

## **FIRE RETARDANT MATERIALS AND SAFETY: PAST, PRESENT, FUTURE -NEW TYPES OF ECOLOGICALLY FRIENDLY FLAME RETARDANTS**

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### **Summary**

The contributors have attempted to discuss modern trends in polymer flame retardancy. They have also tried to reflect the interest that exists in the creation of new forms of ecologically friendly flame retardants for polymers. This interest will give rise to a solution of many practical and political problems in the future. The chapter contains modern ideas and studies focused attention on five trends in polymer flame retardancy: intumescent systems, low-melting glasses systems, polymer nanocomposites, organic char forms, silicon inorganic systems and preceramic additives.

### **1. Introduction**

Our environment has mostly polymeric nature and all polymers burn whether natural or synthetic. The use of polymer flame retardants has an important role in saving lives. There are four main families of flame-retardant chemicals: Inorganic flame retardants including aluminum trioxide, magnesium hydroxide, ammonium polyphosphate and red phosphorus. This group represents about 50% by volume of the global flame retardant production [1].

Halogenated flame retardants, primarily based on chlorine and bromine. The brominated flame retardants are included in this group. This group represents about 25% by volume of the global production [1].

Organophosphorus flame retardants are primarily phosphate esters and represent about

20% by volume of the global production [1]. Organophosphorus flame retardants may contain bromine or chloride.

Nitrogen-based organic flame retardants are used for a limited number of polymers. The flame retardant chemicals' industry has historically been driven by regulations and standards. The normal fire-, smoke-, and toxicity-related standards have been joined by environmental standards caused by the alleged environmental impact of halogens and the alleged toxicity of antimony. Although suitable replacements have not been found for these materials in all cases, the environmental concern has served to depress their growth levels from what it would otherwise have been and/or channel the growth into alternative chemical products. In connection with the amendment of the Ordinance on Dangerous Substances, the federal government of Germany passed a new Ordinance on the ban and restriction of certain chemicals, compounds and products (Chemikalien-Verbots-Verordnung) which became effective on 1-st November 1993 (BGB I, 1720) and has been amended the first time on 6th July 1994 (BGBL I, 1493). The ordinance has replaced the following Ordinances:

1. An ordinance on the Ban of PCB and PCT of 1989
2. An ordinance on the Ban of Pentachlorophenol of 1989
3. First Ordinance on Chloroaliphates of 1991
4. An ordinance on "Dioxins" and "Furans"

In addition to Tetra- up to Hexachlorodibenzo-p-dioxins/furans with Chlorine atoms at position 2,3, 7, 8 (8 substances transferred from the Ordinance on Dangerous Substances, App. V, 3), the amendment of 6-th July 1994 extends the number of congeners of this type by some additional Penta- up to Octachlorodibenzo-p-dioxins/furans. Now the total number of restricted chlorinated PCDD/PCDF-Congeners amounts to 17 substances. The threshold concentrations for these chemicals in substances preparations and products were decreased considerably, depending on their toxic potentials. However, plant treatment agents, intermediates, and a few more products were excluded from this regulation. For the first time, 2, 3, 7, 8 - brominated dioxins and furans are restricted now as well; 8 PBDC/PBCF-.

Congeners were added to the list of the regulation. This was the result of an approximation process to the scientific progress concerning the appearance, environmental fate, toxicity and analytical methodology of these substances.

In December 1992, the European Commission granted Germany an exception under Article 100 (A) (4) of the treaty from EU-legislation issued in 1991 restricting the marketing and use of substances and preparations containing PCP and its compounds (Council Directive 91/173 EEC amending for the ninth time Directive 76/769/EEC). This consent was necessary because the German legislation imposed, differing from the EU-directive, wider restrictions and lower concentrations limits of PCP. After an action of France against the consent, in May 1994 the European Court of Justice annulled the decision by the Commission on the grounds that no adequate reasons had been given for it and thereby Article 190 of the treaty had been violated. In September 1994, the Commission pronounced a new decision and confirmed the German legislation again.

The Commission verifies now the possibility to propose a total ban of PCP for the EU. In this connection one can expect in a near future some new unexpected steps in this direction. It doesn't necessarily mean the total ban of halogenated flame retardants in the next 5 - 10 years. But it actually means a complete reconsideration in a direction of polymers' flame retardancy development. It is obviously, the new efforts will be directed on the ecologically-friendly flame retardant systems. This review is devoted to some new directions in this area.

The main flame retardant systems for polymers currently in use are based on halogenated, phosphorous, nitrogen, and inorganic compounds (Figure 1). All of these flame retardant systems basically inhibit or even suppress the combustion process by chemical or physical action in the gas or condensed phase. To be effective, the flame retardants must decompose near the decomposition temperature of the polymer in order to do the appropriate chemistry as the polymer decomposes, yet be stable at processing temperatures.

Conventional flame retardants, such as halogenated, phosphorous or metallic additives have a number of negative attributes. An ecological issue of its application demands the search of new polymer flame retardant systems. Among the new trends of flame retardancy it can be noticed the use of intumescent systems, polymer nanocomposites, preceramic additives, low-melting glasses, different types of char-formers and polymer morphology modification [1]. However, it should be assumed the close interactions between the different flame retardant types in order to achieve a synergistic behavior. The block scheme of polymer flame retardant systems is given on Figure 1.

