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Polystyrene/graphite Nanocomposites: Effect on Thermal Stability

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Abstract

Nanocomposites consisting of polymer and clay have been shown to exhibit a significant reduction in flammability and an increase in mechanical properties. This work examines the effect of thermal stability and mechanical properties of nanocomposites prepared from potassium graphite and styrene. Synthesis of nanocomposites was accomplished by using potassium graphite (KC₈) as the initiator in the polymerization of styrene. A slight increase in thermal stability is observed but mechanical properties are decreased.

Keywords

Nanocomposites, Polystyrene, Graphite, Thermal stability, Cone calorimetry, Potassium graphite

1. Introduction

Polymer-clay nanocomposites have been shown to exhibit a significant increase in thermal stability and an enhancement in mechanical properties ^[1]. The dispersion of the clay within the polymer has a most significant

influence on the properties of the material. When the clay is not well-dispersed, no nanocomposite is formed; if it is well-dispersed, either an intercalated or a delaminated nanocomposite is formed. Intercalated nanocomposites consists of well-ordered layers in which registry is maintained between the clay layers while this registry is lost in delaminated, also known as exfoliated, nanocomposites. The formation of delaminated nanocomposites seems to lead to a greater enhancement of mechanical properties than is observed for intercalated systems. It has been suggested that layered materials may be beneficial to the enhancement of polymer properties.

Graphite is another layered material and it is thought that an enhancement in properties may be observed. Nyden and Gilman have performed molecular dynamic simulations (MD_REACT) for nanocomposites composed of graphite and polypropylene [2]. They found that the “nanocomposite effect” of this system is best when the graphite layers are separated by ~ 3.0 nm.

Nyden and Gilman have also observed that for a polyamide-6/clay nanocomposite, there is a critical mass fraction value that can not be exceeded to form intercalated structures, once this value is exceeded the nanocomposite becomes delaminated. For intercalated nanocomposites the attractive forces must be stronger than the repulsive forces, otherwise the clay structure will become delaminated and form a hybrid structure. It has been shown that intercalated compounds are more thermally stable than the delaminated nanocomposites [3]. Based on these observations, it would be assumed that there should be an increase in thermal stability observed for the graphite-polymer nanocomposites.

The graphite structure consists of carbon layers in an alternating stacking sequence. The carbon atoms are bonded covalently in a hexagonal arrangement within the layer and these layers are weakly bonded to each other. It is the weak van der Waals forces between the layers which makes intercalation possible. The typical d-spacing between the carbon layers in graphite is approximately 3.35 \AA . Graphite is known to form lamellar compounds with alkali metals, where the carbon has taken on a planar arrangement [4], [5], [6]. Potassium can insert into the graphite structure to give a number of compounds, called stages. The first stage material, KC_8 , has an orthorhombic orientation and the d-spacing increases from 3.35 \AA for graphite to 5.41 \AA for KC_8 . Second stage, KC_{24} , has a spacing of 8.72 \AA , while the third stage material, KC_{36} , has a spacing of 12.1 \AA .

Shioyama has shown that graphite intercalation compounds (GIC) of alkali metals can form ternary compounds with organic molecules [7], [8], [9], [10]. Shioyama's work showed that unsaturated hydrocarbons could be co-intercalated into the graphite layers of alkali metal-GICs. Once the hydrocarbon was intercalated, polymerization could be carried out in the interlayer spacing of graphite. The polymerizations were done using metal-GIC compounds (RbC_{24} , CsC_{24} , KC_{24} , and KC_8) with the vapor of isoprene, 1,3-butadiene, and styrene. Shioyama observed expansion of the graphite layers within “several tens of minutes” [7]. In the case of KC_{24} and KC_8 , polymerized samples resembled exfoliated graphite but lacked a characteristic “gap” and the bulk density of the samples was similar to that of the virgin polymer [7], [8]. X-ray diffraction of the polymers show no peaks due to graphite or the GIC; this is attributed to the layers being separated and disordered due to the polymerization. Thermogravimetric analysis results were similar to the virgin polymers. Reactions of KC_8 and KC_{24} with acrylonitrile, 1-butene, and isobutene were also examined. It was found that these polymers could react for more than a month and no expansion of the GIC was detected [9]. X-ray diffraction patterns showed the co-existence of stages 2 and 3 potassium-GICs and no other phases were observed [9]. It was also found that KC_{24} -polymer (acrylonitrile, 1-butene, isobutene) was stable in water for up to 11 days upon which the potassium-GIC decomposed to a stage 4 compound; this indicates high stability of these systems [9]. This is thought to be due to monomers polymerizing only on the surface of the GIC edge, which would protect the GIC in water [9]. For the polymers prepared using RbC_{24} and CsC_{24} , similar results are observed where the products resemble exfoliated graphite, but the bulk density and thermal properties are similar to those of the commercial polymers [10]. X-ray diffraction patterns of RbC_{24} -polymers show only peaks resembling those of the commercial polymer while

thermogravimetric analysis of these polymers is also similar to the commercial polymer^[10]. The CsC₂₄-polymer systems show peaks in the X-ray diffraction of polymer and additional peaks attributed to higher stage Cs-GICs; suggesting that polymerization is low^[10].

In this work the bulk polymerization of styrene using potassium graphite, KC₈, as the initiator has been examined. Previous work has been carried out using this initiator but, in most cases, the polymer has been washed free of the graphite so it is unknown if a nanocomposite had been formed. Based upon the simulations of Nyden and Gilman, one may anticipate enhanced thermal stability for the nanocomposites.

