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Abstract

Synthetic polymer materials are rapidly replacing more traditional inorganic materials such as metals and natural polymeric materials such as wood. Since these novel materials are flammable, they require modifications to decrease their flammability through the addition of flame-retardant (FR) compounds. Recently, environmental regulation has restricted the use of some halogenated FR additives, initiating a search for alternative FR additives. Nanoparticle fillers are highly attractive for this purpose since they can simultaneously improve both the physical and flammability properties of the polymer nanocomposite. We show that carbon nanotubes can surpass nano-clays as effective FR additives if they form a jammed *network structure* within the polymer matrix, such that the material as a whole behaves rheologically like a gel. We find this kind of network formation for a variety of highly extended carbon-based nanoparticles: single and multi-walled nanotubes, as well as carbon nanofibers.

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Nanoparticle Networks Reduce the Flammability of Polymer Nanocomposites*

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Synthetic polymer materials are rapidly replacing more traditional inorganic materials such as metals and natural polymeric materials such as wood. Since these novel materials are flammable, they require modifications to decrease their flammability through the addition of flame-retardant (FR) compounds. Recently, environmental regulation has restricted the use of some halogenated FR additives, initiating a search for alternative FR additives. Nanoparticle fillers are highly attractive for this purpose since they can simultaneously improve both the physical and flammability properties of the polymer nanocomposite. We show that carbon nanotubes can surpass nano-clays as effective FR additives if they form a jammed *network structure* within the polymer matrix, such that the material as a whole behaves rheologically like a gel. We find this kind of network formation for a variety of highly extended carbon-based nanoparticles: single and multi-walled nanotubes, as well as carbon nanofibers.

Typically, the burning process of a polymer material begins with heating to a temperature at which thermal degradation initiates. The boiling temperatures of most of

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the thermal degradation products of polymers are much lower than thermal degradation temperatures of thermoplastics and the degradation products are then superheated as they form¹. Bubbles nucleate below the heated polymer surface and grow with the supply of more degradation products by diffusion from the surrounding molten plastic² and they further evolve into the gas phase as fuel vapor. These bubbles agitate the outer layer of polymer melt and can interfere with the formation of a solid, char-like heat transfer barrier at the boundary¹. It has been recognized that the use of nanoscale reinforcing fillers, such as nano-clay particles, can help to reduce the flammability of polymer materials by inhibiting this vigorous bubbling process in the course of degradation during combustion¹. The addition of these filler particles often leads to the added benefit of enhancing the physical properties of nanocomposites relative to the polymer matrix^{3,4,5}. On the other hand, this flame retardant effect is not general for all nanocomposite additives. We previously found that poly(methyl methacrylate) PMMA/nanocomposites of nanosilica (13 % mass fraction) exhibited vigorous bubbling during burning as in unfilled materials, leading ultimately to a residue consisting of granular, coarse particles⁶. The effect of these symmetric nanoparticles on flammability was only marginal for this class of fillers. In contrast, nanocomposites based on nano-clay particles formed a continuous protective solid layer on the burning surface or extended island structures made of clay and carbonaceous char during burning^{7,8,9,10} (Several review papers are available that describe the FR effect of these additives^{11,12,13,14}). The presence of the protective layer clearly plays an important role in the flammability reduction by these additives, but these clay particle layers tend to develop large lateral surface cracks in which vigorous bubbling still occurred¹⁵. These extended nanoparticles are clearly

promising flame retardants, but further studies are needed to improve the effectiveness of this type of filler and to understand the physical factors responsible for this flame retardant effect.

Polymer nanocomposites with low levels of single-walled carbon nanotubes (SWNT)^{16, 17, 18, 19}, multi-walled carbon nanotubes (MWNT)^{20, 21, 22, 23, 24}, or carbon nanofibers (CNF)^{25, 26, 27, 28} show significantly increased mechanical properties and electrical conductivity and similarly to clay they have a highly extended structure. Thus, carbon-based nanoadditives provide an additional type of nanoparticle to be examined for potential FR application. The combination of nanotubes with clay particles provide another class of materials worth exploration as FR additives^{29,30}.

