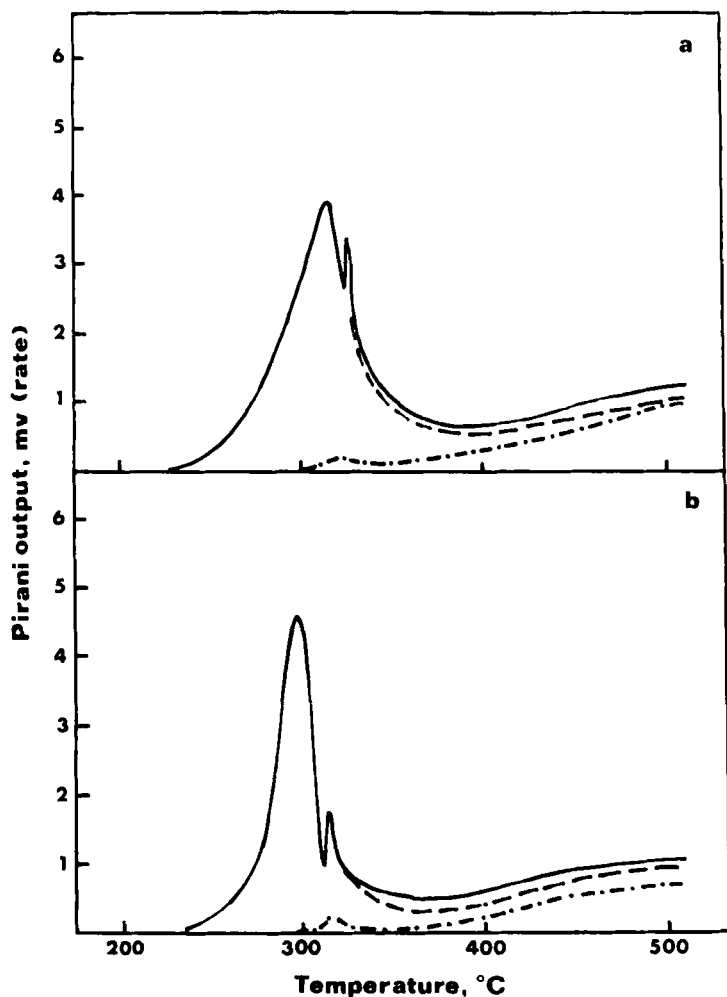
FIG. 2. TVA curves for 1:1 by weight PVC-PAN powder samples, degraded simultaneously in (a) unmixed and (b) mixed condition. Sample size, 50 mg of each polymer; heating rate, 10°C/min.

TG measurements (Fig. 4) confirm the behavior found by TVA. Thus, the mixed polymers show a sharper initial weight loss (attributable to the PVC) followed by a separate second stage of weight loss in the temperature range associated with the sharp PAN breakdown peak in the TVA curve, whereas in the absence of any interaction
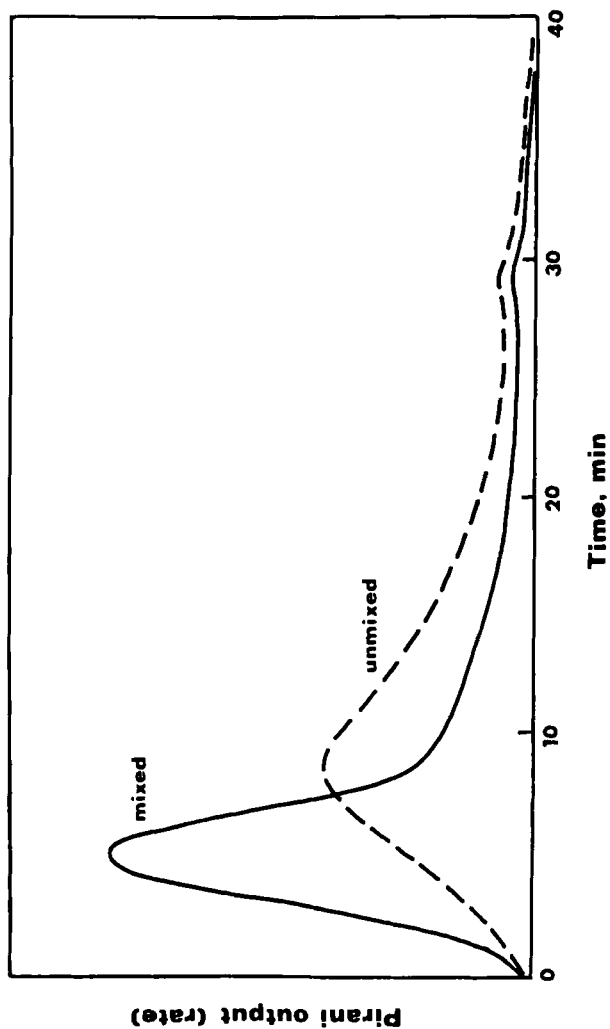
FIG. 3. Isothermal TVA curves for 1:1 PVC-PAN powder samples, degraded simultaneously at 285°C in unmixed and mixed conditions. Sample size, 50 mg of each polymer; heating rate, 10°C/min.
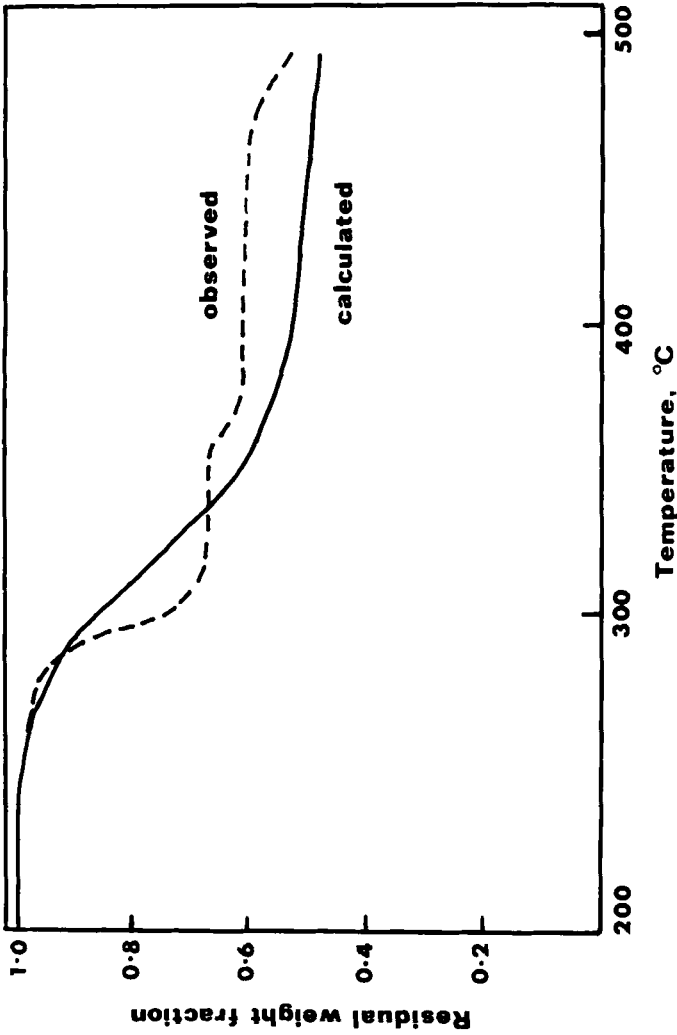
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FIG. 4. Comparison of experimentally observed weight loss in degradation of 1:1 by weight PVC–PAN powder mixtures with curve calculated from TG curves for the polymers degraded separately, assuming no interaction. Sample size, 5 mg of each polymer; heating rate, 10°C/min; dynamic nitrogen flow, 80 ml/min.

