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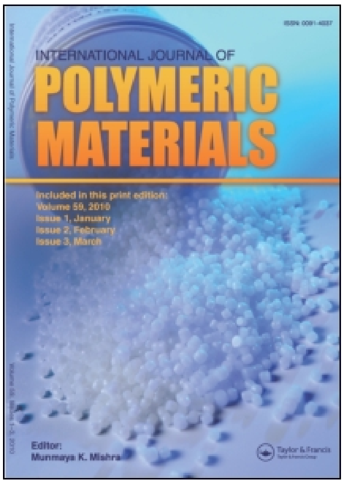

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Thermal and Oxydative Stability of PVA and Nylon 6,6

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Recent advances in the thermal decomposition, pyrolysis in vacuum and in the presence of oxygen, and fire retardancy of PVA and Polyamide Nylon 6,6 are reviewed.

KEY WORDS PVA, Nylon 6,6, thermal decomposition, pyrolysis

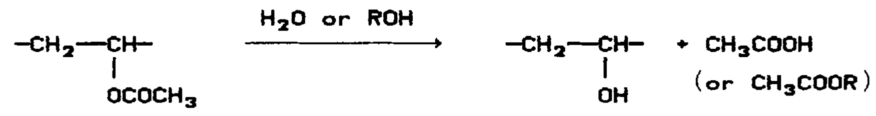
INTRODUCTION

The problems of thermal and oxidative stability under various environmental conditions have been studied for many years. Because of the technological importance and technical complexity of the issues related to polymer stability, it is desirable to present an overview of recent advances in this field.

POLYMER CHARACTERISTICS

I Polyvinyl Alcohol[1]

The monomer, vinyl alcohol ($CH_2{=}CHOH$, tautomeric with acetaldehyde, CH_3CHO), is unknown. But the polymer is a stable substance obtained by hydrolysis or alcoholysis of polyvinyl acetate.



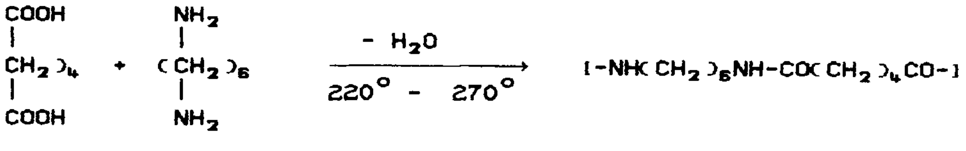
$$-CH_2-\underset{OCOCH_3}{\underset{|}{CH}}- \xrightarrow{H_2O \text{ or } ROH} -CH_2-\underset{OH}{\underset{|}{CH}}- + CH_3COOH \quad (\text{or } CH_3COOR)$$

Properties. The properties of polyvinyl alcohol (PVA) include solubility in water, especially on warming to 70–80°C; plasticiation by moisture and water-soluble hydric alcohols (glycerol, glycol, triethylene glycol, sorbitol), glyceryl lactate, amides (urea), and also calcium chloride acting as a humectant; and swelling by polyhydric alcohols (hot). PVAs are relatively unaffected by almost all organic liquids: hydrocarbons, and chlorinated hydrocarbons, alcohol, acetone, esters, oils and fats and are ozone resistant and decomposed by conc. acids, especially oxidizing acids. PVA burns with a slightly smoky flame and leaves a black residue and unpleasant odor (particularly formaldehyde).

Additional and thermal properties includes specific gravity, 1.25–1.35; fibers, 1.26–1.32; and second-order transition at 85°C. The polymer is serviceable up to 120°–140°C, though it slowly yellows (degrades) above 100°C, and darkens (with evolution of water and conversion to an unsaturated polymer) if kept at 150–200°C. The polymer does not properly melt.

The first-order transition temperature (melting transition) is considerable and depends on the tacticity of the PVA Table I.[1]

II Nylon 6,6[1]



$$\underset{\text{COOH}}{\overset{\text{COOH}}{(CH_2)_4}} + \underset{NH_2}{\overset{NH_2}{(CH_2)_6}} \xrightarrow[220^\circ - 270^\circ]{-H_2O} [-NH(CH_2)_6NH-CO(CH_2)_4CO-]$$

Properties. The properties of Nylon include solubility in phenols and phenol/chlorinated hydrocarbon mixtures (1/3 phenol/tetrachloroethane, by volume), 90% formic acid, hot formamide, hot benzyl alcohol, halohenated alcohols and decomposition by conc. mineral acids, oxidizing agents, and halogens. Nylon is relatively unaffected by hydrocarbons and chlorinated hydrocarbons, esters, ethers, oils and set and upon combustion, melts, darkens, boils, and finally burns with a small flame that is easily extinguished giving a white smoke. Decomposition occurs at 260–300°C., specific gravity is 1.14 and thermal properties include second-order (glass) transition at 37–47°C and a melting point of 250–260°C.