2. Experimental

2.1. Materials

All materials were obtained from Aldrich Chemical Company. The graphite was in the form of a powder of 1–2 μm size. The styrene was used after removal of the inhibitor (4-*tert*-butylcatechol) by passing the monomer through an inhibitor-remover column, followed by distillation. Commercial polystyrene (Aldrich) of 280,000 molecular weight was used to prepare blends and as a reference material. KC₈ was prepared following literature methods^{[7], [8], [9], [10], [11]}.

2.2. Analysis

A Cahn TG-131 thermoanalyzer was used under a flowing inert atmosphere at a scan rate of 20 °C min. Samples were cut from the graphite/polymer nanocomposite. The temperature at which 10% degradation occurs is taken as representative of the onset temperatures of degradation. T_{max} is the temperature at which the maximum rate of degradation occurs and is another measure of thermal stability. All TGA results are the average of at least three runs; typically the temperatures are reproducible to ±3 °C. Cone calorimetry was performed per ASTM E 1354–92 using a Stanton Redcroft/PL Thermal Sciences instrument at 35 KW/m² in the horizontal orientation. The samples were 6.3 mm and mounted using the edge retainer frame and wire grid; the mass was approximately 35 g. Exhaust flow was set at 24 l/s and the spark was continuous until the sample ignited. Infrared spectra were obtained using a Nicolet Magna infrared 560 spectrometer E.S.P. ¹H Nuclear magnetic resonance spectroscopy was performed on a General Electric QE 300 NMR in deuterated chloroform at 300 MHz. X-ray diffraction (XRD) was performed on a Rigaku Geiger Flex, 2-circle powder diffractometer using CuKα radiation. Scans were taken from 2 theta at 0.70–30°, step size 0.1°, and scan time per step of 20 s.

2.3. Preparation of potassium graphite initiator (KC₈)

The preparation of the initiator followed the literature procedures^{[11], [12], [13], [14], [15]}. A 250-ml, 3-neck round bottom flask, glass stirring rod, dropping funnel, and nitrogen inlet/outlet was oven-dried overnight, then assembled and flame dried with a Bunsen burner under a nitrogen atmosphere. To the cooled glassware was added graphite and this was flame dried with a Bunsen burner. The flask and its contents were heated to 120 °C, and potassium was added over approximately a 30 min period with vigorous mechanical stirring. Upon completion of addition the mixture was allowed to stir an additional 2 h. The resulting product was small yellow balls with a light brown coating and a reflective coating had formed on the surface of the flask. The material was used immediately as a polymerization catalyst.

2.4. Polymerization of styrene intercalated with graphite, method I—all graphite as initiator

The polymerization was performed by the addition of styrene to the flask containing the initiator. In a typical reaction, a flask containing the KC₈ (3.66 g) was cooled to 0 °C; to the chilled flask was added, through an addition funnel, 77.0 ml (70.0 g) of purified styrene over 30 min. The Reaction proceeded rapidly. The reaction flask was left overnight, under nitrogen, to permit the completion of the reaction. The flask and its contents

were then exposed to air for 24 h and the polymer was removed from the flask by heating, followed by annealing for 24 h at 120 °C. The reaction products of the potassium, presumably the oxide, hydroxide and carbonate, formed from the reaction of the metal with oxygen, water, and carbon dioxide in air, were not removed.

2.5. Polymerization of styrene intercalated with graphite, method II— addition of graphite during bulk polymerization

The polymerization was performed similar to method I, but using a smaller amount of initiator and adding additional graphite during the polymerization. In a typical reaction, a flask containing the KC_8 (1.07 g) was cooled to 0 °C; to the chilled flask was added, through an addition funnel, 88.0 ml (80.0 g) of purified styrene over 30 min and 1.76 g graphite was added in one portion. The reaction proceeded more slowly than for the method above. The reaction flask was left overnight, under nitrogen, to permit the completion of the reaction. The flask and its contents were then exposed to air for 24 h and the polymer was removed from the flask by heating, followed by annealing for 24 h at 120 °C.

2.6. Polymerization of styrene intercalated with graphite, method III—addition of graphite after bulk polymerization

The polymerization was performed similar to method I. In a typical reaction, a flask containing the KC_8 (1.47 g) was cooled to 0 °C; to the chilled flask was added, through an addition funnel, 100.0 ml (90.9 g) of purified styrene over 30 min. The reaction flask was left overnight, under nitrogen, to permit the completion of the reaction. The flask and its contents were then exposed to air for 24 h and the polymer was removed from the flask by heating. Upon removal from flask the polymer was blended (using a Brabender mixer) with additional 2.57 g of graphite. This sample was annealed for 24 h at 120 °C.

2.7. Preparation of polystyrene using potassium as initiator

The polymerization was performed by the addition of styrene to the flask containing potassium. In a typical reaction, to a flask containing potassium (0.43 g) was added, through an addition funnel, 60.0 ml (54.5 g) of purified styrene over 30 min. Reaction proceeded slowly and was allowed to react for 6 days. Then methanol (150 ml) was added and mixture exposed to air for several days to allow any unreacted potassium to be consumed. Polymer was removed and dried in a vacuum oven at 100 °C over night.

2.8. Preparation of polystyrene/graphite blends

Blends were prepared using a Brabender Plasticorder mixer. The mixer was heated to 220 °C and commercial polystyrene ($M_w=280,000$) and graphite were poured into blender and allowed to mix for 20 min. After the polymer was removed from the Brabender, it was annealed overnight under vacuum at 120 °C. Blends were prepared containing 2 and 5% graphite.