effects a single smooth stage of weight loss with maximum rate at an intermediate point between those observed, would have been expected.

Product analysis by IR spectroscopy indicated no products other than those previously identified for the homopolymer decompositions. The amount of ammonia found was significantly reduced, however, due to the formation of NH_4Cl during collection.

The cold ring fraction (CRF) of high molecular weight products (chain fragments) which collects on the cooled upper part of the TVA degradation tube was examined by IR spectroscopy for both the un-mixed and mixed degradation situations. The spectra in both cases resembled that of the corresponding products from PAN alone, indicating that most of the chain fragments from the blend arise from the PAN. The observed absorptions show that the CRF consists of cyclized nitrile sequences together with unchanged AN units. Small amounts of unsaturated nitrile structures are also present.

The effect of changing the ratio of the two polymers in the powder mixture was examined by TG for a series of blend compositions containing between 20 and 90% by weight of PVC. The results are compared in Fig. 5 with the TG curves for the two polymers.

Two main observations can be made regarding the stability of these blends. First, that the initial weight loss in the blends occurs considerably earlier in the heating program for all the blend compositions than for PVC alone. Second, that the second stage of decomposition, due to PAN fragmentation, is displaced to a higher temperature in each of the blends (by $80°C$ in a 20% by weight PAN blend). Thus chain fragmentation has been separated from the dehydrochlorination of the PVC component, despite the fact that in the polymers degraded alone, the two processes occur in the same temperature range.

The TVA results have already suggested that the exothermic oligomerization process in PAN is delayed when PVC is present and its intensity is reduced. This aspect has been pursued using DTA. The behavior of PVC, PAN, and a 1:1 blend is shown in Fig. 6.

The principal feature of the PVC trace is a small endotherm corresponding to dehydrochlorination, which overlaps with the temperature region in which nitrile oligomerization occurs exothermically in PAN. The blend shows a smaller exotherm than PAN, displaced to higher temperatures. Comparison with the TG results shows that the exotherm is thus separated from the main weight loss process which occurs in the blend at a much higher temperature. Similar observations have been made by Grassie and McGuchan [19] in studies of copolymers of acrylonitrile with chlorinated monomers.

