

Modification of Polyethylene and Incorporation of Fillers for Effective Reinforcement of Mechanical and Better Flame Retardant Properties

Gul Bali Shah, Mohammad Fuzail

Applied Chemistry Laboratories (ACL), Pakistan Institute of Nuclear Science and Technology (PINSTECH), Nilore, Islamabad, Pakistan

Received 1 December 2004; accepted 8 May 2005

DOI 10.1002/app.22672

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of incorporation of the two different fillers, *i.e.* calcium carbonate and magnesium hydroxide, over a concentration range of 0–35% w/w on mechanical and burning properties and hot set test of polyethylene (PE) has been studied. The incorporation of either of these fillers deteriorates mechanical properties such as percent elongation at break and tensile strength of PE. However, modification of PE not only mitigates the reduction in these properties, but brings enhancement in all the aforementioned properties. A clear difference in these properties for the incorporation of each of these fillers to just PE, silane-grafted

but uncured PE, and silane cross-linked PE has been found. These properties follow the order of superiority as: cross-linked PE > silane-grafted uncured PE > physically filled PE. The different properties due to physical bonding of filler, physical bonding in the presence of polar silane grafted onto PE, and that of chemical bonding of filler in cross-linked PE has been discussed and analyzed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1928–1933, 2006

Key words: additives; cross-linking; flame retardant; initiator; mechanical properties; reinforcement

INTRODUCTION

Polyethylene (PE) as well as its copolymer can be extruded into three types of products: cables, pipes, and sheets/films and is widely used in cables and water pipe industries. All these applications are important, but the fact that PE is a thermoplast with low thermo-oxidative stability, poor fire resistance, and some how low mechanical properties limit its service temperature at a lower level. To improve the properties of PE, it is cross-linked in the presence of peroxide, the chemistry of which is well known.^{1–5} A wide range of fillers are used for different purposes, such as improvement in mechanical properties, flame retardancy, and resistivity to polymeric systems, in various environments. In some cases, fillers are modified to make them compatible with the base polymer,^{6–8} which then improves properties such as elongation^{9–12} and processing temperature of polymer.¹³

The fire-safe use of polymers, which are combustible by nature, can be achieved by reducing heat release, smoke, and corrosive gases, delaying or modifying ignition, and flame spread during the early phase of combustion. The halogen-containing compounds, although used in polymers as flame retardant, give rise to the

problems of toxicity, corrosion, and smoke.^{14–16} Halogen-free compounds such as aluminum trihydrate and magnesium hydroxide (MH) when used only at a high loading (60% by weight)^{17,18} fillers can confer adequate flame retardancy on polyolefins. Such high loading leads to decreases in mechanical properties such as tensile properties because of poor compatibility between the filler and the polymer.^{19,20} Recently, interest in using chemically bonded flame retardants has increased because of their established advantages over those of the ordinary additives.^{1,21–23}

To focus on the aforementioned problems, the effect of incorporation of MH and calcium carbonate to simple and silane-grafted PE (cured and uncured) has been studied on mechanical, fire retardant properties and hot set test. The objective was also to differentiate quantitatively, between the detrimental or other wise influence of the filler in PE, on its mechanical and burning behaviors as well as help to develop better halogen-free flame retardant formulations that could be used for cable and wires and hot water pipes.

EXPERIMENTAL

Materials

Magnesium hydroxide (MH) (fine powder), calcium carbonate (ultra fine powder), white powder, ($M = 78$, particle size = 20–250 μ), vinyl triethoxysilanes, (F. Wt. 190.32, assay > 98%) were supplied by Fluka

Correspondence to: G. B. Shah (gbsah.gul@gmail.com).

Chemika. Dibutyltindilaurate (DBTDL; F. Wt. 631.56) of analytical grade was purchased from Merck-Schuchardt. Low density polyethylene (LDPE) (Lotrene) granules were supplied by Qapco Ltd., Qatar. Benzoyl peroxide (BPO) was purchased from Fluka Chemika. These chemicals were used as such without further purification.