2.9. Extraction of polymer

Polymers were extracted from the nanocomposites using THF; typically solvent was poured onto the nanocomposite and allowed to sit for 24 h. The polymer was filtered through Celite to remove graphite and precipitated with methanol. In a typical example 1 g of graphite-containing polystyrene was placed in 200 ml of THF and precipitated with 400 ml of methanol. Infrared spectra of the extracted polymer showed the absence of graphite, peaks typically observed at 1600 and 1360 cm^{-1} are no longer present.

2.10. Determination of molecular weight

Molecular weight determinations were performed using a Ubbelohde viscometer in a water bath maintained at 30.0±0.2 °C. Samples were prepared by dissolving 0.25 g of extracted polystyrene in 25 ml of toluene. Into the

viscometer was placed 10 ml of solution and allowed to come to equilibrium at 30.0 °C. Then the solution was drawn into the observation bulb and allowed to drain and time was recorded. This was repeated three times and the average value used. In this case $[\eta]$ was calculated using the Huggins equation for single point viscosity determination. The k_h (Huggins constant) for the anionic polymerization of styrene in toluene is 0.51^[16].

3. Results and discussion

3.1. Preparation of initiator and polymerization

The preparation of the initiator is a well-known procedure, first introduced by Lancette^{[17], [18]}. Since the first stage compound, KC_8 , is a golden color, it is easy to observe that the preparation was successful. The polymerization was performed using three different techniques for the introduction of graphite into the material. In the first method, all of the graphite was introduced in the form of the initiator. There were two sources of graphite for the other two methods of preparation, the initiator along with the addition of additional graphite. These were used in order to investigate materials with variable amounts of graphite. In the second method, the additional graphite was added during the polymerization while for the third method, additional graphite was added through a melt blending process, post reaction, using a Brabender mixer. It must be noted that the reaction products of potassium, likely the oxide, hydroxide and carbonate, were not removed and may be present in the nanocomposite. The presence of additional graphite during the preparation slows the reaction, however there is little, if any, effect on the molecular weight between the various preparative methods. The molecular weight data will be discussed in a later section of this paper.

3.2. X-ray diffraction

The typical d-spacing for graphite is 3.35 Å and upon conversion to KC_8 , this expands to 5.41 Å. Fig. 1 shows typical plots for graphite and polystyrene; the d001 peak for graphite can be seen at $2\theta=13.35^\circ$. The broad features near $2\theta=10$ and 18° that are apparent in polystyrene are observed in all polystyrene nanocomposites that have been prepared in this laboratory and are attributed to the polymeric phase [19]. Fig. 2 shows the XRD plots for graphite blended with commercially available polystyrene. The XRD of the blends showed no change in d-spacing from that observed in graphite; there is no intercalation through melt blending in this system. This is validated by the observation of peaks for graphite, $2\theta=13.35$ and 26.55° , and polystyrene, $2\theta=10$ and 18° , present without change in position. Fig. 3, Fig. 4, Fig. 5 show the plots for nanocomposites prepared by methods I, II and III, respectively. In these plots two theta is 5.85 and, using Bragg's law ($\lambda=2d\sin\theta$), the d-spacing increases to 15.1 Å. In some instances the spacing is somewhat larger, up to 22.3 Å. From the XRD one can see that intercalated nanocomposites are formed by all three methods. Definitive proof of the formation of a nanocomposite typically requires transmission electron microscopy (TEM) in addition to XRD data; attempts to obtain TEM results for these nanocomposites have been unsuccessful.

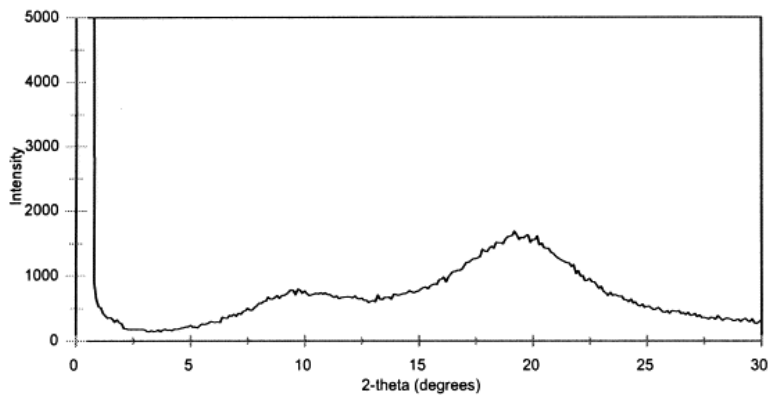
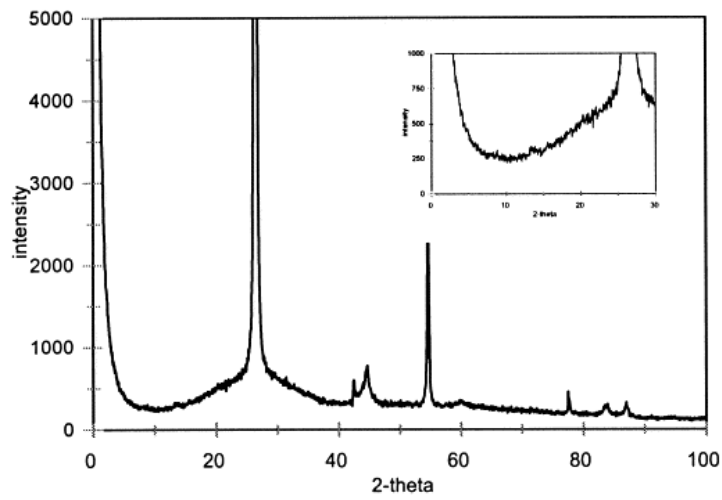


Fig. 1. X-ray diffraction patterns of graphite (top) and polystyrene (bottom). Inset is of expanded region between 2-theta angles 0 and 30.