DECOMPOSITION DATA

I Thermal Decomposition of PVA[2]

Pyrolysis under vacuum. Decomposition of PVA proceeds in two stages. The first stage, which begins at 200°C, mainly involves dehydration accompanied by

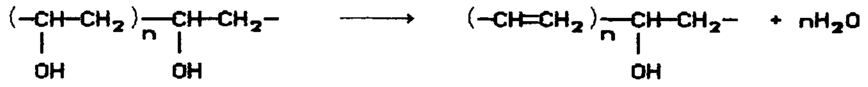
TABLE I

Crystalline melting points of PVA

Experimental Method	T_m (°C)	Sample
DTA	228–240	Atactic
DTA	230–267	Syndiotactic
DTA	212–235	Isotactic

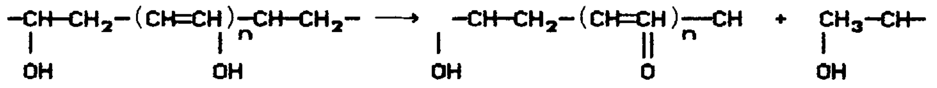
Insolubilized fibers show changes associated with decomposition and melting between 200–260°C.

the formation of some volatile products. The residues are predominantly polymers with conjugated, unsaturated structures. In the second stage, polyene residues are further degraded at 450°C to yield carbon and hydrocarbons. The mechanism involved in thermal decomposition of PVA has been deduced by Tsuchya and Sumi.[2] At 245°C, water is split off the polymer chain, and a residue with conjugated polyene structure results:



$$(\underset{OH}{-CH}-CH_2)_n-\underset{OH}{CH}-CH_2- \longrightarrow (-CH{=}CH_2)_n-\underset{OH}{CH}-CH_2- + nH_2O$$

Scission of several carbon–carbon bonds leads to the formation of carbonyl ends. For example, aldehyde ends arise from the reaction:



$$-\underset{OH}{CH}-CH_2-(CH{=}CH)_n-\underset{OH}{CH}-CH_2- \longrightarrow -\underset{OH}{CH}-CH_2-(CH{=}CH)_n-\underset{\overset{\|}{O}}{CH} + CH_3-\underset{OH}{CH}-$$

In the second-stage pyrolysis of PVA, the volatile products consist mainly of hydrocarbons, i.e. *n*-alkanes, *n*-alkenes and aromatic hydrocarbons (Table II).[2] It was also reported[3] that the formation of volatile vapors, water and acetaldehyde from PVA pyrolysed at 185–350°C, can be fitted into the first-order rate equation. The rate constant is equal to 10^{-4} per minute.

Pyrolysis in the presence of oxygen. Thermal degradation of PVA in the pres-

TABLE II

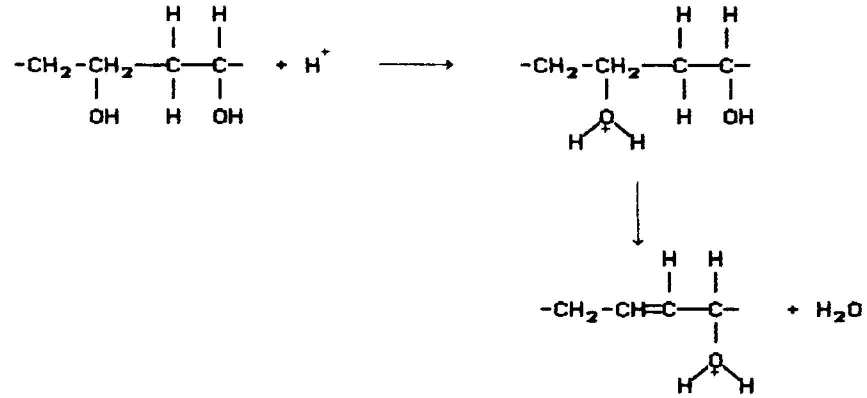
Thermal decomposition products of PVA (240°C, 4h)