Procedure for modification, filling of PE sample, and its characterization

Grafting of silane on to PE was carried out as reported in our recently published paper.¹ In the first step, vinylsilane was grafted on to PE chain through a free radical reaction initiated by BPO. Weighed amount of powdered LDPE, 0.36 g of BPO, 3 mL silane, and 0.2 g of catalyst (DBTDL) were homogeneously mixed for 5 min in a closed brabender mixer type (Rheodrive 5000-Haake, Germany) set at a temperature of 140°C. Weighed amount (5–35% by wt) of the respective filler, i.e. MH or calcium carbonate, was added and mixed for further 5 min in the mixer. The material was pressed into sheet of required thickness in a heat press at 190°C.

In the second stage, the sheets were cured in autoclave at 105°C for 4 h. The organotin catalyst (DBTDL), which decreases the activation energy^{24–26} for hydrolysis and condensation of the ethoxy groups of the silane molecules, resulted in the polymer network formation, i.e. cross-linking.

Tensile measurements

Tensile strength, Hot set test, and burning characteristic were measured according to the respective standards specifications and methods as reported earlier.¹ Specimens for the tensile tests were cut with a dumbbell cutter according to BS 903 Part A2 1956 D. A rubber testing machine (Instran Model 4301 S.No. H2711 High Wycombe, England) was used for measurement of tensile properties. The tests were carried out at a strain rate of 50 mm/min. The load cell of 5 KN was used. The corresponding isothermal stress–strain curve was obtained. The ultimate tensile strength and percent elongation at break (%Eb) were calculated.

Hot set test

Hot set test was carried out on a dumbbell shaped piece of sample according to the standards such as BS 6746F, IEC 540, ISO 6427, (DIN 16,892), ASTM D 2765–90. The specifications of withstanding a load of 20 N/cm² at 200°C for 15 min were monitored for all the tests.

Burning characteristics of the cross-linked samples

The burning properties of the sample were measured by a candle type flammability tester model D made by

Toyo Seiki Seisaku-SHO Ltd., Japan. The pressure of nitrogen and oxygen gas fed to the combustion section was adjusted by regulating valves to 1.5 Kg/cm². After flow of the mixture of gases for 30 s, the upper portion of the specimen having constant dimensions, i.e. 1 × 6.5 × 100 mm³, was ignited. Three specimens for each composition were tested. The combustion time and the visual observations about the burning properties for the samples are recorded in respective Tables I and II.

RESULTS AND DISCUSSION

In the present work, the effect of incorporation of concentration range of 0–35% w/w of Mg(OH)₂ and CaCO₃ on to PE (non cross-linked and cross-linked) was separately studied for mechanical as well as burning properties. In this respect, the results are divided into two categories. In the first category, the graphical representation of mechanical properties, i.e. tensile strength and %Eb, of non cross-linked and cross-linked PE for CaCO₃ and Mg(OH)₂ are presented in Figures 1–4, whereas the results about the second category, i.e. burning characteristics, are recorded in Tables I and II. In the case of each of these filler for each concentration (Figs. 1–4), the respective properties are separately presented for physical incorporation of filler to just PE, to the silane-grafted but uncured PE, and to the silane cross-linked PE. It is clear from these figures that for each of the filler used, its three different mode of incorporation to PE show distinct different values of properties. The mechanical properties (TS and %Eb) and the burning characteristic of the three types of PE (pure, silane grafted, and cross-linked) filled with CaCO₃ or Mg(OH)₂ presented in Figures 1–4 and Tables I and II, respectively, show superiority order as: cross-linked PE > silane-grafted uncured PE > physically filled PE.

A reversion of property from smooth continuous decrease (Figs. 1 and 3) of TS for the increase in concentration of physically incorporated filler (MH or calcium carbonate) in PE to increase in the same property (Figs. 1 and 3) for the modified PE for either of the filler observed is interesting. This reversion in behavior shows that grafting of the silane to PE changes the nature of interaction between the filler and the polymer matrix. Here, the incorporated filler acts as a reinforcing agent in contrast to the case (physical incorporation) where it deteriorated the tensile properties. The cross-linked samples show further superior nature in this respect. The reason for the superior TS of silane-grafted uncured PE samples is that the alkoxy groups attached to silicon impart polarity to PE, which bonds filler effectively. In the case of cross-linked samples, the hydrolysis and polycondensation (cross-linking) of the alkoxy groups on silicon with one another