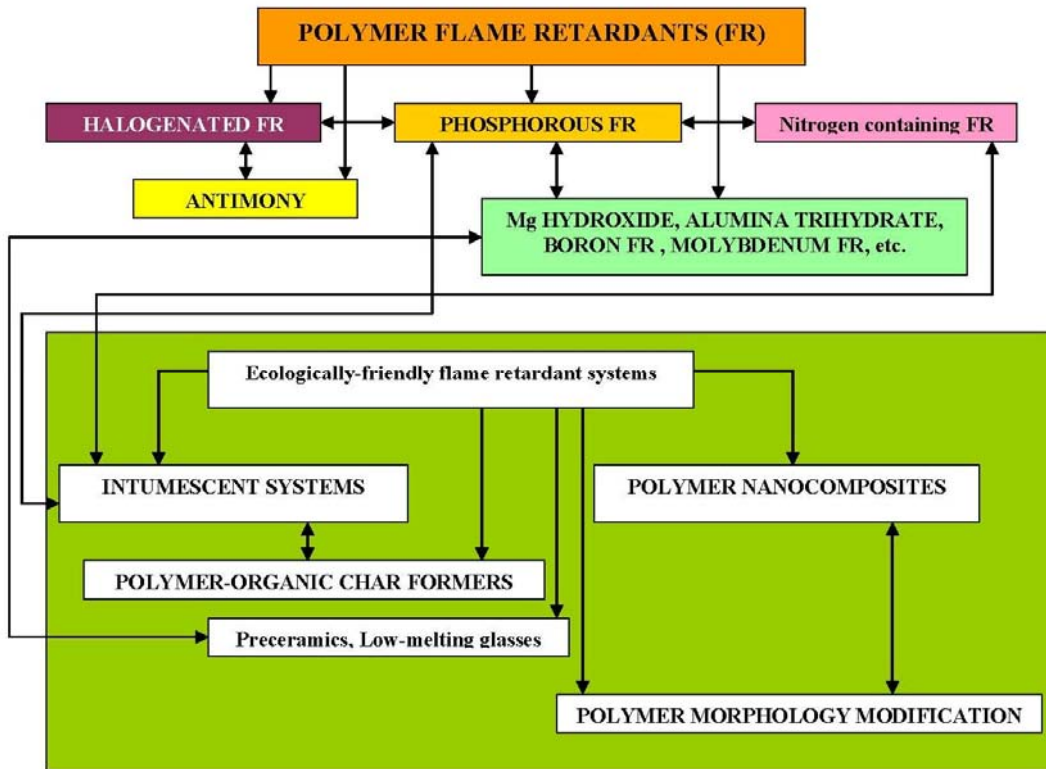
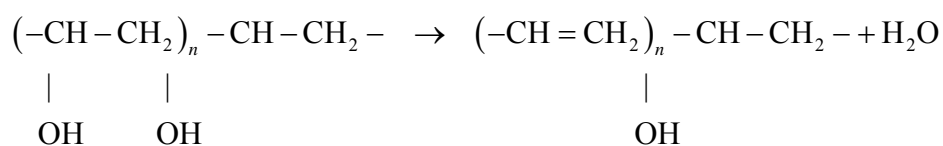


Figure 1. Block-scheme of polymer flame retardant systems

## 2. Organic Char Former

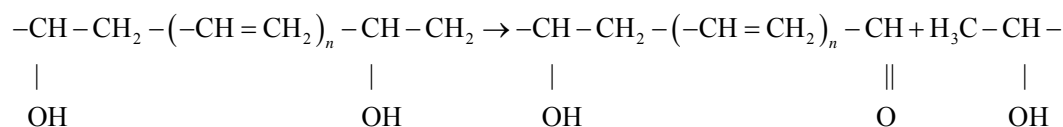
The study of new polymer flame retardants has been directed at finding ways to increase the tendency of plastics to char when they are burned [2, 3]. There is a strong correlation between char yield and fire resistance. This follows because char is formed at the expense of combustible gases and because the presence of a char inhibits further flame spread by acting as a thermal barrier around the unburned material. The tendency of a polymer to char can be increased with chemical additives and by altering its molecular structure. It has been studied polymeric additives (polyvinyl alcohol systems) which promote the formation of char [4-6]. These polymeric additives usually produce a highly conjugated system - aromatic structures which char during thermal degradation and/or transform into cross-linking agents at high temperatures.

Decomposition of PVA goes in two stages. The first stage, which begins at 200°C, mainly involves dehydration accompanied by formation of 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 PVA has been deduced by Tsuchya and Sumi [7]. At 245°C water is split off the polymer chain, and a residue with conjugated polyene structure results:



Scission of several carbon-carbon bonds leads to the formation of carbonyl ends. For example,

aldehyde ends arise from the reaction: In the second-stage pyrolysis of PVA, the volatile products consist mainly of hydrocarbons, i.e.



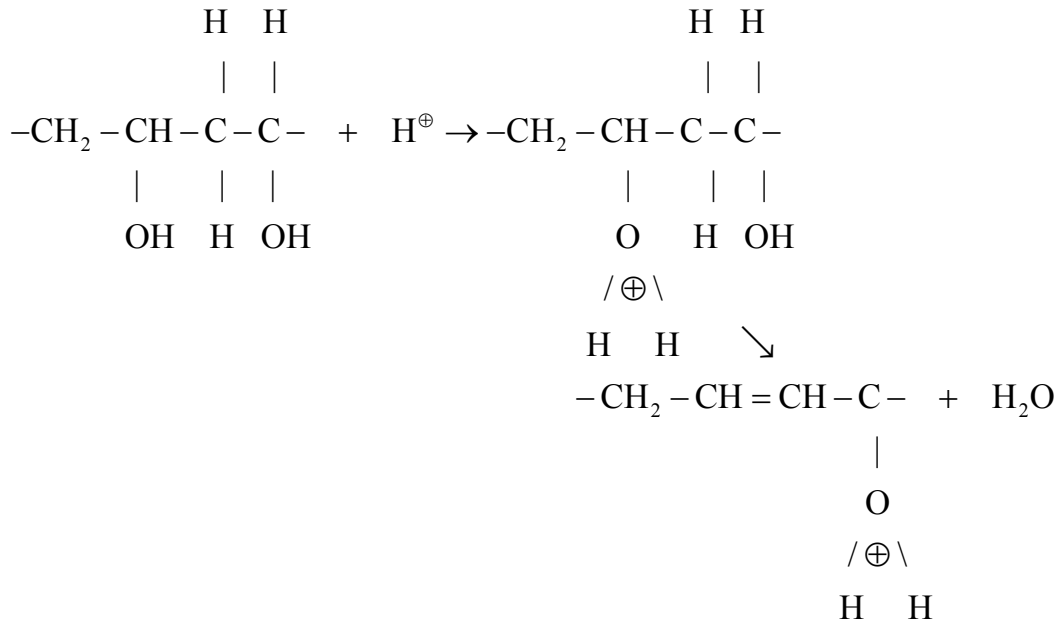
In the second-stage pyrolysis of PVA, the volatile products consist mainly of hydrocarbons, i.e. *n*-alkanes, *n*-alkenes and aromatic hydrocarbons (Table 1) [7]. Thermal degradation of PVA in the presence of oxygen can be adequately described by a two-stage decomposition scheme, with one modification. Oxidation of the 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 a conjugated unsaturated ketone structure [8]. The first-stage degradation products of PVA pyrolyzed in air are fairly similar to those obtained in vacuum pyrolysis. In the range 260°-280°C, the second-order-reaction expression satisfactorily accounts for the degradation of 80% hydrolyzed PVA up to a total weight loss of 40%. The activation energy of decomposition appears to be consistent with the value of 53.6 kcal/mol, which is obtained from the thermal degradation of PVA [8].