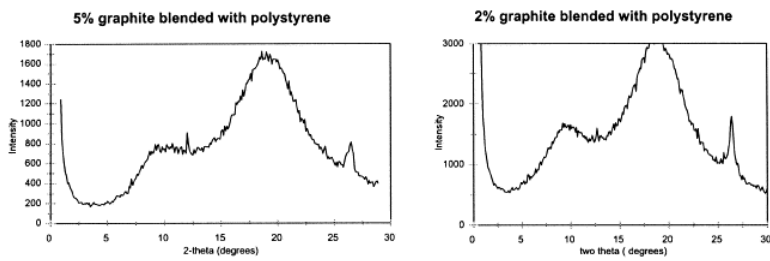


Fig. 2. XRD plots of blends.

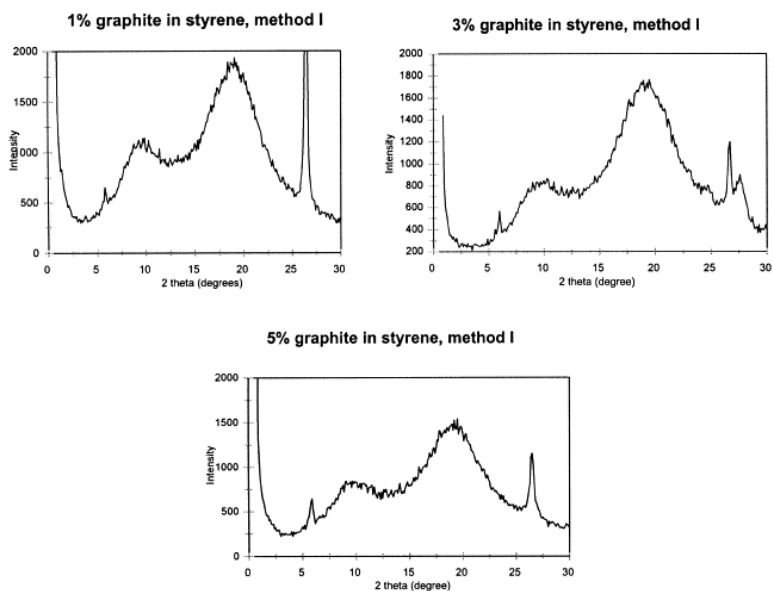


Fig. 3. XRD plots of nanocomposites prepared by method I.

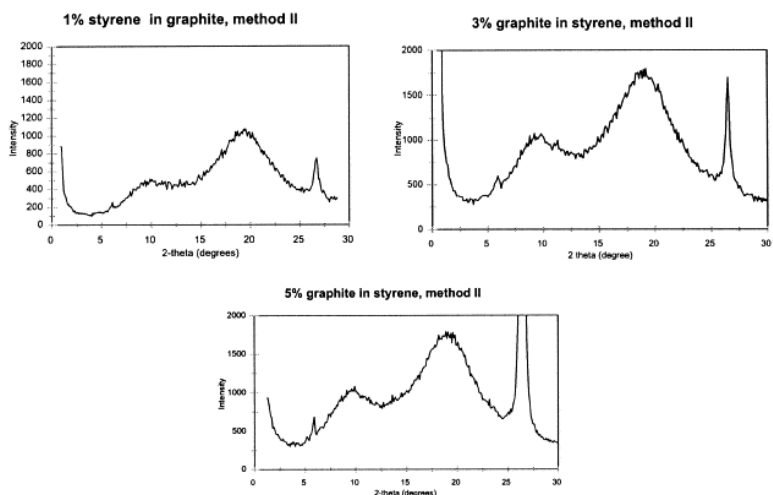


Fig. 4. XRD plots of nanocomposites prepared by method II.

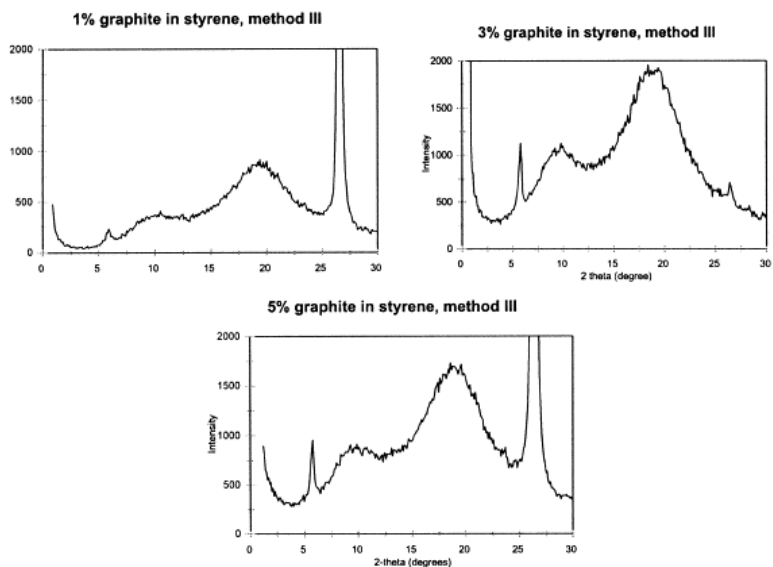


Fig. 5. XRD plots of nanocomposites prepared by method III.