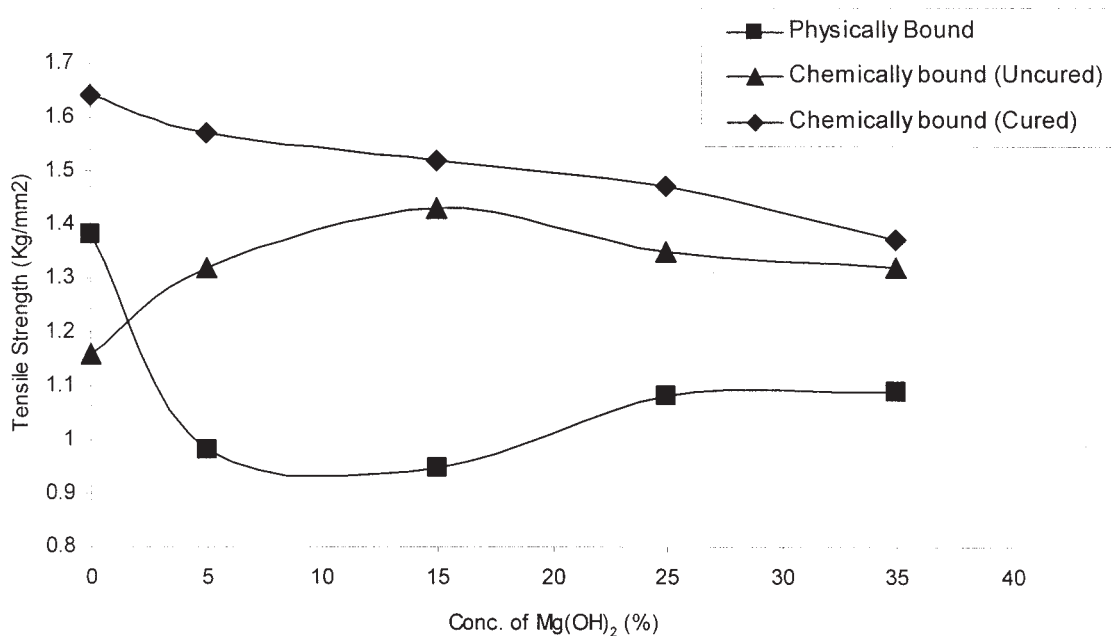


Figure 1 Effect of concentration of Mg(OH)₂ on tensile strength.

and with that of filler carried out in autoclave result in effective cross-links.

These cross-links whether chemical or physical formed because of the interaction between the Si-O of the silane on the PE with the filler promote reinforcement and hence give superior TS to the PE matrix. The effect of reinforcement of fillers on polymeric network is

well documented²⁷⁻³¹ and it is an established^{27,32} fact that it depends upon the chemical nature as well as on the size of the particles. For example, 10 times increase in tensile strength and 100% modulus reported²⁷ for silicone network on incorporation of pyrogenic silica filler have been attributed to the small particle size of the filler (5-30 nm) and high concentration of silanol groups (2-