Changes in the IR spectra of PVA subjected to heat treatment have been reported [8]. After heating at 180°C in air, bands appeared at 1630 cm<sup>-1</sup> (C=C stretching in isolated double bonds), 1650 cm<sup>-1</sup> (C=C stretching in conjugated dienes and trienes), and 1590 cm<sup>-1</sup> (C=C stretching in polyenes). The intensity of carbonyl stretching frequency at 1750 - 1720 cm<sup>-1</sup> increased, although the rate of increase of intensity was less than that of the polyene band at low temperatures. Above 180°C, although dehydration was the predominant reaction at first, the rate of oxidation increased after an initial induction period. The identification of a low concentration of benzene among the volatile products of PVA has been taken to indicate the onset of a crosslinking reaction proceeding by a Diels-Alder addition mechanism [8]. Clearly, benzenoid structures are ultimately formed in the solid residue, and the IR spectrum of the residue also indicated the development of aromatic structures [8].

<b>Products</b>	<b>Weight % of original polymer</b>
Water	33.4
CO	0.12
CO <sub>2</sub>	0.18
Hydrocarbons (C <sub>1</sub> - C <sub>2</sub> )	0.01
Acetaldehyde	1.17
Acetone	0.38
Ethanol	0.29
Benzene	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	0.02
Unidentified	0.082

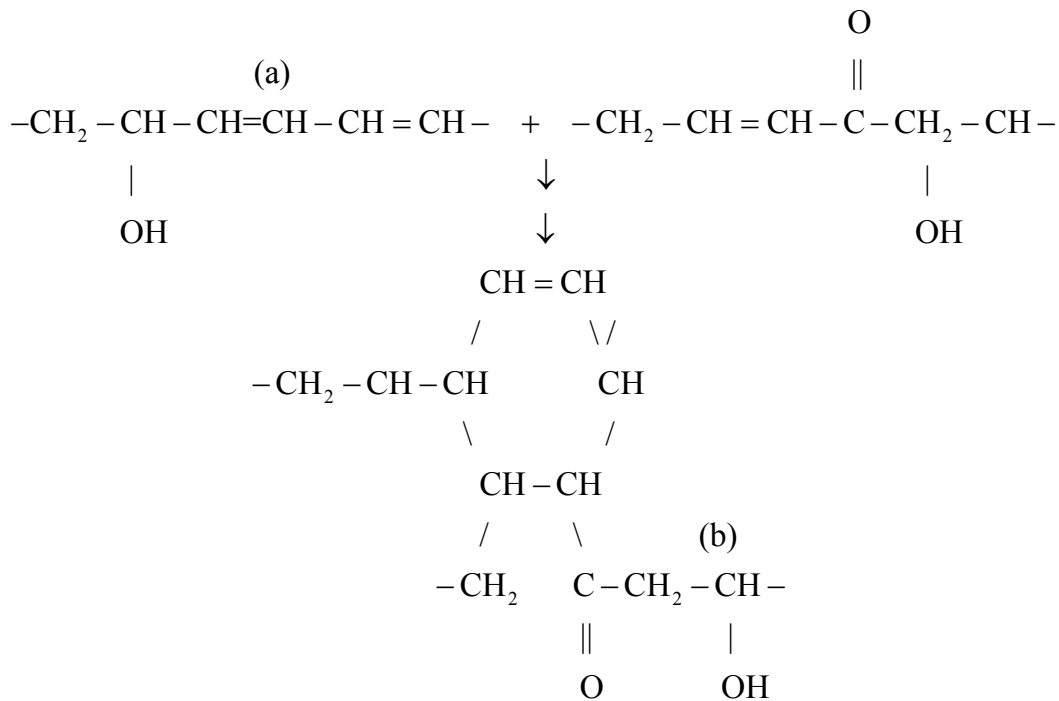
Table 1. Thermal decomposition products (240°C, 4 h.) [7].

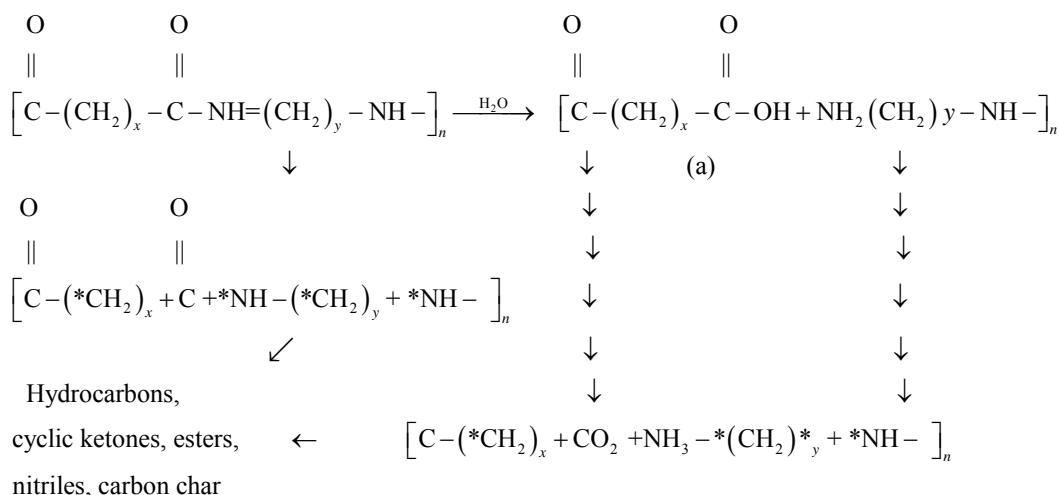
Acid-catalyzed dehydration promotes the formation of conjugated sequences of double bonds (a) and Diels-Alder addition of conjugated and isolated double bonds in different chains may result in intermolecular crosslinking producing structures which form graphite or carbonization (b).