3.3. Thermogravimetric analysis of the nanocomposites and blends

Thermogravimetric analysis data, which is presented in Table 1, shows the onset temperature of the degradation, as measured by the temperature at which 10% degradation occurs, the maximum peak in the derivative, T_{max} , as an indicator of the course of the degradation, and the fraction of non-volatile material which remains at 600 °C, char. The onset temperature of degradation for the polystyrene/graphite nanocomposites increases by about 50 °C compared to commercial polystyrene and similar results are obtained for T_{max} ; these are quite similar to the values that have been previously reported for polystyrene-clay nanocomposites. The polystyrene prepared using potassium as the initiator shows a slightly lower onset of degradation while T_{max} is consistent, except in the case of method III where the values are higher. There is not much difference between the three methods of preparation but a slight enhancement is seen for systems in which not all of the graphite was added in the form of KC_8 . In all cases the reaction products of potassium are present, of course, the amount depends upon the amount of initiator that was used; the amount of initiator has little effect on thermal stability so it must be concluded that the presence of these reaction products do not influence the thermal stability. A large amount of material which is non-volatile at elevated temperature, in many cases significantly more than the amount of graphite that was added, is found in many TGA experiments. The amount of non-volatile does not show any significant variation based on either the mode of preparation or the amount of initiator so it is unlikely to be significantly influenced by the presence of potassium salts. There is also some variability in the amount of char and this must be attributable to sampling problems, which suggests that these nanocomposites are not uniform. It is of interest to note that the materials in which additional graphite has been added post reaction show much more consistent results.

Table 1. Thermogravimetric analysis of graphite–polystyrene nanocomposites prepared by all methods; com. is virgin polystyrene produced commercially of 280,000 molecular weight

% KC_8	% C	$T_{10\%}$ (°C)	T_{max} (°C)	Char (%)
<i>Method I—all graphite from initiator</i>				
0		394	436	1±1
Com.		351	418	0
5.04	3.59	419	446	19±10
5.12	3.67	401	442	7±2
4.17	2.95	417	445	9±3
4.17	2.96	415	445	10±2
3.14	2.19	410	443	19±4
3.39	2.41	410	441	11±3
2.13	1.51	406	442	8±1
1.10	0.779	419	445	9±2
1.39	0.987	408	444	6±1
<i>Method II—additional graphite added during polymerization</i>				
1.89	5.35	442	451	30±8
1.91	5.18	416	444	25±19
1.32	4.31	428	453	26±1
1.41	3.96	425	448	29±5
2.23	3.17	411	451	15±12
1.85	3.08	402	439	22±1
2.21	2.15	418	448	9±2
1.20	1.18	420	453	9±2
1.5	1.3	410	457	5±1
1.20	1.18	416	448	7±4

<i>Method III—additional graphite added post reaction</i>				
1.9	5.53	428	455	12±1
1.6	4.90	431	451	11±1
1.70	3.67	426	457	13±2
1.80	3.00	428	452	6±1
1.24	1.15	419	468	7±1
1.62	0.969	428	447	5±1

The graphite containing polymers were extracted and the extracted materials examined by TGA (Table 2). It is surprising that the extracted polymers show very similar onset temperatures of degradation as observed for the polystyrene-graphite nanocomposites; but upon examination of polystyrene prepared using only potassium the values are as expected. The procedure that was used to remove the graphite will also eliminate any potassium salts so these extracted polymers are pure materials. An even greater surprise is the observation of significant non-volatile residue from the reaction. The fraction of non-volatile residue does, in general, decrease but it does not go to zero as one might have expected. One logical explanation for the enhanced thermal stability and the presence of non-volatile residue is the incomplete removal of graphite from the polymer. Indeed when the nanocomposites were filtered through filter paper, the presence of graphite was obvious from the color of the dried polymer. Filtration through a Celite filter bed allows the complete removal of graphite and this is shown in the infrared spectra by the absence of the peaks due to graphite in the 1500 and 1000 cm^{-1} regions (Fig. 6); the absence of potassium salts is also shown through the lack of anion vibrations in the IR spectra. Peaks corresponding to the graphitic structure in carbon black are typically observed at 1600 and 1360 cm^{-1} [20]. The uncertainties in the amount of non-volatile are the values that one may expect in a typical TGA run and give credence to the absence of either graphite or potassium salts. NMR spectroscopic measurements have been carried out on the extracted polymers and they appear to be completely atactic materials; the apparent higher thermal stability cannot be due to tacticity differences. A possible explanation may be a memory effect, similar to what has been described by Blumstein.

Table 2. Thermogravimetric analysis of the extracted polymer

	% KC_8	% C	$T_{10\%}$ ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)	Char (%)	Mol. wt. (g/mol)
<i>Method I—all graphite from initiator</i>						
5.04		3.59	409	438	2±1	1.7×10^5
5.45		3.67	412	444	7±1	6.1×10^5
4.17		2.95	418	440	4±1	7.5×10^5
4.17		2.96	420	442	4±1	7.1×10^5
3.14		2.19	408	441	5±1	3.2×10^5
3.39		2.41	402	438	2±1	2.4×10^5
2.13		1.51	418	445	4±1	4.4×10^5
1.10		0.779	419	443	5±1	5.0×10^5
1.09		0.987	395	440	4±1	2.8×10^5
<i>Method II—additional graphite added during polymerization</i>						
1.89		5.35	413	442	3±1	3.3×10^5
1.91		5.18	406	447	1±1	4.6×10^5
1.32		4.31	412	449	2±1	4.3×10^5
1.41		3.96	395	434	4±1	8.2×10^5
2.23		3.17	413	441	3±2	6.7×10^5
1.85		3.08	397	451	2±1	6.7×10^5