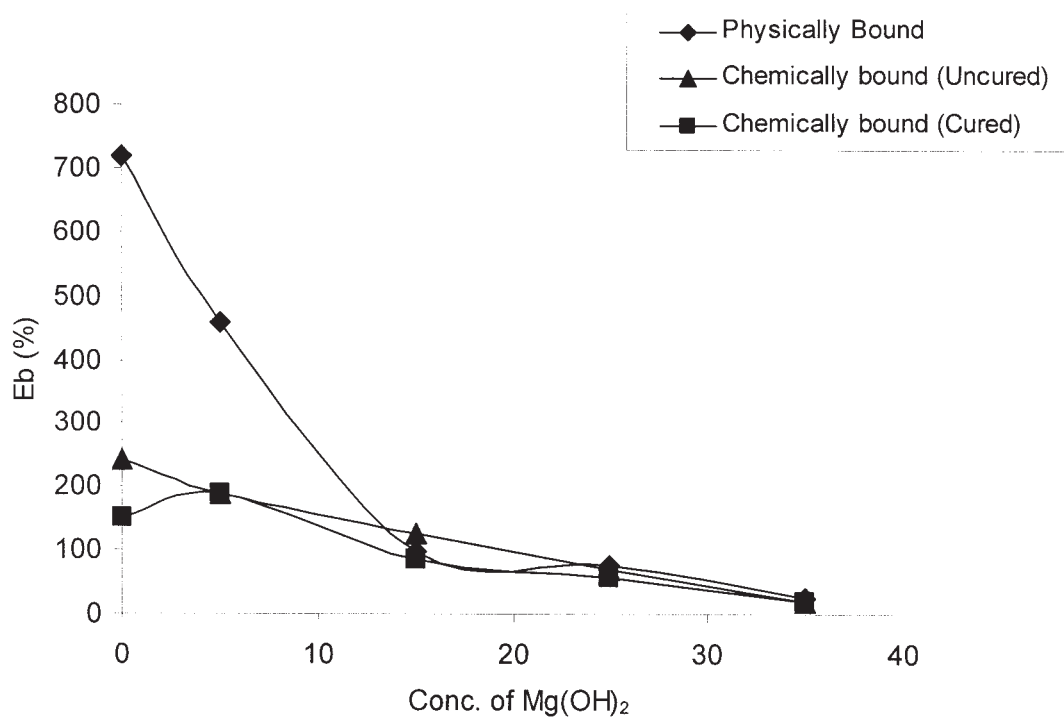


Figure 2 Effect of concentration of Mg(OH)₂ on %Eb.

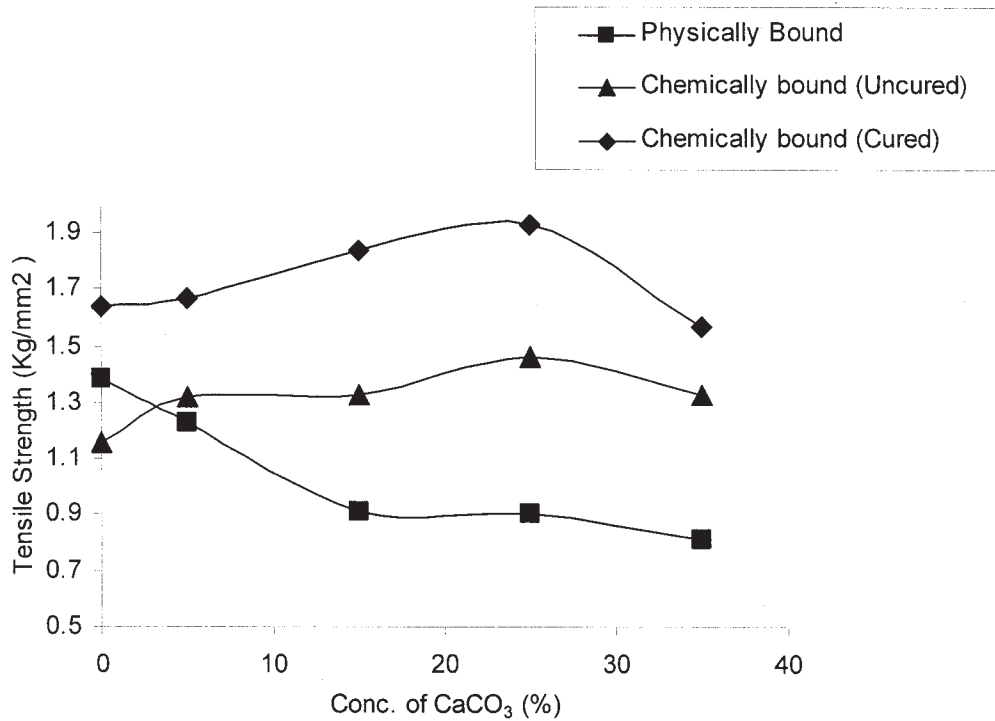


Figure 3 Effect of concentration of CaCO₃ on tensile strength.

3.5/nm²). However, study about incorporation of filler to three different forms of PE and its subsequent effect of differentiation in properties such as mechanical, burning, and hot set test is new, important, and interesting.