Product	% by weight of original polymer
Water	33.4
CO	0.12
CO_2	0.18
Hydrocarbons C_1–C_2	0.01
Acetaldehyde	1.17
Acetone	0.38
Ethanol	0.29
Bensene	0.06
Crotonaldehyde	0.76
3-pentene-2-one	0.19
3,5-heptadiene-2-one	0.099
2,4-hexadiene-1-al	0.55
Benzaldehyde	0.022
Acetophenone	0.021
2,4,6-octatriene-1-al	0.11
3,5,7-nonatriene-2-one	0.020
Unidentified	0.082

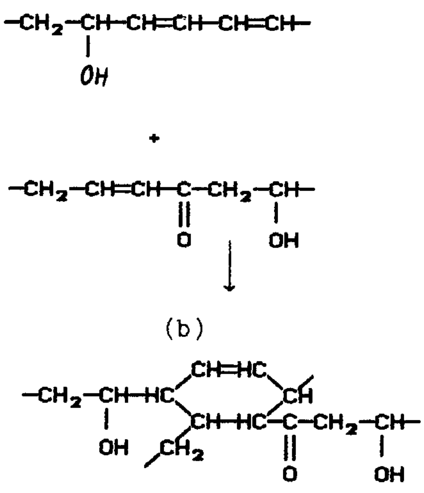
ence of oxygen can be adequately described by a two-stage decomposition scheme, with one modification. Oxidation of unsaturated polymeric residue from dehydration reaction introduces ketone groups into the polymer chain. These groups then promote the dehydration of neighboring vinyl alcohol units producing conjugated unsaturated ketone structure.[1] The first-stage degradation products of PVA pyrolysed in air are fairly similar to those obtained in vacuum pyrolysis. In the range of 260 to 280°C, the second-order reaction expression satisfactorily accounts for the degradation of 80% hydrolysed PVA up to a total weight loss of 40%. The activation energy of decomposition appears to be consistent with the value of 53.6 kkal/mol that is obtained from the thermal degradation of PVA.[1]

Infrared spectroscopic study of the PVA residue. The changes in the IR spectra of PVA subjected to heat treatment were studied.[1] After heating to 180°C in air, the bands appeared at 1630 cm^{-1} (C=C stretching in isolated double bonds), 1650 cm^{-1} (C=C stretching in conjugated diens and triens), and 1590 cm^{-1} (C=C stretching in polyenes). The intensity of the carbonyl stretching frequency at 1750–1720 cm^{-1} increased, although the rate of increase of intensity was less than of the polyene band at low temperatures. Although above 180°C dehydration was the predominant reaction at first, the rate of oxidation increased after an initial induction period.

Mechanism of crosslinking during degradation of PVA. The identification of a low concentration of benzene among the volatile products of PVA [81, 84] has been taken to indicate the onset of a crosslinking reaction proceeding by a Diels-Alder addition mechanism [86]. Clearly, benzenoid structures are ultimately formed in the solid residue, and the IR spectrum of the residue also indicated the development of aromatic structures [85].