2.21	2.15	414	446	4±1	2.0×10 ⁵
1.20	1.18	396	443	2±1	8.4×10 ⁵
1.5	1.3	407	442	3±2	7.6×10 ⁵
1.20	1.18	385	442	1±1	11×10 ⁵
<i>Method III—Additional graphite added post reaction</i>					
1.9	5.53	423	449	2±1	18×10 ⁵
1.6	4.90	415	445	1±1	28×10 ⁵
1.70	3.67	391	445	2±1	7.5×10 ⁵
1.80	3.00	391	436	4±1	7.7×10 ⁵
1.24	1.15	421	448	2±1	14×10 ⁵
1.62	1.27	427	451	1±1	6.6×10 ⁵

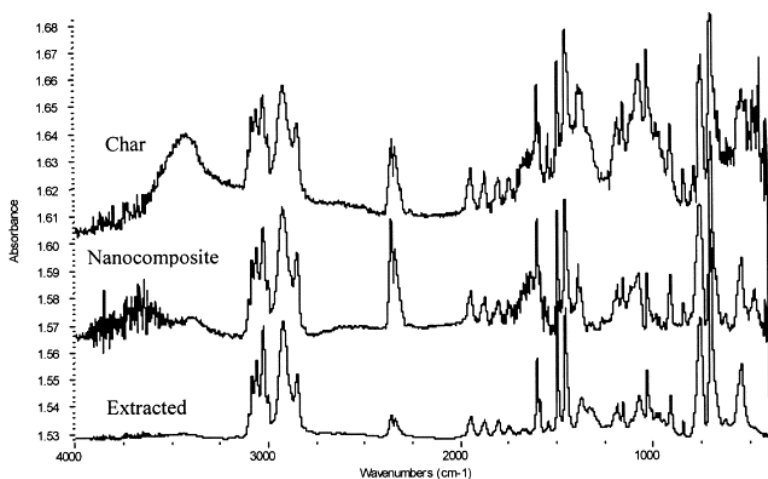


Fig. 6. Infrared spectra of extracted polystyrene (bottom), graphite/polystyrene nanocomposite (middle), and char of nanocomposite at 600 °C (top).

Blumstein has studied the polymerization of methyl methacrylate by adsorption onto montmorillonite clay [21], [22], [23], [24], [25], [26]. He observed that as monomer is adsorbed onto the surface there is an oriented growth of the polymer which results in a polymer that still possesses the memory of the monomer-substrate interactions and organization within the adsorbed layers. This was seen in the architecture and stereospecificity of the polymer. The polymer retained within the clay did not degrade under conditions where poly(methyl methacrylate) does undergo thermal degradation. When the polymer was extracted from the clay, it was observed to have a higher thermal stability than bulk polymerized poly(methyl methacrylate). It was suggested that the insertion polymer and the crystalline surface on which polymerization occurred may be replicas, i.e., the internally trapped monomer polymerizes replicating the surfaces on which it is adsorbed. This can be seen in the specificity of the polymer versus what would be expected. He suggests that isotactic triads were formed due to the templating effect of the clay cations. Therefore, the way in which a polymer is prepared will affect its properties, leading to what is called a “memory effect”.

Viscosity measurements have been performed on the extracted polymers to determine the molecular weight of polystyrene (Table 2). The viscometric molecular weights range from 1×10^5 to over 1×10^6 g/mol. This molecular weight is consistent with what has been previously reported for polymers initiated by potassium graphite and with the molecular weight determined for polystyrene prepared with potassium (5.2×10^5 g/mol). There does not appear to be any correlation between the amount of initiator and the molecular weight of the polymer.

Thermogravimetric analysis of the blends prepared with the Brabender mixer have similar onset temperatures of degradation and char formation (amount of non-volatile residue remaining in TGA pan) to those prepared by

method I (Table 3). The onset temperature is a little higher for the nanocomposite than for the blends but there is not a large difference. From XRD measurements, these blends do not show any expansion of the d-spacing of graphite so nanocomposites are not formed in the blending process. Perhaps the microdispersion in the blends offers the same barrier properties as observed in the nanocomposites with graphite. Very good dispersion of the clay is essential to obtain good thermal properties but this may not be essential for graphite.

Table 3. TGA data for blends

% C	T _{10%} (°C)	T _{max} (°C)	Char (%)
5.0	397	439	8±1
4.8	407	444	9±1
2.1	402	438	9±1
2.0	402	439	7±1

The TGA curves for representative nanocomposites prepared by all three methods are shown in Fig. 7 while the curves for a blend and a nanocomposite prepared in which all of the graphite comes from the initiator are shown in Fig. 8.

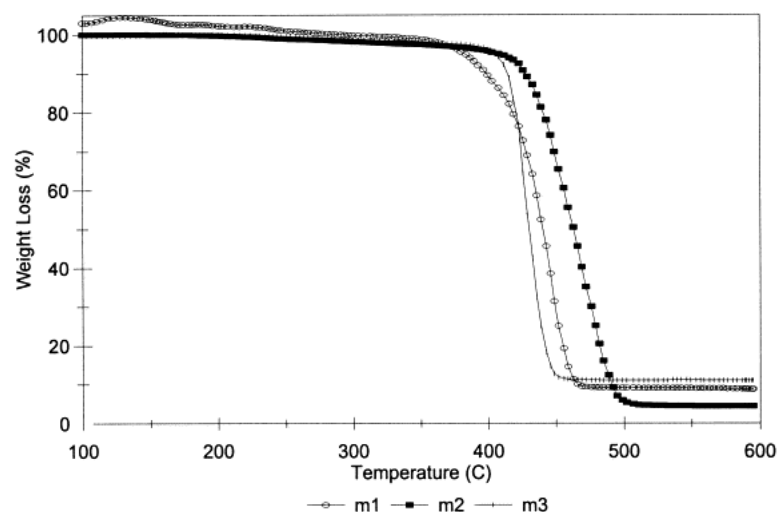


Fig. 7. TGA curves for polystyrene—graphite nanocomposites prepared by all three methods; the legends refers to the methods of preparation.