In contrast to PVA, it was

found [9-11] 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<sub>2</sub> and NH<sub>3</sub> suggested that the degradation mechanism must have been highly complex. Further research has led to a generally accepted degradation mechanism for aliphatic polyamides [12]:

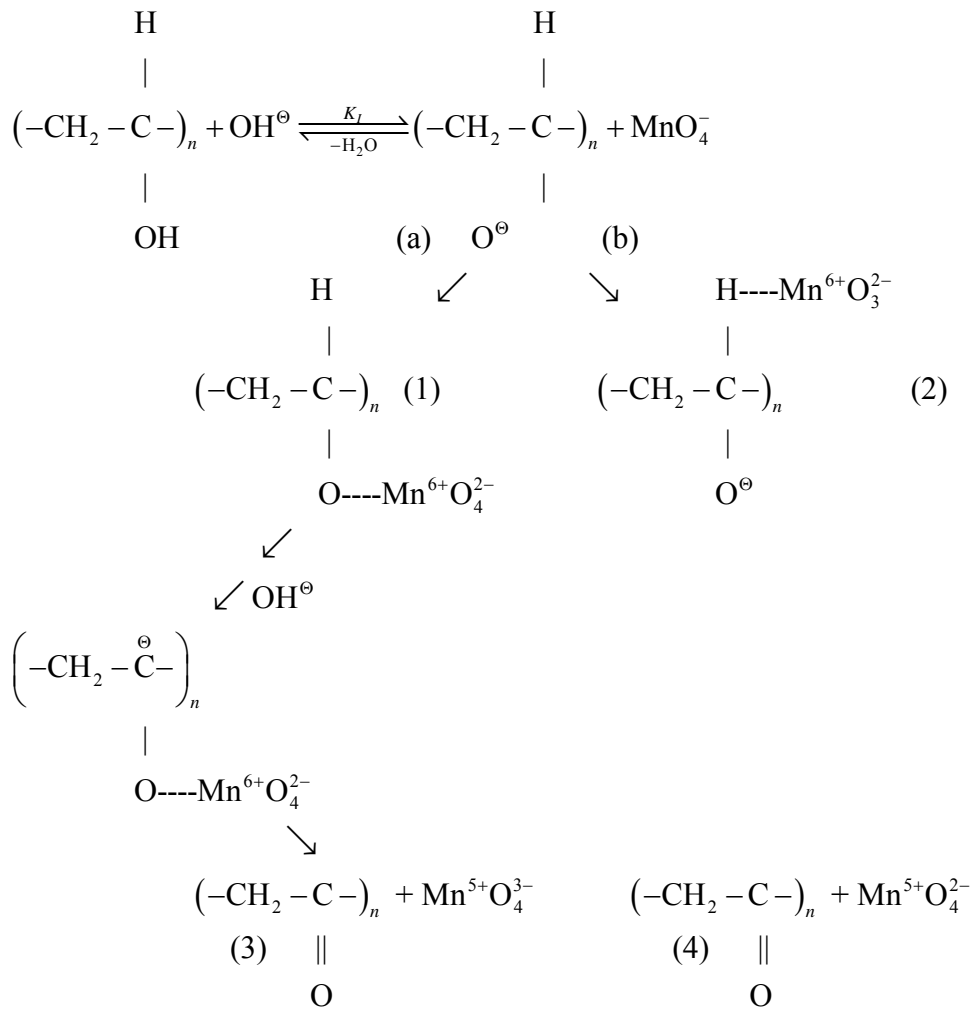




1. Hydrolysis of the amide bond usually occurred below the decomposition temperature;
2. Homolytic cleavage of C-C, C-N, C-H bonds generally began at the decomposition temperature and occurred simultaneously with hydrolysis;
3. Cyclization and homolytic cleavage of products from both of the above reactions occurred;
4. Secondary reactions produced CO, NH<sub>3</sub>, nitriles, hydrocarbons, and carbon chars.

An idea of introducing poly(vinyl alcohol) into nylon-6,6 composition was based on the possibility of high-temperature acid-catalyzed dehydration. This reaction can be provided by the acid products of nylon 6,6 degradation hydrolysis which would promote the formation of intermolecular crosslinking and char. Such a system we have called "synergetic carbonization", because the char yield and flame suppression parameters of the polymer blend of poly (vinyl alcohol) and nylon 6,6 are significantly better than that of pure poly(vinyl alcohol) and nylon-6,6 polymers.

It is well-known that nylons have poor compatibility with other polymers because of their strong hydrogen bonding characteristics. The compatibility of nylon-6 with poly(vinyl-acetate) (PVAc) and poly(vinyl alcohol) (PVA) has been studied [13]. Compatibility was judged from the melting temperature depression. The results indicate that nylon-6/polyvinyl alcohol blends are partially compatible. "Compatibility" in this work does not mean thermodynamic miscibility but rather ease of mixing blends to achieve small size domains. To improve the flame resistant properties of the poly(vinyl alcohol) - nylon-6,6 system the substitution of pure poly(vinyl alcohol) by poly(vinyl alcohol) oxidized by potassium permanganate (PVA-ox) has been offered.. This approach was based on the fire behavior of the (PVA-ox) itself. It was shown experimentally using a cone calorimeter that there was a dramatic decrease of the rate of heat release and significant increase in ignition time for the oxidized PVA in comparison with the original PVA. The literature on the oxidation of macromolecules by alkaline permanganate presents little information about these redox-systems. One set of workers [14, 15] investigated the oxidation of PVA as a polymer containing secondary alcoholic groups by KMnO<sub>4</sub> in alkaline solution. It was reported that the oxidation of PVA by permanganate in alkaline solutions occurs through formation of two intermediate complexes (1) and/or (2) [16]:

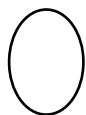


The reactions (a) and (b) lead to the formation of poly(vinyl ketone) (3) as a final product of oxidation of the substrate. Poly(vinyl ketone) was isolated and identified by microanalysis and spectral data [17].

Preliminary cone calorimeter tests for PVA and PVA oxidized by  $\text{KMnO}_4$  were carried out at heat fluxes of 20, 35 and 50  $\text{kW/m}^2$  (Table 2) [18-20]. The carbon residue (wt. %) and peak of heat release rate (Peak R.H.R.  $\text{kW/m}^2$ ) suggest substantial improvement of fire resistance characteristics for PVA oxidized by  $\text{KMnO}_4$  in comparison with PVA. PVA oxidized by  $\text{KMnO}_4$  gives about half the peak of heat release rate (Peak R.H.R.  $\text{kW/m}^2$ ), when compared with pure PVA. Even at 50  $\text{kW/m}^2$ , the yield of char residue for PVA oxidized by  $\text{KMnO}_4$  was 9.1%. One reason for this phenomenon may be the ability for PVA oxidized by  $\text{KMnO}_4$  (polyvinyl ketone structures) to act as a neutral (structure 1) and/or monobasic (structure 2) bidentate ligand [21].