Although the magnitude of the PAN exotherm is reduced in the blend, the peak is broader, and DSC measurements indicate that ΔH is increased by some 50% compared to PAN alone. Thus it may be concluded that the oligomerization process, although delayed and
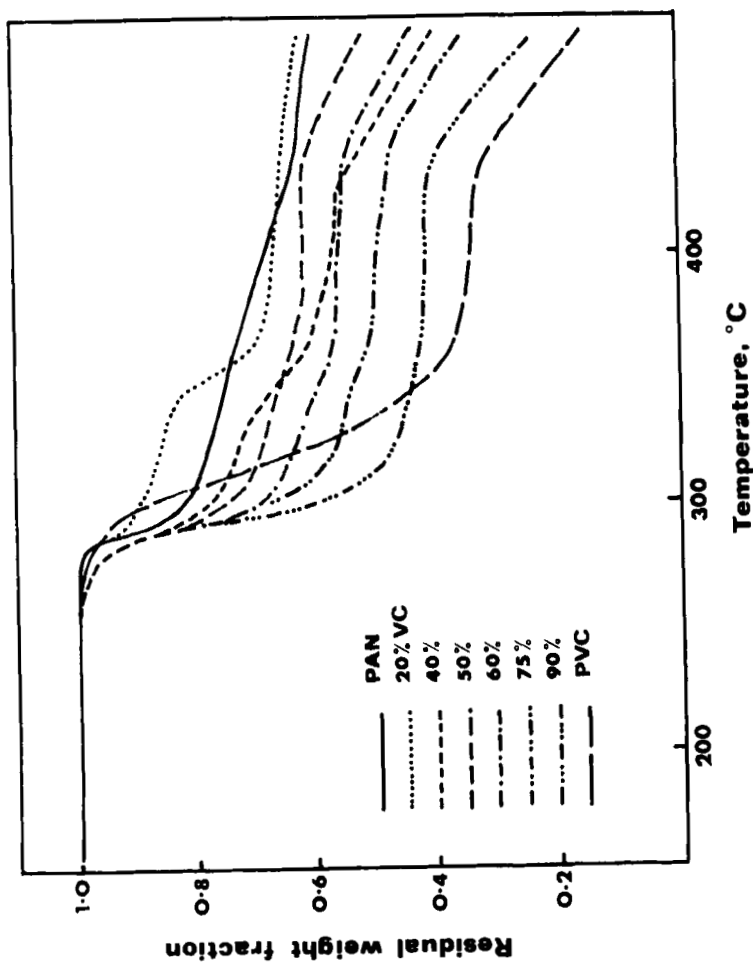
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FIG. 5. TG data for PVC–PAN mixtures of various compositions. Total sample size, 10 mg; heating rate, 10°C/min; dynamic nitrogen flow, 80 ml/min.
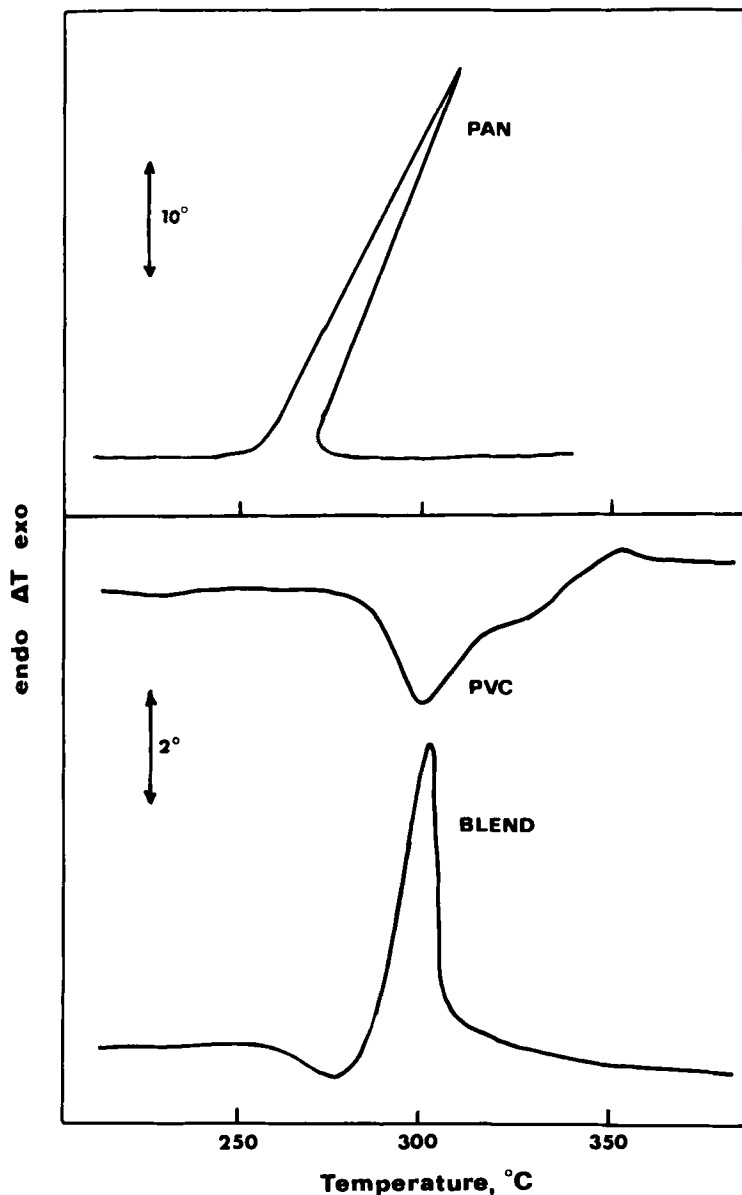
FIG. 6. DTA data for PAN, PVC and a 1:1 PVC-PAN mixture. Sample size, 10 mg; heating rate, 10°C/min; dynamic nitrogen flow, 80 ml/min.

occurring over a broader temperature range, is in fact more exten-
sive in the blend.

Considerable caution has to be exercised in correlating results
obtained by TVA and TG, in which the ammonia and hydrogen chloride
escape readily from the degrading polymer, with those from DTA and
DSC where escape is difficult.

Degradation of PAN as a blend with poly(vinylidene chloride),
chlorinated rubber, and poly-α-chloroacrylonitrile, respectively [19],
gave similar effects to those of PVC on PAN; these polymers all
evolve hydrogen chloride during degradation.

Effect on PAN. The PVC-PAN blends are so highly incom-
patible that the interaction effect on PAN can only reasonably be
attributed to the PVC reaction product, HCl. This view is supported
by the fact that simultaneous, unmixed degradation of the two poly-
mers gives a marked effect.

The results suggest that the nitrile oligomerization process only
begins to reach a significant rate when HCl evolution has almost
ceased. When it begins, it occurs less sharply than for PAN alone;
it is difficult to decide whether this is due to the effect of small
residual amounts of HCl or whether the oligomerization mechanism
is fundamentally altered. HCl is apparently an inhibitor of the
oligomerization process; there is an interesting correlation here
with an early observation of Grassie and McNeill [20] that colored,
soluble polymethacrylonitrile polymers, in which nitrile oligomeriza-
tion has occurred, when in solution, lose their color instantly on
addition of small amounts of aqueous HCl. This was interpreted in
terms of a reversion of the oligomerization process. Such an explana-
tion would account for the fact that PAN apparently does not undergo
nitrile oligomerization in the presence of HCl.

Effect on PVC. The presence of PAN reduces the stability
of PVC very considerably. Again, the extreme heterogeneity of the
polymer mixture leads to the conclusion that if this is a chemical
effect, it can only be due to volatile products from PAN breakdown.
Ammonia and hydrogen cyanide begin to be produced (not in large
amounts) when PAN is heated alone at 10°C/min, at about 220°C.
Base catalysis of dehydrochlorination in PVC in the presence of
ammonia is a possibility which must be considered.