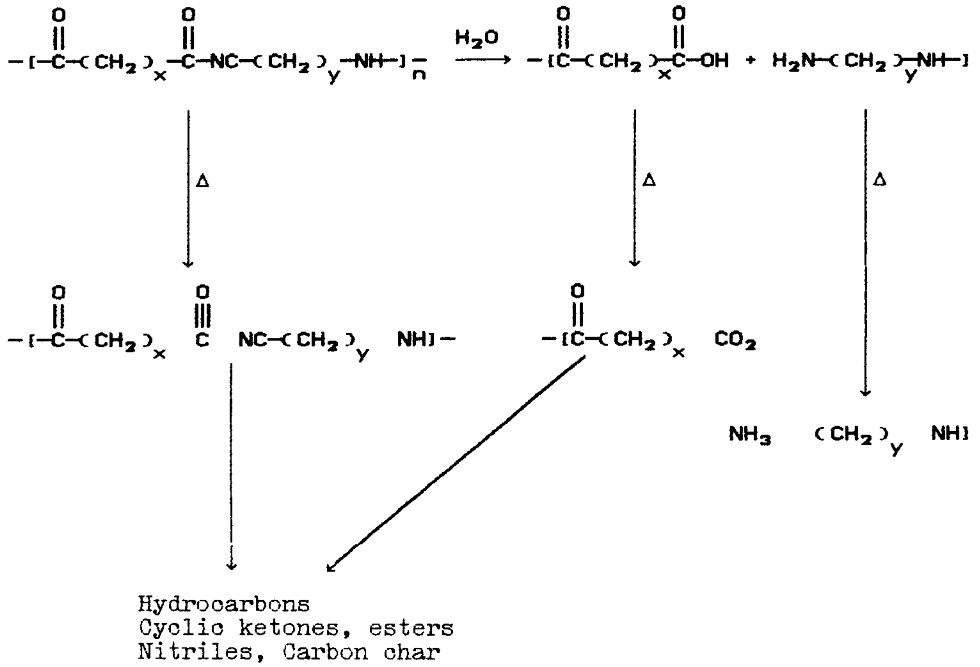


Acid-catalyzed dehydration promotes the formation of conjugated sequences of double bonds (a) and Diels-Alder addition of conjugated and isolated double bonds in different chains may result in intermolecular crosslinking producing structures that form graphite on carbonization (b)



II Thermal Decomposition of NYLON 6,6

It was found[3,4] that when nylon 6,6 was subjected to temperatures above 300°C in an inert atmosphere, it completely decomposed. The wide range of degradation products, which included several simple hydrocarbons, cyclopentanone, water, CO, CO_2 and NH_3, suggested that the degradation mechanism must have been highly complex. Further research has led to a generally accepted degradation mechanism for the aliphatic polyamides[5]:



1. Hydrolysis of the amide bond occurred below the decomposition temperature and could have been alleviated if proper care had been taken in purification;
2. Homolitic cleavage of C—C, C—N, and C—H bonds generally began at the decomposition temperature and occurred simultaneously with hydrolysis;
3. Cyclization and homolitic cleavage of products from both of the above reactions occurred;
4. Secondary reactions produced CO, NH_3, nitriles, hydrocarbons, and carbon chars.

FIRE RETARDANCY OF POLYAMIDE 6,6

The fire retardancy of polymers can be achieved by various methods:

1. Modifying the pyrolysis scheme, to produce non-volatile or non-combustible products that dilute the flame oxygen supply;
2. Smothering the combustion, through dilution of the combustible gases or the occurrence of the barrier (char), which hinders the supply of oxygen;
3. Trapping the active radicals in vapor phase (and eventually in condensed phase);
4. Reducing the thermal conductibility of the material to limit the heat transfer (char).

In Polyamide 6,6 (NYLON) several types of flame retardants are used[6]: phosphorus compounds, halogenated compounds with inorganic synergists, and miscellaneous compound (non phosphorus and non halogenated).

Phosphorus compounds retard burning essentially in the condensed phase, influencing pyrolysis and char formation, according to the following mechanisms[7]:

In the condensed phase: 1. they form phosphoric and related acids that act as a "heat sink" as they undergo endothermic reduction; and 2. they form a thin glassy coating that is a barrier that lowers the concentration of combustible gases in vapor phase, limits the diffusion of oxygen, and limits the heat transfer.

In vapor phase, where PO radicals are likely to exist: 3. they stop the free-radical oxidation process of carbon into carbon monoxide only, avoiding the highly exothermic reaction of carbon dioxide formation.

Halogenated compounds are known to be essentially active in vapor phase by trapping the active radicals, and so inhibiting the combustion of the matrix.

There is a well-known synergy between Sb_2O_3 and the halogenated compounds: Sb_2O_3 promotes the halogen volatilisation in the form of metallic halides (SbX_3) or oxyhalides ($Sb_xO_yx_z$). In the case of chlorinated compounds, $SbCl_3$ traps H to produce HCl, SbCl, $SbCl_2$ and Sb. Sb reacts with O· and Oh· to give SbOH and SbO·, which traps radicals again.[8]

Miscellaneous systems concerns the flame retardants that act through the production of diluting non-combustible gases: 1. Hydroxides decompose endothermically, thus the heat level, producing water which dilutes the combustible gases, and inert oxide. In the case of $Mg(OH)_2$, it has been reported that its morphology has an influence on the LOI but no effect on the UL94 test.[9] It is also claimed that $Mg(OH)_2$ promotes char formation and gives lower smoke levels than $Al(OH)_2$.[10]

2. Melamine cyanurate retards burning in the vapor phase by producing uncombustible diluting gases (NH_3) and condensation products in the condensed phase, which undergo further degradation steps.[11]