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### **Bibliography and Suggestions for further study**

1. Lomakin S.M., Zaikov G.E., *Ecological Aspects of Flame Retardancy*, V S P International Science Publishers, Zeist Holland, pp. 170, (1999).
2. Lomakin S.M., Brown J.E., Breese R.S. and Nyden M.R., *Polymer Degrad. And Stab.* **41**, 229-243 (1993).
3. Factor A., Char Formation in Aromatic Engineering Polymers, in *Fire and Polymers*, Ed. Nelson G.L. (Ed.), pp. 274-287, ACS Symposium Series 425, ASC, Washington DC (1990).
4. Lomakin S.M., Zaikov G.E. and Artsis M.I., *Intern. J. Polym. Mater.* **32** (1-4) 173-202 (1996).
5. Lomakin S.M., Zaikov G.E., Artsis M.I., Ruban L.V. and Aseeva R.M., *Oxidation Comm.* **18** (2), 105-112 (1995).
6. Lomakin S.M., Zaikov G.E. and Artsis M.I., *Intern. J. Polym. Mater.* **26** (3-4), 187-194 (1994).
7. Tsuchiya Y. and Sumi K., *J. Polym. Sci., A-1* **7**, p. 3151 (1969).
8. Finch, C.A. (Ed.), *Polyvinyl Alcohol. Properties and Applications*, p.622, John Wiley London (1973).
9. Achhammer B.G., Reinhard F.W. and Kline G.M., *J. Appl. Chem.* **1**, 301 (1951).
10. Goodman I., *J. Polym. Sci.* **13**, 175 (1954).
11. Conley, R.T.(Ed.) *Thermal Stability of Polymers*. Vol.1, p. 350, Marcel Dekk., New York, (1970).
12. Grassie N. and Scott G., *Polymer Degradation and Stabilization*, Cambridge University Press, Cambridge (1985).
13. Chang-Sik Ha, Won-Ki Lee, Tae-Woo Roe and Won-Jei Cho, *Polymer Bulletin* **31**, 359 (1993).
14. Hassan R.M., *Polym. Intern.* **30**, 5 (1993).
15. Hassan R.M., El-Gaiar S.A. and El-Summan A.M., *Polym. Intern.* **32**, 39 (1993).
16. Hassan R.M., Abd-Alla M.A. and El-Gahmi M.A., *J. Mater.Chem.* **2**, 613 (1992).
17. Zaikov G.E. and Lomakin S.M., *Plasticheskie Massy* **39**, 211 (1996).
18. Zaikov G.E. and Lomakin S.M., *Polym. Degrad. And Stab.* **51**, 359 (1997).
19. Lomakin S.M. and Zaikov G.E., *Khimicheskaya Fizika* **14** (10), 39-47 (1995).
20. Zaikov G.E. and Lomakin S.M., *Intern. J. Polym. Mater.* **31**, 119-129 (1996).
21. Lomakin S.M. and Zaikov G.E., *Polym. Degrad. And Stab.* **41**, 229-243 (1996).
22. Zaikov G.E. and Lomakin S.M., ACS Symposium Series, Vol. 559: *Fire and Materials*, p.186, Washington, DC (1995).
23. Zaikov G.E. and Lomakin S.M., *Intern. J. Polym. Mater.* **38**, 321-328 (1997).
24. Kashiwagi T., *Fire Calorimetry*, Proceedings of a special Symposium on Fire Calorimetry, Report no. DOT/FAA/CT-95/46, 1995, p. 48.
25. Buch R.R., *Fire Calorimetry*, Proceedings of a special Symposium on Fire Calorimetry, Report no. DOT/FAA/CT-95/46, 1995, p. 154.
26. Lomakin S.M., Zaikov G.E. and Artsis M.I., *Intern. J. Polym. Mater.* **32**, 354-368 (1996).
27. Lomakin S.M., Zaikov G.E. and Artsis M.I., *Intern. J. Polym. Mater.* **32** (1-4), 213-220 (1996).
28. Voorhoeve R. J. H. *Organohalosilanes Precursors to Silicones*, pp. 122-132. Elsevier, Amsterdam (1967).

29. Sax N. I. and Lewis R. J., *Dangerous Properties of Industrial Materials*, 7-th edn., Van Nostrand Reinhold, New York (1989).
30. Lyons J. W., *The Chemistry and Uses of Fire Retardants*, pp. 15-16, Wiley-Interscience, New York (1970).
31. McHale E. T., *Survey of Vapor Phase Chemical Agents for Combustion Suppression*, Fire Research Abstracts and Reviews, Vol.11, pp. 90-104 (1969).
32. Morrison M. E. and Scheller K., *Comb. and Flame* **18**, 3-12 (1974).
33. Ebsworth E. A. V., *Volatile Silicon Compounds*, pp. 336-337. Academic Press, New York (1975).
34. Rochow E. G. in *Comprehensive Inorganic Chemistry*, Vol.11. Pergamon Press, New York (1973).
35. Zaikov G.E. and Lomakin S.M., *Polym. Degrad. and Stab.* **54** (2-3), 223 (1996).
36. Kroenke W.J., *J. Mater. Sci.* **21**, 1123 (1986).
37. Gilman J.W., Ritchie S.J, Kashiwagi T. and Lomakin S.M., *Fire and Mat.* **21**, 233 (1997).
38. Gilman J.W., Lomakin S.M., Kashiwagi T., VanderHart D.L. and Nagy V., *ACS Polymer Preprints* **38**, 802 (1997).
39. Scung K.P., Mantheimer-Timnat Y., Yaccarino P and Glassman I., *Combustion Sci. Technol.* **22**, 235 (1980).
40. Laine R.M., *Nature* **353**, 642 (1991).
41. Compton G., British patent; 2,203, 157 (1988).
42. Weil E.D. and Navin P., *Proceedings of the ADDITIVES' 95 International Conference* (1995).
43. Anderson Jr., C. E., Dziuk Jr., J., Mallow W. A., Buckmaster J. *J. Fire Sci.* 1985, 3, 151.
44. Tramm H., Clar C., Kuhnel, P., Schuff W. U. S. Pat. 1938; 2106938.
45. Kay M., Price A. F., Lavery, I. *J. Fire Retard. Chem.* 1979, 6, 69.
46. Camino G., Costa L., Trossarelli L. *Polym. Deg. Sta.* 1984, 7, 25.
47. Camino G., Martinasso G., Costa L., Cobetto R. *Polym. Deg. Sta.* 1990, 28, 17.
48. Levchik S. V., Costa L., Camino G. *Polym. Deg. Sta.* 1992, 36, 31.
49. Cagliostro D. E., Riccitiello S. R., Clark K. J., Shimizu A. B. *J. Fire Flam.* 1975, 6, 205.
50. Delobel R., Le Bras M., Quassou N., Alistigsa F. *J. Fire Sci.* 1990, 8, 85.
51. Delobel R., Le Bras, M., Quassou N., Descressain R. *Polym. Deg. Sta.* 1990, 30, 41.
52. Heinrich H. Deutsch. Pat. 1991; DE4015490A1.
53. Rychly J., Matisova-Rychla L., Vavrekova M., *J. Fire Retard. Chem.* 1981, 8, 82.
54. Cullis C. F., Hirschler M. M., Khattab M. A. A. M. *Eur. Polym. J.* 1992, 145
55. Vandersall, H. L., *J. Fire & Flamm.* 2:97-140 (1971).
56. Cagliostro, D. E., Riccitiello, S. R., Clark, K. J. and Shimizu, A. B., *J. Fire & Flamm.* 6:205-220 (1975).
57. Butler K.M., Baum H.R., Kashiwagi T., International Association for Fire Safety Science. Fire Safety Science. Proceedings. Fifth International Symposium. March 3-7, 1997, Melbourne, Australia, Intl. Assoc. for Fire Safety Science, Boston, MA, Hasemi, Y., Ed., 523-534 p, (1997).
58. White T.E.K., Gasiewicz T.A., *Biochem. Biophys. Res. Comm.* **193**, 956-962 (1993).
59. Anderson, C., Ketchum, D. E. and Mountain, W. P., *J. Fire Sciences* 6:390-410 (1988).
60. Williams, M. L., Landel, R. F. and Ferry, J. D., *J. Am. Chem. Soc.* 77:3701 (1955).
61. Anderson, C. E., Dziuk, J., Mallow, W. A. and Buckmaster, J., *J. Fire Sci.* 3:161-194 (1985).