We previously found that nanocomposites based on carbon nanotubes are likewise capable of forming a continuous network-structured protective layer *without* the formation of cracks that compromise the FR effectiveness. This resulted in a significant reduction in heat release rate (a flammability measure related to the fire intensity) with a carbon nanotube mass concentration as low as 0.5 %^{31,32,33}. This protective layer mainly consisted of carbon nanotubes and it appeared to act as a heat shield for the virgin polymer below the layer^{32,33,34}. Poorly dispersed carbon nanotubes resulted in the formation of a discontinuous layer consisting of fragmented islands (with sizes from one to 10 mm) rather than the continuous network protective layer³³. Very low concentrations of the tubes yielded the same fragmented island structures as found in the clay nanocomposite measurements. The FR performance of the nanocomposites containing the island structures was much poorer than that of the nanocomposites forming a *continuous* protective network layer. Thus, the formation of the network-structured

protective layer during burning, without any openings or cracks, seems to be crucial for the large reduction in heat release rate. In the present study, we hypothesize that this network forms within the original sample under appropriate fabrication conditions and that this structure provides the main source of the protective layer that forms during the burning process. This hypothesis is systematically tested with various sizes and concentrations of carbon-based nanoparticles in a PMMA matrix.

The selected nanoparticles all had a common carbon chemistry: SWNT, MWNT, and CNF. The effects of the size of the tubes on the physical structure of the protective layer and on the FR effectiveness were determined. Carbon black particles (CB) were also included for comparison to gain insight into the role of particle anisotropy in the FR effect.

A selected sequence of video images of a sample during gasification tests is shown in Figure 1 for an external radiant flux of 50 kW/m^2 in nitrogen (no flaming but sample heating similar to fire conditions). The PMMA had a viscosity average nominal molecular mass of 100,000 g/mol and the mass fraction of SWNT, MWNT, CNF and CB was 0.5 % in each case. Pristine PMMA behaved like a liquid with vigorous bubbling and no residue was left in the container at the end of the test. The PMMA/SWNT(0.5 %) nanocomposite was solid-like and did not exhibit noticeable bubbling except for a short period after initial exposure to the external radiant flux. The final residue, though having a slightly undulating surface, had no deep cracks and was slightly thinner than the thickness of the original sample. The residue mainly consisted of SWNTs with a network structure that was porous, transmitting about 20 % of the external radiant flux through its the about 6 mm thick layer³³. On the other hand, numerous small island structures (black

spots in Figure 1c) were formed in the case of the PMMA/MWNT(0.5 %) and the islands coagulated with the progress of the test, leading to the formation of large islands having many deep cracks. Vigorous bubbling was observed through the cracks between the islands. Both the PMMA/CNF(0.5 %) and the PMMA/CB(0.5 %) formed slightly viscous liquids with vigorous bubbling occurring under heating. A thin, small, coagulated, network-like residue was left at the bottom of the container for the PMMA/CNF(0.5 %) and a thin black coating over the container surface with several small islands was left after the test for the PMMA/CB(0.5 %), as shown in Figure 1e.

The mass loss rate of each sample tested in the gasification test was calculated by taking the time derivative of the measured sample mass history; the results are plotted in Figure 2. Only the PMMA/SWNT(0.5 %) formed the network-structured layer which suppressed bubbling; its mass loss rate was the least among the five samples, followed by the PMMA/MWNT(0.5 %). Mass loss rates of both the PMMA/CNF(0.5 %) and the PMMA/CB(0.5 %) were not appreciably different from that of the pristine PMMA. From these observations, we clearly see that the formation of a network-structured protective layer during burning is crucial for the improvement in flammability properties.