The contribution of effective cross-links, whether chemical or physical, from the filler (Mg(OH)₂ or

CaCO₃) and PE interaction tips the balance between chain tightening due to cross-linking and chain flexibility. As a result, a decrease in %Eb is observed for all the three kinds of PE with increase in concentration of filler. In the case of physical incorporation of filler to PE, there is a drastic decrease in %Eb when compared

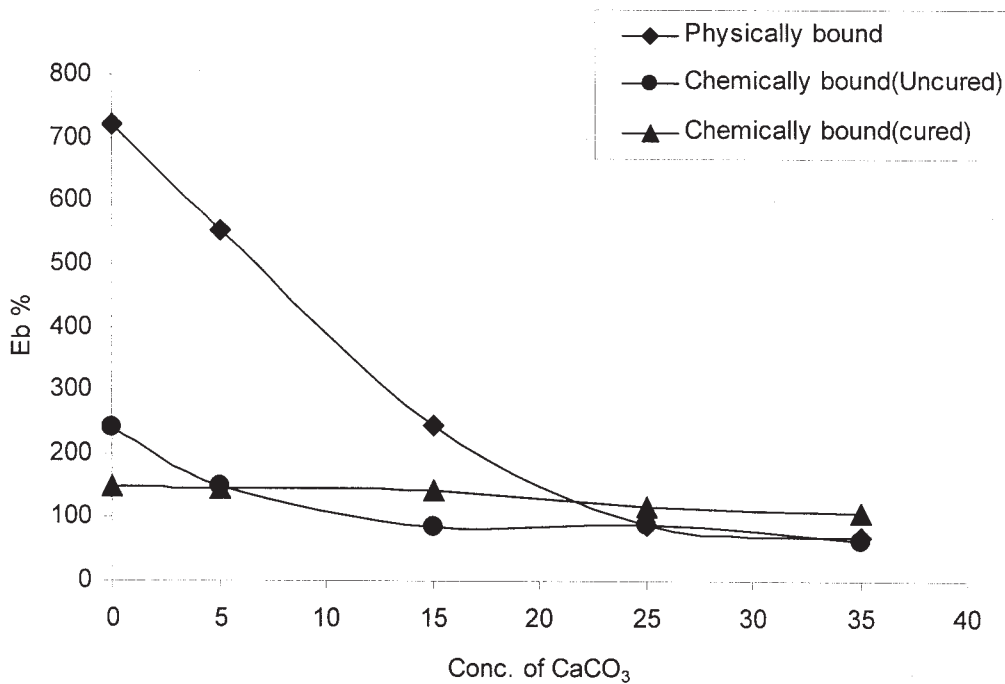


Figure 4 Effect of concentration of CaCO₃ on %Eb.

TABLE I
Effect of Concentration of Mg(OH)₂ on Burning Properties of Polyethylene

Filler concentration (Mg(OH) ₂) (%)	Oxygen setting (LOI)	Sample		
		Physically bound	Chemically bound	
			Un-cured	Cured
0 (Control)	19.5	Sample rolls over itself, small flame, no smoke, falls within 41 s	Sample withstands its standing position, no rolling off, burning time 92 s	Sample withstands its standing position, no rolling off, burning time 100 s
5	19.5	Sample rolls over itself, small flame, no smoke, falls within 65 s	Sample withstands its standing position, no rolling off, burning time 125 s	Sample withstands its standing position, no rolling off, burning time 160 s
15	20.0	Sample rolls over itself, falls within 40 s, small flame, no smoke	Sample rolls over itself dripping from the top burning time 90 s	Sample withstands its standing position, no rolling off, burning time 150 s
25	24.0	Sample rolls over itself, falls within 60 s, medium flame, no smoke	Sample dripping from the top, burning time 65 s	Sample withstands its standing position, no rolling off, burning time 120 s
35	28.0	Sample rolls over itself, falls within 60 s, medium flame, no smoke	Sample rolls over itself, dripping observed, burning time 120 s	Sample withstands its standing position, no rolling off, burning time 128 s

with the corresponding other two types of PE. As presented in Figures 2 and 4, the %Eb within the concentration range of 0–25% w/w Mg(OH)₂ shows that the sample having physically incorporated filler presents higher values than that containing silane-grafted filled sample, which in turn are higher than the cross-linked one. For higher loading, i.e. >25% w/w, all the three kinds of PE samples irrespective of its form show more or less the same %Eb.

The observations about the burning characteristic of the PE having Mg(OH)₂ and CaCO₃ loaded through different mode of incorporation are recorded in Tables I and II. During burning characteristics, the PE physically loaded with Mg(OH)₂ or CaCO₃ (Tables I and II) shows

insignificant effect, compared with pure PE. The silane-grafted filled PE for each additive presents better fire resistivity, while the cross-linked samples show further improvement in this respect. Thus, the same order of superiority for the three kinds of PE in reference to fire retardancy was observed as that for the TS.