This hypothesis was tested by degrading PVC in the presence of a
polymer which yields large amounts of NH$_3$ at temperatures below
that at which PVC alone begins to break down. Such a polymer is
polyacrylamide (PAM), and TVA curves for PVC-PAM powders in
the mixed and unmixed conditions are presented in Fig. 7. The strik-
ing increase in HCl production in the temperature range in which
PAM begins to evolve ammonia provides convincing support for the
hypothesis that ammonia can initiate or catalyze PVC dehydrochlori-
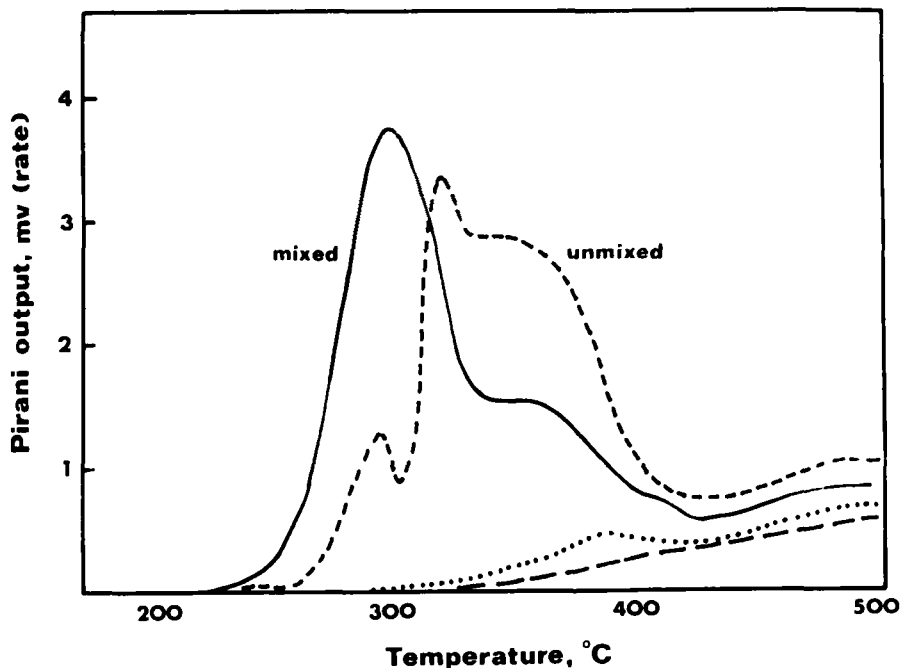nation.

FIG. 7. TVA curves for 1:1 PVC-PAM powder samples degraded simultaneously in unmixed and mixed condition. Sample size, 25 mg of each polymer; heating rate, 10°C/min.

The view that volatiles from PAN reduce the stability of PVC-PAN blends is apparently untenable, however, despite the convincing support for the role of ammonia, because in presence of PVC, the reaction which leads to ammonia formation [21] is suppressed until dehydrochlorination is nearly complete, as discussed above.

An alternative explanation may be found in the physical state of the system. If the presence of PAN makes it more difficult for HCl to escape out of the powder sample, then the autocatalytic effect of HCl will be increased. PVC alone shows a marked decrease in stability when degraded as a powder, compared to a thin film [2], and this has been explained in the same way.

PVC-PBMA System

The degradation of poly(n-butyl methacrylate) has been investigated under isothermal conditions by Grassie and MacCallum [22].

These workers found that, in addition to monomer, butene-1 is a minor product of degradation, due to the occurrence, to a small extent, of an ester decomposition reaction in which methacrylate acid units are left in the chain, in competition with the predominant depolymerization. These acid units can subsequently decompose.

The TVA curve for PBMA (Fig. 8) illustrates the breakdown of this material under programmed heating conditions. The rather involatile monomer gives the limiting rate effect [17] observed in the -45°C trace. Butene production is seen from the -75°/-100°C traces to commence at about 270°C. The distinctive small peak in the -196°C curve results from the decomposition of the small amounts of poly(methacrylic acid) type structures.

PVC-PBMA blends were prepared as films cast from a common solution in freshly distilled cyclohexanone. Thus the degree of heterogeneity in this system is much less than for the three systems just considered.

TVA traces for 1:1 by weight PVC-PBMA samples degraded together in the "unmixed" and "mixed" states are shown in Fig. 9, where, for simplicity, only the traces for 0°C and -100°C trap temperatures are reproduced. For both systems, the peaks for the -100°C traces around 330°C are due to HCl volatilization, while the 0°C trace results from both BMA monomer and HCl. It can be seen that there is a considerable increase in the size of the 0°C peak around 350°C in the mixed system. Since the amount of HCl evolved is similar in both cases, this extra volatilization in the mixed system is due to a product of lower volatility. Spectroscopic examination indicated only BMA monomer in the products condensable at -75°C. This early acceleration of monomer production in PBMA has the consequence, clearly seen in the TVA curve, that less BMA is produced in the later stages of the heating program, for the blend.

About 400°C in the trace for the mixed polymers, there is increased production of material noncondensable at -100°C (and at -196°C, although this is not shown on the figure). This probably results from decomposition of poly(methacrylic acid) structures (or the corresponding anhydride) produced by interaction of HCl with the PBMA ester groups. Thus in the blend, this type of structure is formed by two routes, viz., ester decomposition and by reaction with HCl from the PVC.

The results above are entirely consistent with processes analogous to the mechanism previously proposed (Table 1 and ref. [3]) for the interaction of PVC with PMMA and with the results of Guyot et al. [23] for the degradation of graft copolymers of PVC and PBMA.