In order to validate the hypothesis that a jammed network is formed in the initial samples, we performed viscoelastic measurements on the samples as a function of particle type and concentration. The viscoelastic properties of the PMMA nanocomposites containing SWNT, MWNT, CNF, or CB are presented in Figure 3 for a range of filler mass fractions. The storage modulus G' provides a measure of nanocomposite 'stiffness' and its frequency dependence characterizes whether the material is in a liquid-like or solid-like state²⁴. At 200 °C and low frequencies, the

PMMA/CB composites have nearly the same rheological response as pure PMMA, regardless of the CB concentration, exhibiting the typical rheological response of a Newtonian liquid behavior with $G' \sim \omega^2$ at low frequencies. This scaling was also observed for PMMA/CNF nanocomposites with intermediate concentration loading (i.e., 1 %) and for nanocomposites with low loadings of these tubular fillers (i.e., 0.1 %). However, for the composites containing a higher concentration of these extended fillers, this liquid-like low frequency scaling of G' disappeared and G' became nearly *constant* at low frequencies. This indicates a transition from a Newtonian liquid to an ideal Hookean solid, which accompanies the formation of a mechanically stable network structure^{24, 35} ('jammed network' or 'dispersion gel')³⁶. We term the composition at which this rheological state is achieved the "gel concentration", ϕ_g . Specifically, we define ϕ_g as the concentration at which G' becomes independent of ω for an extended low frequency range.

Besides the filler type and loading, the filler dimension also had a significant effect on the rheological response of the nanocomposite. With the same 0.5 % filler loading, the SWNT nanocomposite had solid-like behavior, while the MWNT nanocomposite had a much reduced elastic response as indicated by the smaller G' at low frequencies relative to the SWNT nanocomposite, while the CNF nanocomposite exhibited only a liquid-like behavior. An increase in the concentration of MWNT and CNF from 0.5 % to 1 % and 0.5 % to 4 %, respectively, both yielded a gel-like rheological response for both MWNT and CNF nanocomposites. Our estimate of ϕ_g has the same order of magnitude as previously reported values of the percolation concentration for electrical conductivity

(0.26 vol%³⁷ with SWNT and 1 %²⁴ and 2 %³⁸ with MWNT), but our nanoparticle concentration is much less than the reported percolation threshold (between a mass fraction of 10 % and 20 %) for CNF³⁹. The addition of CB for the concentration range considered in this study did not lead to dispersion gelation. A relatively high percolation concentration of 9 vol % has been reported for CB⁴⁰.

Previous work has shown that there should be a general tendency of ϕ_g to decrease with decreasing tube diameter in this class of extended particles³⁶. We can roughly understand this trend from the increase in the interfacial area and for tubes of a smaller diameter. It is estimated that the interface areas of the MWNTs and the CNFs are about 70 % and about 10 % of that of the SWNTs, respectively, in 0.5 % mass fraction of each type of tubes in PMMA. The fact that the SWNT tends to form bundles/ropes of nanotubes mitigates the effect of having a small ratio of the SWNT diameter to the diameter of the MWNT to some extent. The relationship between flammability properties and the total interfacial area is discussed in Supplemental Information.

The results of the gasification experiments with various concentrations of SWNT, MWNT, and CB in PMMA are shown in Figure 4 a. The PMMA/SWNT(0.2 %), which did not form gelled nanocomposites (see Figure 3), formed island structures (Figure 4 b(a)) rather than a continuous network protective layer. Its mass loss rate was also much higher than that of the PMMA/SWNT(0.5 %) which formed a continuous protective layer. The PMMA/MWNT(1 %) and the PMMA/CNF(4 %) also formed a network layer (Figure 4 b (b) and 4 b (c), respectively) and their mass loss rates were at least as low as that of the PMMA/SWNT(0.5 %). However, the PMMA/CB(4 %) formed a thin layer consisting of the accumulation of a large amount of coagulated granular particles.

Additionally, bubbling was observed between the granular particles; this sample's mass loss rate was as high as that of the PMMA/SWNT(0.2 %).