Comparing the burning properties of the PE loaded at the same level with Mg(OH)₂ and CaCO₃, it seems unexpectedly that both types of samples exhibit similar characteristics despite the fact that the former is better flame retardant than the latter. However, the fact of the matter is that as stated in the experimental part, the CaCO₃ used was of ultra fine nature, while Mg(OH)₂ was used as fine powder. Hence, the smaller

TABLE II
Effect of Concentration of CaCO₃ on Burning Properties of Polyethylene

Formulations (CaCO ₃) (%)	Oxygen setting (LOI)	Sample		
		Physically bound	Chemically bound	
			Uncured	Cured
0 (Control)	19.5	Sample rolls over itself, small flame, no smoke, burning time 40 s	Sample withstands its standing position, No rolling off, burning time 90 s	Sample withstands its standing position, No rolling off, burning time 100 s
5	19.5	Sample rolls over itself, small flame, no smoke, falls within 50 s	Sample withstands its standing position, no rolling off, burning time 120 s	Sample withstands its standing position, no rolling off, burning time 135 s
15	22.0	Sample rolls over itself, falls within 60 s, small flame, no smoke	Sample withstands its standing position, no rolling off, burning time 120 s	Sample withstands its standing position, no rolling off, burning time 150 s
25	24.0	Sample rolls over itself, falls within 60 s, medium flame, no smoke	Sample withstands its standing position, no rolling off, burning time 135 s	Sample withstands its standing position, no rolling off, burning time 155 s
35	27.5	Sample rolls over itself, falls within 60 s, medium flame, no smoke.	Sample withstands its standing position, no rolling off, burning time 110 s	Sample withstands its standing position, no rolling off, burning time 120 s

particle size of the CaCO_3 used, compared with $\text{Mg}(\text{OH})_2$, has compensated the other wise inferior flame retardant behavior of the former and has brought its properties at par with the latter in the present circumstances.

The migration of various components from the bulk of materials to the surface and its transformation to an inorganic coating during burning make the mechanism of fire retardancy complex. However, various theories have been put forward and in general it is believed that flame retardant materials reduce the flammability by the endothermic evolution of water, which then dilutes the fuel gases and oxygen in the flame, while the residues stabilize the polymers melts as an inert filler.³³ According to Marchal et al.,³⁴ the produced water acts not only as a thermal shield but protect the bulk materials from external heat flux and moreover inhibits the oxygen diffusion. This protection is generally believed to be the result of creation of an expanded carbonaceous structure on the flame front. In some cases, the reduction in flammability of polymers has been attributed to the plasticity of the char formation at higher temperature.^{35,36}

It is an established^{1,21-23} fact that fire retardants that inhibit the combustion process by chemical methods are more effective than those that do the same job by physical methods. As a manifestation of this point, physically dispersed filler and the silane-grafted filled PE samples do not qualify hot set test, whereas the cross-linked one having either of the filler at any concentration from the aforementioned range passes hot set tests according to the standards.

CONCLUSIONS

Modification of PE is important to achieve effective reinforcement of mechanical properties, flame retardancy, and hot set test qualification with incorporation of fillers such as MH and calcium carbonate. Grafting of silane to PE and incorporation of filler in the uncured as well as in the cured (cross-linked) state not only mitigate mechanical properties reduction of samples caused due to physical loading of filler but actually enhances these properties. The easy, simple, and effective methodology used in this study has manifested a clear difference in mechanical, flame retardant, and hot set test properties for both of these fillers for physical, silane-grafted uncured, and cross-linked filled PE. These properties in general follow the order of superiority as: cross-linked PE > silane-grafted uncured PE > physically filled PE.

Hot set test has shown that the incorporation of calcium carbonate or MH to PE makes qualify the sample to pass the said test only when it is cross-linked. This demonstrates that cross-linking increases

thermal stability much more than when these compounds are dispersed in simple or even in silane-grafted PE.