62. Aseeva R.M., Zaikov G.E., "Combustion of polymer materials", Munchen, Karl Hanser Verlag, 1986, 389 pp.
63. Levchik S.V., Camino G., Costa L. and Levchik G.F., *Fire and Mater.* **19**, 1-8 (1995).
64. Levchik S.V., Levchik G.F., Balabanovich A.I., Camino G., Costa L., *Polymer Degrad. And Stab.* **54**, 205-215 (1996).
65. Levchik S.V., Costa L., Camino G., *Polymer Degrad. And Stab.* **36**, 229 (1992).
66. Levchik S.V., Levchik G.F., Selevich A.F., Leshnikovich A.I., *Vesti AN Belarusi, Ser. Khim.* **3**, 34-39 (1995).
67. Williams I.G., *Plastics Rubber Process. Application* **4**, 239 (1984).
68. Levchik S.V., Levchik G.F., Selevich A.F., Leshnikovich A.I., *Thermochim. Acta* **39**, 41 (1994).
69. Levchik S.V., Levchik G.F., Camino G., Costa L., *J. Fire Sci.* **13**, 43 (1995).
70. U.S. Environmental Protection Agency, *Interim procedures for estimating risks associated with exposures to mixtures of chlorinated dibenzo-p-dioxins and dibenzofurans (CDDs and CDFs) and 1989 update*. Risk Assessment Forum, EPA/625/3-89/016. PB90-145756. National Technical Information Service, Springfield, VA (1989).
71. Levchik S.V., Balabanovich A.I., Levchik G.F., Camino G., Costa L., *Polymer Degrad. And Stab.*, 1998, in press.
72. G. Camino, G. Martinasso, L. Costa, *Polym. Degrad. Stab.*, 27:285-296, 1990.
73. H.E. Baumgarten, R.A. Setterquis L., *J. Am. Chem. Soc.*, 79:2605-2608, 1957.
74. A.E. Canavan, B.F. Dowden, C. Eaborn. *J. Chem. Soc.* 331-334, 1962.
75. C.E. Higgins, V.M. Baldwin, *J. Org. Chem.*, 30:3173-3176, 1965.
76. K.D. Berlin, J.G. Morgan, M.E. Peterson, W.C. Pivonka., *J. Org. Chem.*, 34:1266 - 1271, 1969.
77. P. Haake, C.E. Diebert. *J. Am. Chem. Soc.* 93:6931-6937, 1971.
78. V. Lhomme, C. Bruncau, N. Soyer, A. Brault. *Ind. Eng. Chem. Prod. Res. Dev.* 23:98 -102, 1994.
79. J. Rychly, L.M. Rychla, M. Vavrekova., *J. Fire Retard. Chem* 8: 82-92, 1981.
80. Modern Plastics, *Encyclopedia-2000*, pp.62-c71
81. T. Kashiwagi, J. W. Gilman, Silicon-Based Flame Retardants, In: *Fire Retardancy of Polymeric Materials*. Ed. By A.F. Grand, C.A. Wilkie, Marcel Dekker, Inc., New York, p.353-389, (2000).
82. J.W. Gilman, T. Kashiwagi, R.H. Hams Jr, S. Lomakin, ID Lichtenhan, P Jones, A Bolf. In: S Al-Malaika, C Wilkie, CA Golovoy, eds. *Chemistry and Technology of Polymer Additives*. London: Blackwell Science, 1999, pp. 135-150, (1999)
83. W Kowbel, R Viadyanathan, JR Patel, JC Withers. *Proceedings of 43-rd International SAMPE Symposium, Anaheim, 1998*, pp. 1018 -1028.
84. T.C. Chao, SK Sarmah, RP Boisvert, GT Burns, DE Katsoulis, WC Page. *Proceedings of 43-rd International SAMPE Symposium, Anaheim, 1998*, pp. 1029-1041.
85. R.P. Kambour, W.V. Ligon, R.P. Russell. *J. Polym Sci Polym Lett Ed* 16, 327-333, (1978).
86. RP Kambour. *J Appl Polym Sci* 26, 861-877, (1981).
87. D.W. Van Krevelen. *Polymer* 16:615-620, (1975).
88. D.R. Olson. *Proceeding of the Fifteenth International Conference on Fire Safety, 1990*, pp. 328-336. (1990).
89. R. Gardiner, R Buch, D Romenesko. In: *INTERFLAM 93*. London: Interscience Communications, pp. 675-687, (1993).
90. M.R. MacLaury, A.L. Schroll. *J Appl Polym Sci* 30:461-472, (1985).