Industrial Flame Retardants for NYLON 6,6

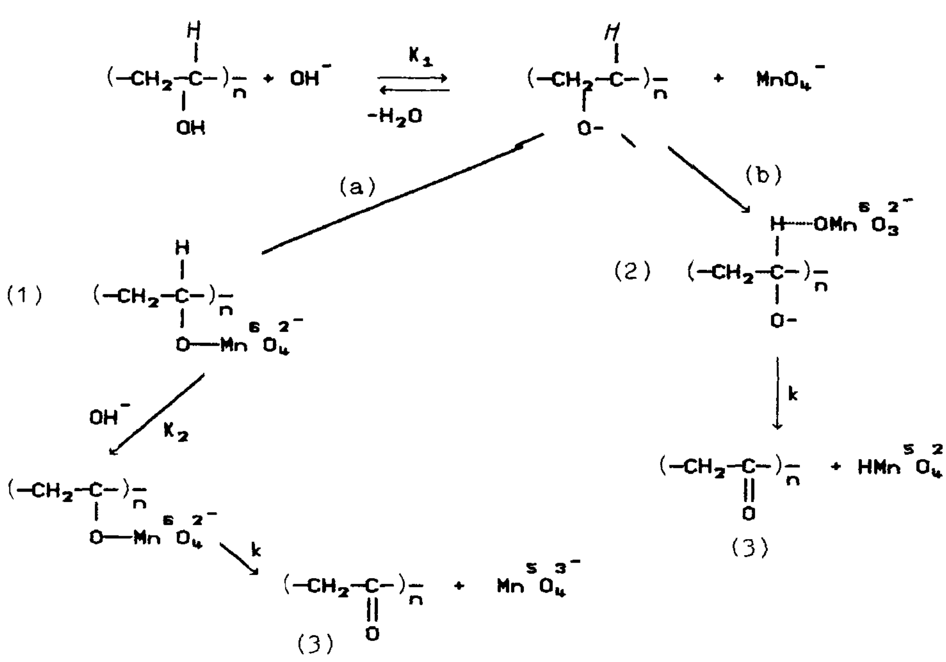
1. Red phosphorous (6–9% wt.) in reinforced and non-reinforced formulations (0–35% wt. glass fibers).[6]
2. Dechlorane (10–25% wt.) $C_{10}Cl_{12}$.[6]
3. Decabromodiphenyl oxide (10% wt.) $C_{12}OBr_{10}$.[6]
4. Decabromodiphenyl $C_{12}Br_{10}$ or brominated polystyrene (7–24% wt.), in synergy with antimony oxide (0.6 to 6% wt.) or a mixture of antimony oxide with zinc borate in various proportions, in reinforced and non-reinforced formulations (0–35% wt.).[6]
5. Halowax 1006 (a mixture of penta and hexachloronaphtalene, with 63% chlorine)—10% wt. with: SnO 10% wt.,[13] PbO 10% wt.,[13] and ZnO 15% wt.[13]
6. Archlor 1268 (chlorinated biphenyl – 68% chlorine)—10% with SnO_2 - 10% wt.[12]
7. Pentabromophenol—5% wt. with PbO—5% wt.[12]
8. Octachloronaphthalene—5% wt. with Cu_2O—3% wt.[12]
9. Melamine cyanurate (10% wt.).[6]
10. Magnesium hydroxide (50–60% wt.) is used in reinforced formulations.[6]

Requirements for Flame Retarded Formulations Based on Nylon 6,6

Property	Requirement
Thermostability	Nylon process T° (300°C)
Volatility	Non volatile below 300°C
Flame retardancy	LOI $\geq$ 28, UL94: VO or V1
Mechanical properties	Impact Strength $\geq$ 40 kJ/m^2
Hazard	Safe handling, no toxicity, no pollution
Possibility of filler	Yes
Cost	Not expensive

OXIDATION OF POLY(VINYL ALCOHOL) BY PERMANGANATE IONS IN ALKALINE SOLUTIONS

The literature available on the oxidation of macromolecules by alkaline permanganate presents little information about these redox systems. The oxidation of PVA as a polymer containing secondary alcoholic groups by $KMnO_4$ in alkaline solution was investigated.[13,14] It was reported that the oxidation of PVA by MnO_4^- in alkaline solutions occurs through formation of two intermediate complexes (1) and/or (2).[14] Hence, two alternative mechanisms for the decomposition were suggested. The first corresponds to a fast deprotonation for the intermediate by the alkali followed by electron transfer from PVA$^-$ to Mn^6 (a). The second mechanism corresponds to the transfer of hydride ions from PVA to MnO_4^{2-} as the rate-determining steps (b):



The reactions (a) and (b) lead to the formation of poly(vinyl ketone) (3) as a final product of oxidation of the substrate. Poly (vinyl keton) was isolated and identified by microanalysis and spectral data.[15]

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