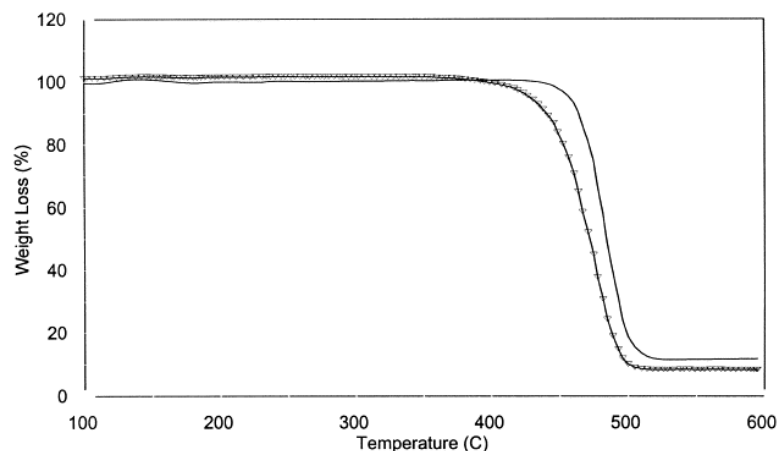


Fig. 8. Thermogravimetric analysis of blend (∇) and nanocomposite (—).

In comparing the methods of preparation, it is clear that the nanocomposite prepared by the addition of graphite during the polymerization has a slightly higher onset temperature and T_{max} than do the other preparative modes.

3.4. Cone calorimetry of the nanocomposites and blends

The graphite containing polymers were examined by Cone calorimetry and the results are shown in Table 4. From this data, one can see that the peak heat release rate, PHRR, for the graphite-containing polystyrene nanocomposites is lower than that of the virgin polystyrene, typically about 35% lower. The increased time to burnout and an overall decrease in mass loss and mass loss rate suggest that the graphite is acting to slow down the thermal degradation of the polystyrene. The specific extinction area (SEA, a measure of smoke produced) of the graphite-containing polymers is lower than for the virgin polymer. From these results, it appears that the graphite does introduce some stability to the polymer. The typical error in Cone measurements is $\pm 10\%$, based upon thousands of measurements [27]. The uncertainties reported in the tables of Cone data are within the typical range, indicating that these much larger samples avoid the sampling problem noted from the TGA data. For polystyrene-clay nanocomposites, the reduction in peak heat release rate, at the 3 and 5% clay level is about 50% so these graphite systems do not offer the same reduction as in the clay nanocomposites.

Table 4. Cone calorimetry results for nanocomposites

% KC ₈	t_{ignition} (s)	t_{PHRR} (s) ^a	PHRR ^a (kW/m ²)	Mean HRR ^a (kW/m ²)	Avg. SEA ^a (m ² /kg)	Mass loss %	Mass loss rate (mg/s)
Method I—all graphite from initiator							
PS	35	165	1024	479	1572	86.0	127
5.08	33±4	197±0	635±14	332±10	1193±133	80.0±2.5	107±1
4.17	25±0	190±17	670±36	352±10	976±36	82.7±1.8	114±6
3.26	30±7	181±3	665±13	352±19	1034±26	84.9±2.6	108±1
1.10	28±11	183±0	668±20	376±15	1009±18	82.5±3.1	110±1
Method II—additional graphic added during polymerization							
1	30±7	169±0	579±29	308±34	815±111	80.7±4.4	98±2
3	22±10	170±2	669±47	308±19	906±34	84.2±2	119±3
5	22±3	175±8	710±25	449±34	1033±13	84.2±2.1	118±2
Method III—additional graphite added post reaction							
1	22±10	187±12	682±30	352±24	1006±20	87.2±8.8	115±8
3	22±10	182±8	657±30	332±34	927±63	85.5±0.1	119±2
5	8±3	169±27	657±41	332±34	908±90	81.6±3.2	113±4

t_{ignition} , Time to ignition; t_{PHRR} , time to peak heat release rate; PHRR, peak heat release rate; Mean HRR, mean heat release rate; SEA, specific extinction area (a measure of the amount of smoke released).

The heat release rate for the blends (Table 5) is slightly higher than that of those prepared by method I, but, still significantly lower than that of virgin polystyrene. Also observed is a slightly higher mass loss for the blends than for method I, suggesting that the polymers prepared by method I may have somewhat higher stability.

Table 5. Cone calorimetry data for the blends

%KC ₈	% C	t _{ignition} (s) ^a	t _{PHRR} (s) ^a	PHRR ^a (kW/m ²)	Mean HRR ^a (kW/m ²)	Avg. SEA ^a (m ² /kg)	Mass loss (%)
PS		35	165	1024	479	1572	86
Blends	5	35	190	702	381	1008	84
	4.8	30	182	727	342	918	84
	2.1	30	178	693	352	950	85
	2.0	30	167	762	361	974	87

a_{t_{ignition}}, Time to ignition; t_{PHRR}, time to peak heat release rate; PHRR, peak heat release rate; mean HRR, mean heat release rate; SEA, specific extinction area (a measure of the amount of smoke released).