91. P.K. Huester. *J Cell Plastic* 10:186-193, July/August, (1974).
92. B Prokai, PK Huester, B Kanner. In: VM Bhamagar, ed., *Proceedings of 1975 International Symposium on Flammability and Fire Resistance*. Technomic Publication, Westport, Conn., pp. 264-281, (1975)
93. M. Iji, S Serizawa. *Poym Adv Technol*,9,593-600, (1998).
94. G. Camino,, S.M. Lomakin, M. Lazzari, *Polymer*, 42, p. 2395–2402, (2001).
95. G. Camino,, S.M. Lomakin, M. Lageard, *Polymer*, 43, p. 2011–2015, (2002).
96. Lewis R.N., *J. Am. Chem. Soc.*, 1948, 70, 1115.
97. Andrianov K.A., *Visokomolec. Soed.*, 1971, A14, 253
98. Thomas T.H., Kendrick T.C., *J. Pol. Sci.*, 1969, 7, 537
99. Grassie N., MacFarlane J., *Eur. Pol. J.*, 1978, 14, 875
100. Kissinger H.E., *Anal Chem.*, 1959, 29, 1702
101. Ismail I.M.K., Rodgers S.L., *Carbon*, 1992, 30, 229
102. Osthoff R.C., Grubb W.T., Burkhard C.A., *Physical Properties of Organosilicon Compounds. I. Hexamethylcyclotrisiloxane and Octamethylcyclotetrasiloxane*, *J. Am. Chem. Soc.*, 1953, 75, 2227-2229
103. Farneth W.E., Herron N. and Wang Y., *Chem. Mater.*, 1992, 4, 916
104. Bunker D.L. Simple kinetic models from Arrhenius to the computer, *Accts.Chem. Res.* 1974, 7, 195
105. Korshak V.V., *The Chemical Structure and Thermal Characteristics of Polymers*, Keter Press, Jerusalem, 1971, 460 p.
106. Zhang, H.; Pantano, C. G. *J. Am. Ceram. Soc.* 1990, 73, 958; *Mater. Res. Soc. Symp. Proc.*, 1992, 271, 783.
107. Renlund, G. M. French Patent 2,647,777, 1990.
108. Burns, G. T.; Taylor, R. B.; Xu, Y.; Zangvil, A.; Zank, G. A. *Chem. Mater.* 1992, 4, 13.
109. Hurwitz, F. I.; Farmer, S. C.; Terepka, F. M. *J. Mater. Sci.* 1991, 26, 1247.
110. Kasemann, R.; Schmidt, H.; Wintrich, E. *Mater. Res. Soc. Symp. Proc.* 1994, 346, 915.
111. Shi, W. Ph.D. Thesis, Rensselaer Polytechnic Institute, 1995.
112. Renlund, G. M.; Prochazka, S.; Doremus, R. H. *J. Mater. Res.* 1991, 6, 2716; 1991, 6, 2723.
113. Birot, M.; Pillot, J.-P.; Dunogue's, *J. Chem. Rev.* 1995, 95, 1443-1477.
114. Laine, R. M.; Babonneau, F. *Chem. Mater.* 1993, 5, 260-279.
115. White, D. G.; Oleff, S. M.; Boyer, R. D.; Budinger, P. A.; Fox, J. R. *Adv. Ceram. Mater.* 1987, 2, 45.
116. Babonneau, F.; Bois, L.; Yang, C.-Y.; Interrante, L. V. *Chem.Mater.* 1994, 6, 51.
117. Babonneau, F. In *Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic Publishers: The Netherlands, 1995; p 103.
118. Belot, V.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Mater. Sci. Lett.* 1990, 9, 1052; *J Polym. Sci. Part A: Polym. Chem.* 1992, 30, 613.
119. Babonneau, F.; Soraru, G. D.; D'Andrea, G.; Dire, S.; Bois, L. *Mater. Res. Soc. Symp. Proc.* 1992, 271, 789.
120. Corriu, R. J. P.; Mutin, P. H.; Vioux, A. *J. Mater. Sci.* 1995, 30, 2313-2318.

121. Whitmarsh, C. W.; Interrante, L. V. U.S. Patent 5,153,295, 1992.
122. Whitmarsh, C. K.; Interrante, L. V. *Organometallics* 1991, 10, 1336.
123. Yang, C.-Y.; Marchetti, P.; Interrante, L. V. *ACS Polym. Prepr.* 1992, 33, 208.
124. Shen, Q.; Interrante, L. V. Preprints of 35th IUPAC International Symposium on Macromolecules, Akron, 1994; p 345; *Polym. Prepr.* 1995, 36, 378.
125. Wu, H.-J.; Interrante, L. V. *Chem. Mater.* 1989, 1, 564; *Macromolecules* 1992, 25, 1840.
126. Q. Liu, W. Shi, F. Babonneau, L. V. Interrante, *Chem. Mater.* 1997, 9, 2434-2441.
127. Burns, G. T.; Taylor, R. B.; Xu, Y.; Zangvil, A.; Zank, G. A. *Chem. Mater.* 1992, 4, 1313.
128. J. Wen and J. E. Mark, Precipitation of silica-titania mixed-oxide fillers into poly(dimethylsiloxane) networks, *Rubber Chem. & Tech.*, **67**, 806-819 (1994).
129. Z. Pu, J. E. Mark, J. M. Jethmalani, and W.T. Ford, Mechanical properties of a poly(methyl acrylate) nanocomposite containing regularly-arranged silica particles, *Polymer Bulletin*, **37**, 545-551 (1996).
130. W. Helbert, J. Y. Cavaille, and A. Dufresne, Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: Processing and Mechanical Behaviour, *Polymer Composites*, **17**, 604-611 (1996).
131. P. Hajji, J. Y. Cavaille, V. Favier, C. Gauthier, and G. Vigier, Tensile behaviour of nanocomposites from latex and cellulose whiskers, *Polymer Composites*, **17**, 612-619 (1996).
132. H. L. Frisch and E. J. Mark, Nanocomposites prepared by threading polymer chains through zeolites, mesoporous silica, or silica nanotubes, *Chem. Mater.*, **8**, 1735-1738 (1996).
133. E. Ruckenstein and Y. Yuan, Nanocomposites of rigid polyamide dispersed in flexible vinyl polymer, *Polymer*, **38**, 3855-3860 (1997).
134. Y. Godovski, Electron behaviour and magnetic properties of polymer nanocomposites, *Thermal and Electrical Conductivity of Polymer Materials (Germany)*, Springer-Verlag, Heidelberg, p 79-122 (1995).
135. B. K. G. Theng, *Formation and properties of clay-polymer complexes*, Elsevier, Amsterdam, p 133 (1979).
136. A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, and O. Kamigaito, Nylon 6-clay hybrid, *Mater. Res. Soc. Proc.*, **171**, 45-50 (1990).
137. K. G. Theng. *Formation and properties of clay-polymer complexes*. Elsevier, Amsterdam, 1979.
138. B. K. G. Theng. *Chemistry of clay-organic reactions*. Wiley, New York, 1974.
139. K. Strawhecker and E. Manias. *Chem. Mater.*, 12:2943-2949, 2000.
140. R.A. Vaia, S. Vasudevan, W. Krawiec, L.G. Scanlon, and E.P. Giannelis. *Adv. Mater.*, 7:154, 1995.
141. E.P. Giannelis, R.K. Krishnamoorti, and E. Manias. *Advances in Polymer Science*, 138:107-148, 1998.
142. M. Alexandre and P. Dubois. *Mat. Sci. & Eng. R: Reports*, 28:1, 2000.
143. W. E. Worall, *Clays: their nature, origin and general properties*, MacLaren & sons, London (1968).
144. H. Van Olphen, *An introduction to clay colloids chemistry*, Wiley, New York (1977).
145. E. Busenberg and C. V. Clemency, Determination of the cation-exchange capacity of clays and soil using ammonia electrode, *Clays and clay minerals*, **21**, 213-215 (1973).
146. M. M. Mortland and J. L. Mellor, Conductometric titration of soils for cation-exchange capacity, *Soil Sci. Soc. Proc.*, **18**, 363-364 (1954).
147. J. L. McAtee, Inorganic-organic cation-exchange on montmorillonite, *Am. Miner.*, **44**, 1230-1236,