References

- Shah, G. B.; Fuzail, M.; Anwar, J. *J Appl Polym Sci* 2004, 92, 3796.
- Duval, M.; St-Onge, H. *IEEE Trans Electr Insul* 1979, EI-14, 264.
- Sluszny, A.; Silverstein, M. S.; Kababya, S.; Schmidt, A.; Narkis, M. *J Polym Sci Part A: Polym Chem* 2001, 39, 8.
- Hjertberg, T.; Palmlof, M.; Sultan, B. A. *J Appl Polym Sci* 1991, 42, 1185.
- Sen, A. K.; Mukherjee, B.; Bhattacharyya, A. S.; DE, P. P.; Bhowmick, A. K. *J Appl Polym Sci* 1992, 44, 1153.
- Wang, Z.; Shen, X.; Fan, W.; Hu, Y.; Qu, B.; Gui, Z. *Polym Int* 2002, 51, 653.
- Wang, J.; Tung, M. Y.; Fuad, A.; Hornsby, P. R. *J Appl Polym Sci* 1996, 60, 1425.
- Hornsby, P. R.; Mihupa, A. *Plast Rubber Process Appl* 1996, 25, 347.
- Cook, M.; Harper, J. F. *Plast Rubber Process Appl* 1996, 25, 99.
- Demjien, Z.; Pukanszky, B. *Polym Comp* 1997, 18, 741.
- Wang, Z. Z.; Qu, B. J.; Fan, W. C.; Li, Z. *Gong Neng Gao Fen Zi Xue Bao* 2001, 14, 47.
- Chuah, A. W.; Leong, Y. C.; Gan, S. N. *Eur Polym Mater* 2000, 36, 789.
- Levchik, S. V.; Weil, E. D. *Polym Int* 2000, 49, 1033.
- McGarry, K.; Zilberman, J.; Hull, T. R.; Woolley, W. D. *Polym Int* 2000, 49, 1193.
- Woolley, W. D.; Fardell, P. J. *Fire Safety J* 1982, 5, 29.
- Delfosse, L.; Baillet, C.; Brault, A.; Brault, D. *Polym Degrad Stabil* 1989, 23, 337.
- Hornsby, P. R. *Fire Mater* 1991, 18, 269.
- Wang, Z. Z.; Qu, B. J.; Fan, W. C.; Huang, P. *J Appl Polym Sci* 2001, 81, 206.
- Hornsby, P. R.; Watson, C. L. *Plast Rubber Process Appl* 1986, 6, 169.
- Wang, J.; Tung, M. Y.; Fuad, A.; Hornsby, P. R. *J Appl Polym Sci* 1996, 60, 1425.
- Liu, Y. L.; Hsiue, G. H.; Lee, R. H.; Chiu, Y. S. *J Appl Polym Sci* 1997, 63, 895.
- Mikroyannidis, J. A.; Kourtidis, D. A. *J Appl Polym Sci* 1984, 29, 197.
- Lewin, M.; Atlas, S. M.; Pearce, E. H. *Flame Retardant Polymeric Materials*; Plenum: New York, 1975; p 22.
- Shah, G. B.; Winter, R. W. *J Appl Polym Sci* 1996, 61, 1649.
- Shah, G. B. *J Appl Polym Sci* 1998, 70, 2235.
- Scott, H. G.; Humpries, J. F. *Mod Plast* 1973, 50, 82.
- Shah, G. B. Ph.D. Thesis, University of Wales College of Cardiff (UWCC), UK, 1990.
- Bonstara, B. B.; Cochrane, H.; Dannenberg, E. M. *Rubb Chem Technol* 1975, 48, 558.
- Smallwood, W. M. *J Appl Phys* 1944, 15, 758.
- Buche, F. *J Appl Polym Sci* 1960, 4, 107.
- Kraus, G. *Reinforcement of Elastomers*; Wiley-Interscience: New York, 1965.
- Mark, J. E. *Pure Appl Chem* 1981, 53, 1495.
- Rothon, R. N. In *Particulate-Filled Polymer Composites*; Longman: Harlow, 1995; Chapter 6.
- Marchal, A.; Delobel, R.; Bras, M. L.; Leroy, J. M.; Price, D. *Polym Degrad Stabil* 1994, 44, 263.
- Anna, A.; Marosi, Gy.; Bourbigot, S.; Bras, M. L.; Delobel, R. *Polym Degrad Stabil* 2002, 77, 243.
- Anna, P.; Marosi, Gy.; Csontos, I.; Bourbigot, S.; Bras, M. L.; Delobel, R. *Polym Degrad Stabil* 2001, 74, 423.