The heat release rate data is presented in graphical form for all modes of preparation and blends in Fig. 9. For all systems the peak heat release rate is reduced, but not as much as seen in the typical polystyrene-clay nanocomposite [19]. It is of interest to note that the shape of the peaks is quite different for these materials when compared to polystyrene-clay nanocomposites. For the clay systems, the heat release rate curve rises very quickly and stays at a somewhat high level for most of the time. On the other hand, in these graphite systems the curve rises slowly and this can be seen by the reduction in the mean heat release rate.

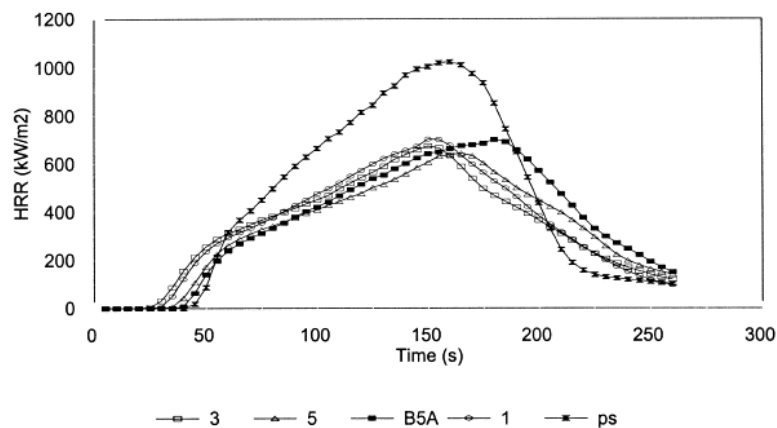


Fig. 9. Heat release rate curves for nanocomposites and blends compared to virgin polystyrene. Samples 1, 3, and 5 refer to nanocomposites containing that amount of graphite while sample B5A is a blend containing 5% graphite.

3.5. Mechanical properties

The mechanical properties of clay-polymer nanocomposites are increased relative to that of the virgin polymer, and this is especially true for exfoliated materials. In work from this laboratory, we have observed a 300% increase in strength at break along with a 45% increase in elongation at break for an exfoliated clay nanocomposite. An intercalated polystyrene-clay nanocomposite gives 120% increase in strength at break with no change in elongation at break [28]. Fig. 10, Fig. 11 display the elasticity modulus and tensile strength, respectively, as a function of the amount of graphite for all methods of preparation compared to commercial polystyrene. The tensile strength and elasticity modulus are lower for the nanocomposites compared to commercial polystyrene. As the amount of graphite increases, there is a decrease in mechanical properties. Increasing the amount of graphite appears to help the thermal stability, but it detracts from the performance of the polymer.

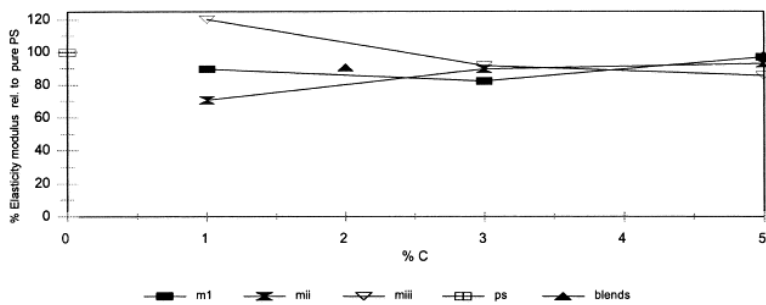


Fig. 10. Elasticity modulus as a percentage compared to commercial polystyrene.

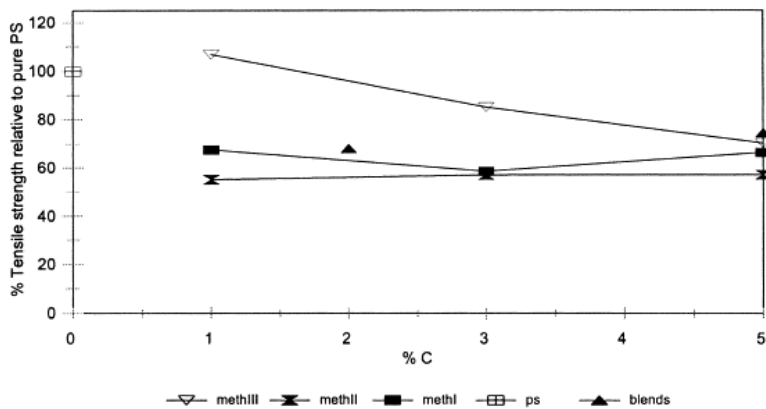


Fig. 11. Tensile strength as a percentage compared to commercial polystyrene.

4. Conclusions

Polymers of very high molecular weight are produced when potassium graphite is used as an initiator. Nanocomposites may be prepared in which all of the carbon comes from the initiator or by the addition of graphite after the reaction has commenced. There is a larger effect on thermal stability when additional graphite is added. The thermal stability, as measured by TGA, is slightly better for nanocomposites than for blends and the same is also true of fire properties, as measured by Cone calorimetry. Gilman and Nyden have stated that the “nanocomposite effect” is best when the graphite layers are separated by about 3 nm^[2].

The separation in this study, has been only one-half of this value. Our results show that intercalated nanocomposites have been formed and an increase in thermal stability is observed; this is in accord with work done by Nyden and Gilman, where an increase in thermal properties should be observed for intercalated structures. The use of clay nanocomposites as fire retardants is unique in the fact that not only is an enhancement in thermal properties observed but also an increase in mechanical properties. Unfortunately a decrease in mechanical properties is observed for these nanocomposites. Further work will attempt to increase the spacing to see if this has an effect.

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