- (1959).
148. J. W. Jordan, Organophilic bentonites, *J. Phys. Colloid Chem.*, **53**, 294-306 (1949).
  149. A. Weiss, Organic derivatives of mica-type layer silicates, *Angew. Chem. internat. Edit.*, **2**, 134-143 (1963).
  150. T. Lan, P. D. Kaviratna, and T. J. Pinnavaia, Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites, *Chem. Mater.*, **7**, 2144-2150 (1995).
  151. Z. Wang and T. J. Pinnavaia, Hybrid organic-inorganic nanocomposites: exfoliation of magadiite nanolayers in an elastomeric epoxy polymer, *Chem. Mater.*, **10**, 1820-1826 (1998).
  152. G. Lagaly, Interaction of alkylamines with different types of layered compounds, *Solid State Ionics*, **22**, 43-51 (1986).
  153. R. A. Vaia and E. P. Giannelis. *Macromolecules*, 30:7990–7999, 1997.
  154. R. A. Vaia and E. P. Giannelis. *Macromolecules*, 30:8000–8009, 1997.
  155. A.C. Balazs, C. Singh, and E. Zhulina. *Macromolecules*, 31:8370–8381, 1998.
  156. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigato, *J. Mater. Res.*, **8**, 1993, p. 1185.
  157. R. A. Vaia, H. Ishii, and E. P. Giannelis, Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates, *Chem. Mater.*, **5**, 1694-1696 (1993).
  158. R. A. Vaia, K. D. Jandt, E. J. Kramer, and E. P. Giannelis, Kinetics of polymer melt intercalation, *Macromolecules*, **28**, 8080-8085 (1995).
  159. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, O. Kamigaito, and K. Kaji, Fine structure of nylon 6-clay hybrid, *J. Poly. Sci.: Part B*, **32**, 625-630 (1994).
  160. L. Liu, Z. Qi, and X. Zhu, Studies on nylon 6/clay nanocomposites by melt-intercalation process, *J. Appl. Polym. Sci.*, **71**, 1133-1138 (1999).
  161. R. A. Vaia, K. D. Jandt, E. J. Kramer, and E. P. Giannelis, Microstructural evolution of melt intercalated polymer-organically modified layered silicates nanocomposites, *Chem. Mater.*, **8**, 2628- 2635 (1996).
  162. M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, and A. Okada, Preparation and mechanical properties of polypropylene-clay hybrids, *Macromolecules*, **30**, 6333-6338 (1997).
  163. R.A. Vaia, Ishii H., and Giannelis E.P. *Chem. Mater.*, 5:1694–1696, 1993.
  164. T. Lan, P.D. Kaviratna, and T.J. Pinnavaia. *Chem. Mater.*, 7:2144, 1995., M.S. Wang, T.J. Pinnavaia, *Chem. Mater.* 6: 2216, 1994., T.J. Pinnavaia, *Science* 220: 365, 1983.
  165. E.P. Giannelis *et al.* (a) *Chem. Mater.*, 8:1728, 1996. (b) *Adv. Mater.* 8: 29, 1996; (c) *J. Pol. Sci. B*: 38: 1595, 2000.
  166. R.A. Vaia, H. Ishii, and E.P. Giannelis. *Chem. Mater.*, 5:1694, 1993., R.A. Vaia, K.D. Jandt, E.J. Kramer, E.P. Giannelis, *Macromolec.* 28:8080, 1995., R.A. Vaia, G. Price, P.N. Ruth, H.T. Nguyen, J. Lichtenhan, *Appl. Clay Sci.* 15:67, 1999.
  167. M.G. Kanatzidis, C.-G. Wu, H.O. Marcy, D.C. DeGroot, and C.R. Kannewurf. *Chem. Mater.*, 2:222, 1990. (b) *ibid.* 3: 992, 1991. (c) *ibid.* 8: 525, 1996.
  168. J.W. Gilman, C.L. Jackson, A.B. Morgan, R. Harris, E. Manias, E.P. Giannelis, M. Wuthenow, D. Hilton, and S.H. Philips. *Chem. Mater.*, 12:1866–1873, 2000.
  169. K. Strawhecker and E. Manias. *Chem. Mater.*, 12:2943–2949, 2000.
  170. R. Xu, E. Manias, A.J. Snyder, and J. Runt. *Macromolecules*, 34:337–339, 2001.
  171. E.P. Giannelis, *Advanced Materials*, 1996, 8, (1), p. 29.
  172. Gilman, J. W., Kashivagi, T., Nyden, M., Brown, J. E. T., Jackson, C. L., Lomakin, S., Giannelis,

- E. P., Manias, E., “*Chemistry and technology of Polymer Additives*”, Chapter 14, Edited by Al-Malaika, S., Golovoy, A., Wilkie, C. A., Blackwell Science Ltd., Oxford 1999.
173. Gilman, J. W., Kashivagi, T., C. L., Giannelis, E. P., Manias, E., Lomakin, S., Lichtenhan, J. D., Jones, P., *Fire Retardancy of Polymer*, (Edited by Le Bras, M., Camino, G, Bourbigot, S., Delobel, R.) The Royal Society of Chemistry, 1998, Cambridge. p. 233
174. Zaikov G.E., Lomakin S.M., Thermal degradation and combustion behavior of polypropylene/multi-walled carbon nanotube composites, *Proceeding of 14 International conference of polymeric materials (15-17 September 2010, Halle-Saale, Germany)*, Ed. by H.-J. Radusch, Martin Luther University Publishing House, 2010, pp. 167