There is a small effect in this system on the breakdown of the PVC component. The rate maximum is displaced slightly to higher temperatures (as for PVC-PMMA blends) but HCl evolution begins a little earlier in the blend. The latter effect was also observed in
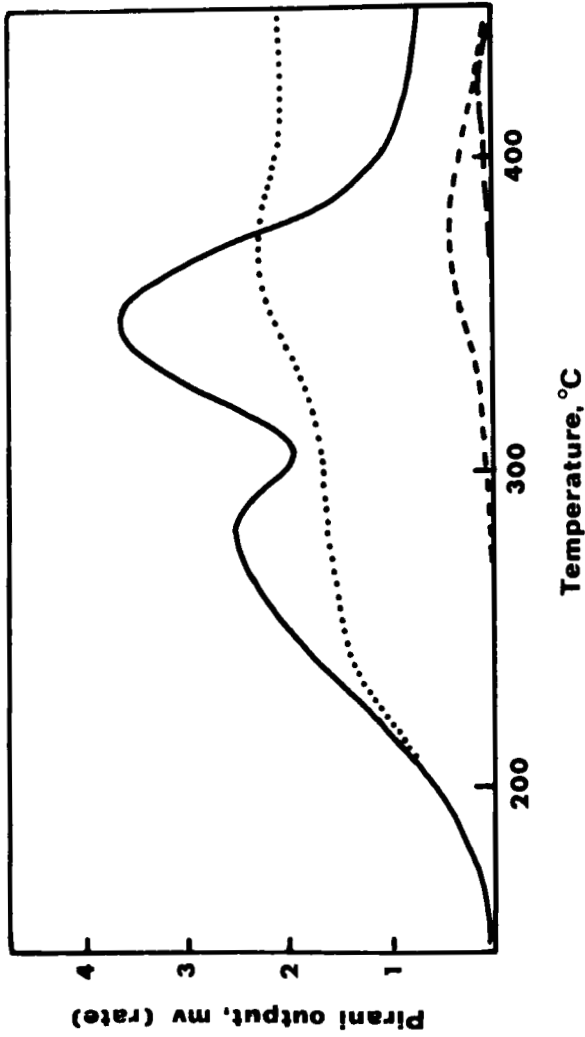
FIG. 8. TVA curve for a PBMA film. Sample size, 50 mg; heating rate, 10°C/min.
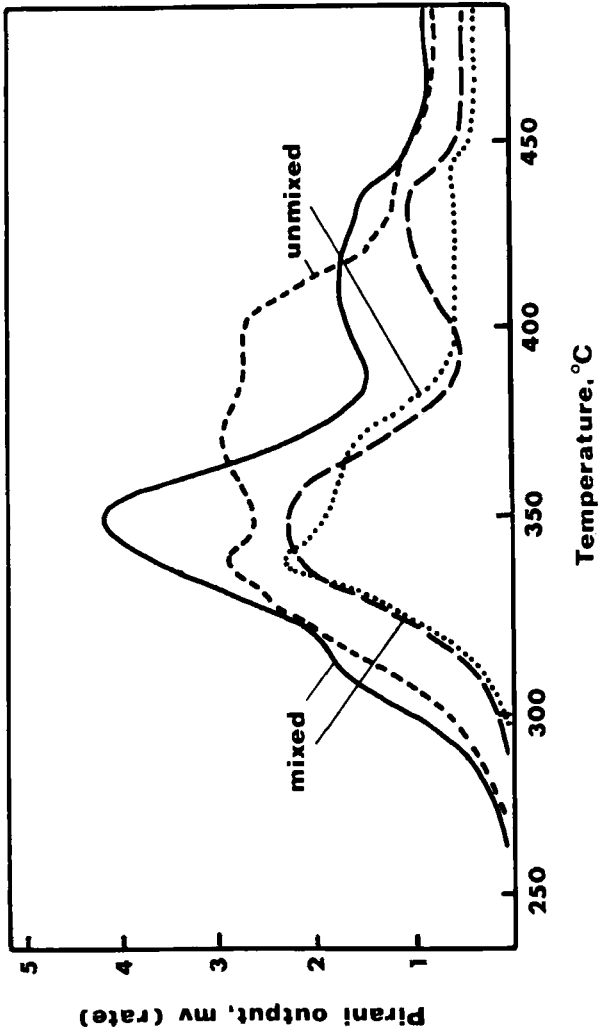
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FIG. 9. TVA curves for 1:1 PVC–PBMA film samples (solvent: cyclo-hexanone) degraded simultaneously in (a) unmixed and (b) mixed condition. Samples size, 25 mg of each polymer; heating rate, 10°C/min.

PVC-PBMA graft copolymers and has been explained by Guyot [24] as due to a reaction of methacrylate monomer with PVC.

PVC - PMA System

The mechanism of degradation of PMA has been discussed by Cameron and Kane [25, 26]. The principal feature of the breakdown of this polymer is a rapid fall in molecular weight due to scissions of the chain backbone. Small amounts of volatiles are formed (methanol, carbon dioxide, traces of monomer) and the presence of these has been explained in terms of free radical processes.

The behavior of 1:1 by weight blends of PVC and PMA, degraded simultaneously in the unmixed and mixed states in the form of films cast from cyclohexanone is shown in Fig. 10.
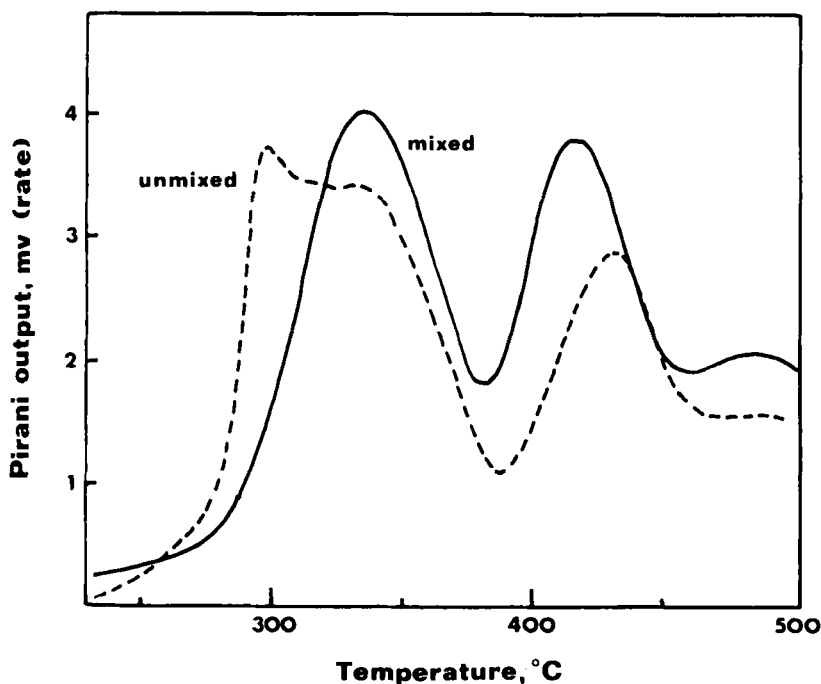
FIG. 10. TVA curves for 1:1 PVC-PMA film samples (solvent: cyclohexanone) degraded simultaneously in (a) unmixed and (b) mixed condition. Sample size, 20 mg of each polymer; heating rate, 10°C/ min.

These results indicate a marked stabilization of the PVC in the blend, but PMA breaks down at somewhat lower temperatures. Product analysis by gas-phase IR spectroscopy gave no indication of any change in the products due to mixing of the polymers.

The observed behavior can be adequately explained if the main interactive process in the blend consists of reaction of chlorine radicals, produced by the PVC, which diffuse into the PMA phase and abstract H atoms. Thus as in the cases of PMMA, PBMA, PS, and PAMS, the PVC is stabilized by loss of a chain carrier. It would be expected that the drop in molecular weight for the PMA would be more rapid in the blend than for PMA alone, but measurements have not been made for this blend system.