These observations indicate that a large reduction in nanocomposite flammability requires a sufficient nanoparticle concentration ϕ_g to form a jammed network within the polymer network. We next quantify how this flammability reduction depends on ϕ to show the transition between the low flammability reduction regime for small ϕ and the high flammability reduction regime for large ϕ . We normalize the nanoparticle concentration by ϕ_g for each type of nanoparticle. From Fig. 3 we estimate $\phi_g = 0.5\%$ for SWNT, 1% for MWNT, and 4% for CNF. Although the CB concentration used in this study was not sufficient for gelation, we chose a relatively large concentration of this filler ($\phi_g = 9\%$) to compare with the extended nanoparticle additives. The relationship between the normalized concentration of nanoparticles and the normalized peak mass loss rate is shown in Figure 5. The peak mass loss rate m''_{peak} is related to the peak heat release rate that is a key flammability measure. This figure shows that an increase in the total surface area sharply decreases the peak mass loss rate until the nanocomposite reaches the critical composition ϕ_g . Then, it appears that a further increase in the concentration of the nanoparticle does not significantly affect the mass loss rate. (Actually, a further increase in the concentration of MWNT in polypropylene increased the peak heat release rate probably due to an increase in thermal conductivity of the nanocomposites³².) These results confirm that achieving ϕ_g in the initial sample is critical for obtaining maximally reduced flammability properties. It appears that the network structure in the initial sample remains intact during burning, though it was somewhat compacted after the PMMA was degraded and its degradation products were gasified.

The integrity of the network at high temperatures can be expected to be influenced by the molecular mass of the polymer matrix. We thus examine the effect of molecular mass, M_w , of the resin on the flammability properties of carbon-based nanocomposites. In particular, we anticipate that a high M_w resin (high viscosity) enhances the formation of the network layer through entanglement of the polymer chains with the nanotube bundles³³. The low M_w resin (low viscosity) should have a reduced network integrity due to the destabilizing effect of the formation and convective motion of bubbles in the molten nanocomposite under burning condition³⁴. The movement of nano-clay particles induced by bubbles was observed in previous measurements on the gasification of polyamid 6 – clay nanocomposites¹⁵. Similar effects could occur for the extended carbon-based nanocomposites if the integrity of the network is not sufficiently strong to resist the movement of bubbles. In order to examine the effects of M_w on the formation of a network and on flammability properties, PMMA nanocomposites (25,000 g/mol and 350,000 g/mol) were prepared with SWNTs; these were subjected to the rheological analysis. The G' of the PMMA(350k)/SWNT(0.2%) was roughly an order of magnitude larger than that of the PMMA(100k)/SWNT(0.2%) and it also showed a weak dependency on frequency in the range of low frequencies ($< 10^{-1}$ rad/s). The G' of the PMMA(25k)/SWNT(0.5%) was roughly an order of magnitude less than that of the PMMA(100k)/SWNT(0.5%) and showed nearly same dependency on ω as the PMMA(100k)/MWNT(0.5%).

The measured mass loss rates of the PMMA(350k)/SWNT(0.2%) and the PMMA(25k)/SWNT(0.5%) are plotted in Figure 6, including the PMMA(100k)/SWNT(0.2%) from Figure 4 and the PMMA(100k)/SWNT(0.5%) from

Figure 2 for comparison. Mass loss rates of the nanocomposites with higher $M_w=350k$ PMMA were clearly lower than those with lower $M_w=100k$ PMMA. Even with 0.2 % of SWNT, the nanocomposites with $M_w=350k$ PMMA formed a very wavy, network-structured layer during burning compared to the formation of islands for $M_w=100k$ PMMA. At a mass fraction of 0.5 % of SWNT, the nanocomposite with $M_w=25k$ PMMA formed a network layer, but its mass loss rate was about 20 % higher than that of the nanocomposite with $M_w=100k$ PMMA as shown in Fig. 6. Although the nanocomposites having the characteristic composition of ϕ_g are required for significantly reducing flammability properties, it appears that there is no direct correlation between G'_p (plateau in G' at low frequencies) at ϕ_g and the extent of flammability reduction with the nanoparticles. For example, the mass loss rate of the PMMA(100k)/SWNT(1%) was about the same as that of the PMMA(100k)/SWNT(0.5%) even though the former G'_p at ϕ_g was about four times higher than the latter G'_p . Furthermore, the PMMA(100k)/CNF(4%) nanocomposite has the lowest mass loss rate, but its G'_p at ϕ_g was lower than those of PMMA/SWNT(1%) and PMMA/MWNT(1%) at ϕ_g .