PVC-PBMAM System

Degradation of PBMAM. The behavior on degradation of PBMAM alone does not appear to have been studied previously. The TVA curve (Fig. 11) shows three main stages of breakdown under programmed heating. The first stage, however, probably involves two phases of reaction since the main peak at T_{max} = 258°C is preceded by a shoulder around 190°C. Products identified by IR analysis up to 265°C consisted of butylamine, monomer, and ammonia. Ammonia is noncondensable at -100°C, so that it is clearly a minor product. The part of the TVA curve between the -75 and -100°C curves is probably due to butylamine, whereas BMAM monomer is condensed between -45 and -75°C. Quantitatively, butylamine and monomer seem to be produced in comparable amounts.

In the remaining stages of degradation of PBMAM (peaks with T_{max} 370, 432°C, respectively) the products identified by IR analysis were butylamine, ammonia, monomer, isobutene, ethylene, butene-1 (and/or propylene), and possibly methacrylonitrile. The noncondensable fraction consisted of carbon monoxide and methane.

The mechanism shown in Eqs. (1) accounts satisfactorily for the observed products. Process (1b) probably proceeds via formation of the primary amide unit (methacrylamide unit) by a reaction analogous to the ester decomposition reaction in PBMA in which butene-1 is also split out (leaving a methacrylic acid unit), followed by cyclization involving adjacent methacrylamide and BMAM units with elimination of butene-1 and ammonia.

The positive IR identification of butene-1 is prevented by the fact that characteristic bands are obscured by strong absorptions of ammonia.

Fragmentation of the cyclic imide in the stage III region, at high temperatures, accounts for the appearance of the noncondensable materials indicated by the TVA traces. The temperature of the rate
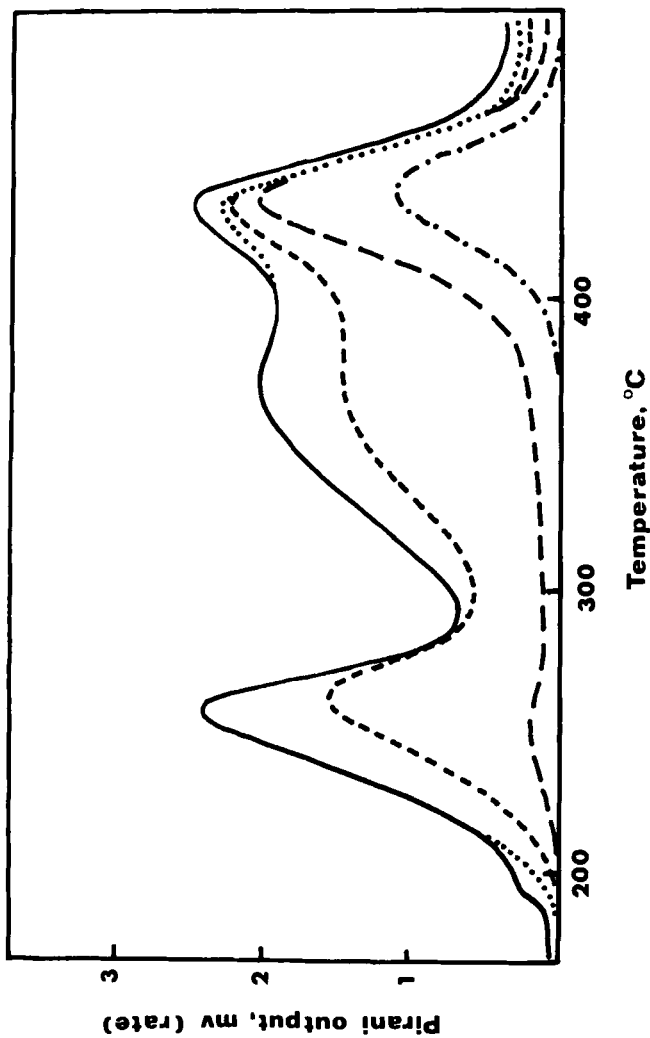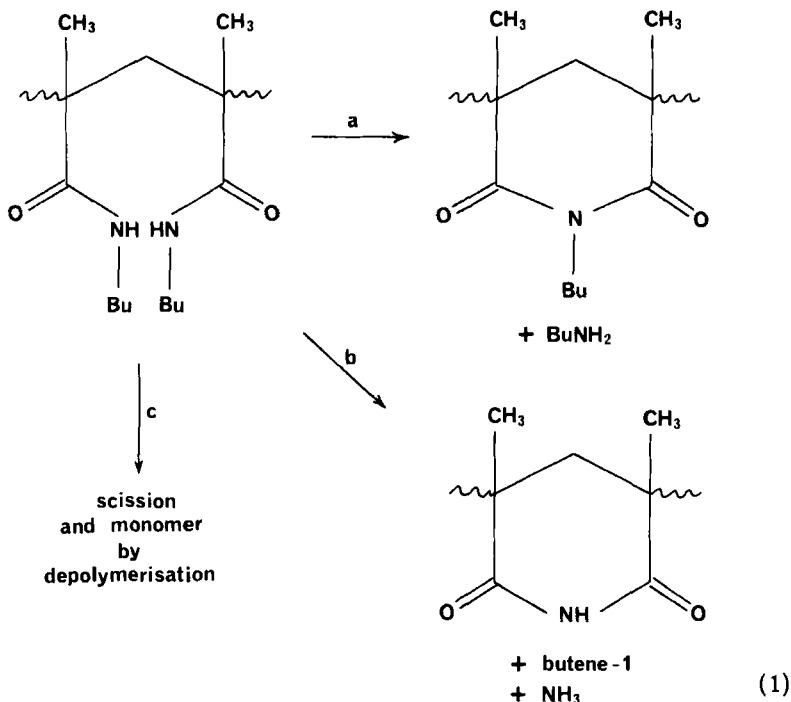
FIG. 11. TVA curve for PBMAM. Sample size, 25 mg (powder), heating rate, 10°C/min.

$$CH_3 \quad CH_3 \qquad \xrightarrow{a} \qquad CH_3 \quad CH_3$$

scission
and monomer
by
depolymerisation

+ BuNH₂

+ butene-1
+ NH₃

$$(1)$$

maximum for stage III, and the pattern of breakdown, are comparable
with the behavior of the corresponding anhydropoly(methacrylic acid)
structure [27].

Dehydration of primary amide units to give methacrylonitrile units
in the chain accounts for the appearance of some methacrylonitrile
in the products.

The products at stages I and II do not differ greatly in their pro-
portions. It is possible that the initial depolymerization process is
end-initiated but that this mode of monomer production becomes
blocked by ring structures formed in the concurrent imidization re-
actions; at stage II temperatures, however, main-chain scission may
initiate further depolymerization, while imidization continues.

Behavior of 1:1 Blends. In this system, as for the PVC-
PAN case, there is no common solvent, so that blends were made by
grinding together the two polymers. These blends were studied only
by TVA and analysis of volatile products.

The TVA curves for the two polymers degraded simultaneously in
the unmixed and mixed states are shown in Fig. 12. Two main features
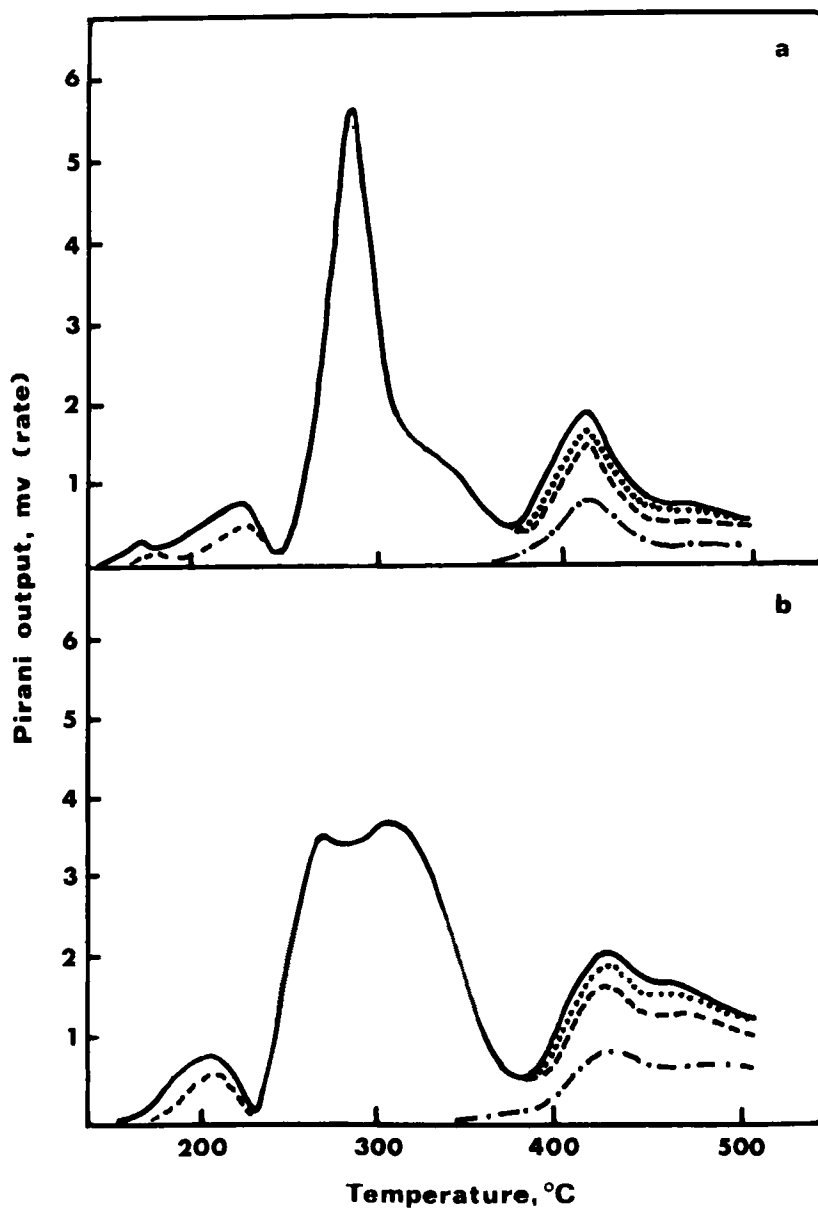are immediately obvious: (a) the T_{max} for the initial stage of PBMAM

FIG. 12. TVA curves for 1:1 PVC-PBMAM powder samples, degraded simultaneously in (a) unmixed and (b) mixed condition. Sample size, 15 mg of each polymer; heating rate, 10°C/min.

breakdown is shifted from 231°C in the unmixed case to 209°C for the mixed polymers; (b) the dehydrochlorination peak (HCl noncondensable at -100°C) moves from T_{max} 292°C to give a double peak in the blend with T_{max} values 270 and 313°C, respectively.

Even for the polymers in the unmixed form, T_{max} for butylamine and monomer production is about 27°C below the value for the PBMAM homopolymer so that the shift to lower temperatures is not due to any interaction in the polymers themselves. It is likely that the flow of butylamine to the Pirani gauges is curtailed as soon as dehydrochlorination begins because of the formation of the amine hydrochloride [Eq. (2)].

$$BuNH_2 + HCl \longrightarrow (BuNH_3)^+ Cl^- \tag{2}$$
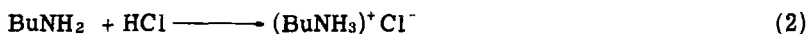
This effect is also evident in the blend, where, because of the earlier loss of HCl, evolution of butylamine ceases to be observed at even lower temperatures resulting in a downward shift in T_{max}.

For the same reasons, the intermediate stage of PBMAM breakdown (T_{max} = 370°C), where butylamine is again a major product, appears to have been removed in both the mixed and unmixed cases.

Dehydrochlorination begins at least 20°C sooner in the blended sample, and the splitting of the HCl peak suggests that two stages of HCl loss are occurring. The first of these may be butylamine-catalyzed and possibly occurs in that part of the PVC closest to the phase boundaries, where butylamine diffusion is more likely. The second stage probably represents the normal dehydrochlorination in the parts of the PVC sample less accessible to butylamine.

The effect of butylamine on PVC thus parallels that of ammonia produced in PAN and PAM breakdown.