The propensity to form jammed network structures from extended nanoparticles should not be limited to tubular shape additives and in future work we plan to examine our network hypothesis for the reduced flammability of polymer nanocomposites in the case of clay (plate) and carbon sheet additives. We also plan to investigate the role of particle flexibility and size polydispersity on the critical concentration ϕ_g describing the gel concentration. Finally, we point out that our observation suggest that we screen for promising flame retarded polymer nanocomposites by performing viscoelastic measurements on the initially fabricated samples.

Methods

The matrix polymer is PMMA (Polyscience[#]). The SWNTs were synthesized by HiPCo and provided from Carbon Nanotechnologies Incorporated and Foster Miller Company. The MWNTs were purchased from Nano Laboratory and the CNFs (PR-I) were purchased from Applied Science Incorporated. The CBs were N299 provided by Sid Richardson Carbon Company. The coagulation method was used to produce all samples³⁵. Dimethylformamide (DMF) was chosen to dissolve the PMMA and to permit dispersion of the particles by sonication for 24 h. Concentration of 0.2 mg/ml (particles/DMF) was used to make all samples with good dispersion of the particles in the sample. Rheology measurements were performed on a Rheometric Solid Analyzer (RSAII) in oscillatory shear with a sandwich fixture. Samples 12.5 mm × 16 mm × 0.5 mm were run at 200 °C with a strain of 0.5 %. Results were reproducible after one frequency sweep, indicating that there was no chain degradation or additional filler alignment during measurement.

A radiant gasification apparatus was designed and constructed at NIST to study the gasification processes of samples (75 mm diameter with 8 mm thick) by measuring sample mass and recording the sample behavior using a video camera. The apparatus consists of a stainless-steel cylindrical chamber that is 1.70 m tall and 0.61 m in diameter. All tests were conducted at 50 kW/m² in nitrogen; more detailed discussion of the apparatus is given in our previous study⁴¹. The standard uncertainty of the measured mass loss rate is ± 10 %. The peak mass loss rate m''_{peak} is related to the peak heat release rate that is a key flammability measure. One peak was observed without the formation of a protective network layer, while two peaks were observed with samples having a jammed network, as shown in Figures 2 and 4 a. The second, late stage peak occurs after the formation of the protective network layer and in this case we chose this peak to define m''_{peak} .

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Competing financial interests

The authors declare that they have no competing financial interests.

[#] Certain commercial equipment, instruments, materials, services or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.

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Figure legends

Figure 1. Selected sequences of sample behavior during the gasification and collected residues. Top two rows are sample behavior and the bottom row consists of pictures of the residues. The nanocomposite samples were PMMA with 0.5 % mass fraction of each nanoparticle. The tests were conducted at 50 kW/m^2 in nitrogen.

Figure 2. Effects of the nanoparticle type on mass loss rate. The tests were conducted at external radiant flux of 50 kW/m^2 in nitrogen.

Figure 3. Effects of the nanoparticles type and concentration on the viscoelastic measurements. The sample with solid symbols shows a gel behavior at low frequencies.

Figure 4. Effects of the nanoparticle type and concentration on mass loss rate and the configuration of the residues. The tests were conducted at external radiant flux of 50 kW/m^2 in nitrogen. (a) mass loss rate and (b) pictures of the residues.

Figure 5. Relationships between normalized peak mass loss rate and normalized concentration of nanoparticles. Mass loss rates were measured at 50 kW/m^2 in nitrogen. The peak mass loss rate is normalized by the peak mass loss rate of PMMA. The concentration is normalized by the concentration of ϕ_g at which Hookean solid gel is formed. The relationship of $m''_{\text{peak}}/m''(\text{PMMA})_{\text{peak}} \approx 1 - (2/3)(\phi/\phi_g)$ provides a fair representation of our data for the pre-gel concentration range, $0 \leq \phi/\phi_g < 1$.