GENERAL DISCUSSION

The degradation behavior of five PVC blend systems has previously been reported in detail; a further five systems are discussed above. In addition to these, the systems PVC-poly(methacrylic acid), PVC-rubber, PVC-cis-polybutadiene, and PVC-polychloroprene have been examined briefly by the TVA twin-limbed tube approach without any evidence having been obtained, by this method, for chemical interaction effects.

With this amount of data now available, it is appropriate to consider more generally the degradation of PVC in different polymeric

TABLE 2. Summary of Interaction Effects for Ten PVC Blends

Blend PVC with	State[a]	Effects on polymers				Product interaction?
		PVC		Second polymer		
		Δ stability	By reaction of	Δ stability	By reaction of	
Cl rubber	F	-	HCl	none		no
PVA	F	-	CH₃COOH	-	HCl	no
PS	F	+	loss of Cl·	+	Cl· ⎫	no
PAMS	F	+	loss of Cl·	-	polyene ⎬	no
PMMA	F	+	loss of Cl·	+	Cl· ⎫	no
PBMA	F	δ+	loss of Cl·	-	HCl ⎫	no
PMA	F	+	loss of Cl·	+	Cl· ⎬	no
PAN	P	-	NH₃	-	HCl	yes
PAM	P	-	NH₃			yes
PBMAM	P	-	BuNH₂			yes

[a] F = film; P = powder.

environments, with particular reference to the comments made in the introduction about the types of interaction which might be expected.

None of these systems shows any evidence for polymer + polymer molecular reaction. Polymer + macroradical reaction may be occurring in the case of PVC-PS, where radicals (presumably macroradicals) involved in PS degradation appear to be stabilized by reaction with the conjugated residue of PVC dehydrochlorination.

There are several systems in which Cl· radicals produce considerable effects on the second polymer, and still more examples of effects due to reaction of HCl with the second polymer. Small molecules from the second polymer can influence PVC behavior–the effects of ammonia and butylamine in destabilizing PVC are especially notable and perhaps surprising in view of the use of related compounds as PVC stabilizers. The destabilizing effect of HCl· produced from chlorinated rubber (which is less stable than PVC) is not unexpected. In systems where Cl· radicals are used up in attack on the second polymer, there is a slight consequent stabilization of the PVC. Acrylic monomers destabilize PVC to a small extent [24].

Direct interaction of products from two different polymers occurs in the PVC-PAN, PVC-PAM, and PVC-PBMAM systems. In cases where this can occur, interaction of the secondary product with one or other polymer is a possibility. In the above systems, this possibility exists but could not be tested.

The degree of heterogeneity has some bearing on the extent of interaction. Thus for PVC-PMMA, for example, interaction of Cl· radicals with PMMA is more significant in films than in powder mixtures. It is clear, however, that many highly heterogeneous polymer mixtures show very large interaction effects.

The observed interactions for the ten PVC blends are summarized in Table 2. These results illustrate clearly that when a polymer is used in an environment in which a second polymer is present, considerable effects on the stability of either or both polymers may result.

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REFERENCES

[1] N. Grassie, I. C. McNeill, and I. Cooke, J. Appl. Polym. Sci., 12, 831 (1968).

[2] I. C. McNeill and D. Neil, Eur. Polym. J., 6, 143 (1970).

[3] I. C. McNeill and D. Neil, Eur. Polym. J., 6, 569, (1970).

[4] D. L. Gardner and I. C. McNeill, Eur. Polym. J., 7, 603 (1971).

[5] A. Jamieson and I. C. McNeill, J. Polym. Sci. Polym. Chem. Ed., 12, 387 (1974).

[6] B. Dodson, I. C. McNeill, and T. Straiton, J. Polym. Sci. Polym. Chem. Ed., 12, 2369 (1974).

[7] B. Dodson and I. C. McNeill, J. Polym. Sci. Polym. Chem. Ed., 14, 353 (1976).

[8] I. C. McNeill, D. Neil, A. Guyot, M. Bert, and A. Michel, Eur. Polym. J., 7, 453 (1971).

[9] A. Jamieson and I. C. McNeill, J. Polym. Sci. Polym. Chem. Ed., 14, 603 (1976).

[10] A. Jamieson and I. C. McNeill, J. Polym. Sci. Polym. Chem. Ed., 14, 1839 (1976).

[11] N. Grassie and W. B. H. Leeming, Eur. Polym. J., 11, 819 (1975).

[12] D. H. Richards and D. A. Salter, Polymer, 8, 127 (1967).

[13] L.-P. Blanchard, V. Hornof, Hong-ha Lam, and S. Malhotra, Eur. Polym. J., 10, 1057 (1974).

[14] Y. Mizutani, S. Matsuoka, and K. Yamamoto, Bull. Chem. Soc. Japan, 38, 2045 (1965).

[15] G. H. Stempel, R. P. Cross, and R. P. Mariella, J. Amer. Chem. Soc., 72, 2299 (1950).

[16] M. M. Koton, T. A. Sokolova, M. N. Savitskaya, and T. M. Kiseleva, J. Gen. Chem. USSR, 27, 2297 (1957).

[17] I. C. McNeill, Eur. Polym. J., 6, 373 (1970).

[18] N. Grassie and R. McGuchan, Eur. Polym. J., 6, 1277 (1970).

[19] N. Grassie and R. McGuchan, Eur. Polym. J., 9, 507 (1973).

[20] N. Grassie and I. C. McNeill, J. Polym. Sci., 27, 207 (1958).

[21] N. Grassie and R. McGuchan, Eur. Polym. J., 7, 1091 (1971).

[22] N. Grassie and J. R. MacCallum, J. Polym. Sci., 2, 983 (1964).

[23] A. Guyot, M. Bert, A. Michel, and I. C. McNeill, Eur. Polym. J., 7, 471 (1971).

[24] A. Michel, M. Galin, and A. Guyot, J. Appl. Polym. Sci., 13, 929 (1969).

[25] G. G. Cameron and D. R. Kane, Makromol. Chem., 109, 194 (1967).

[26] G. G. Cameron and D. R. Kane, Makromol. Chem., 113, 754 (1968).

[27] D. M. Grant and N. Grassie, Polymer, 1, 125 (1960).