Figure 6. Effects of M_w of PMMA on mass loss rate. The tests were conducted at external radiant flux of 50 kW/m^2 in nitrogen.

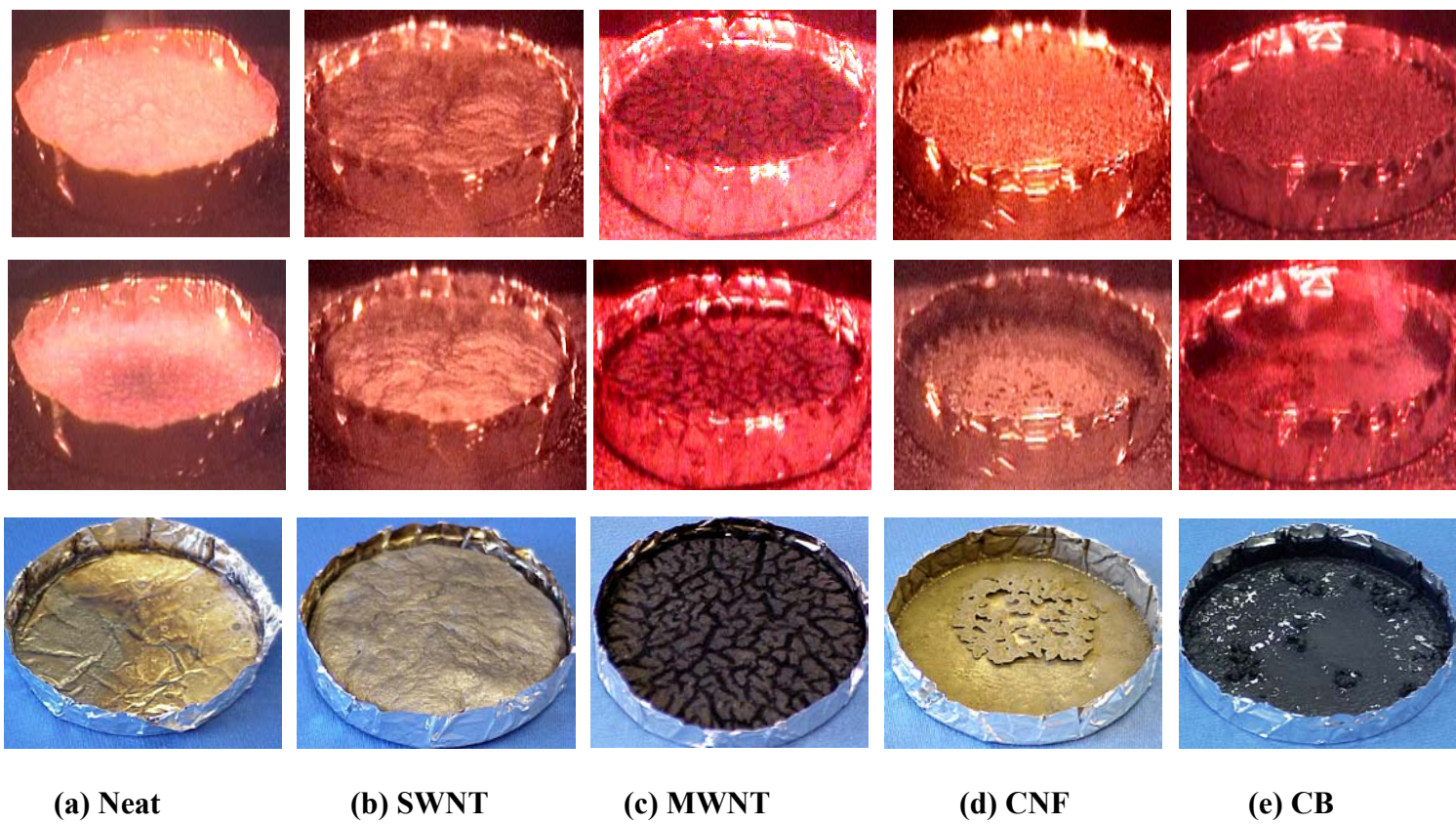


Fig. 1

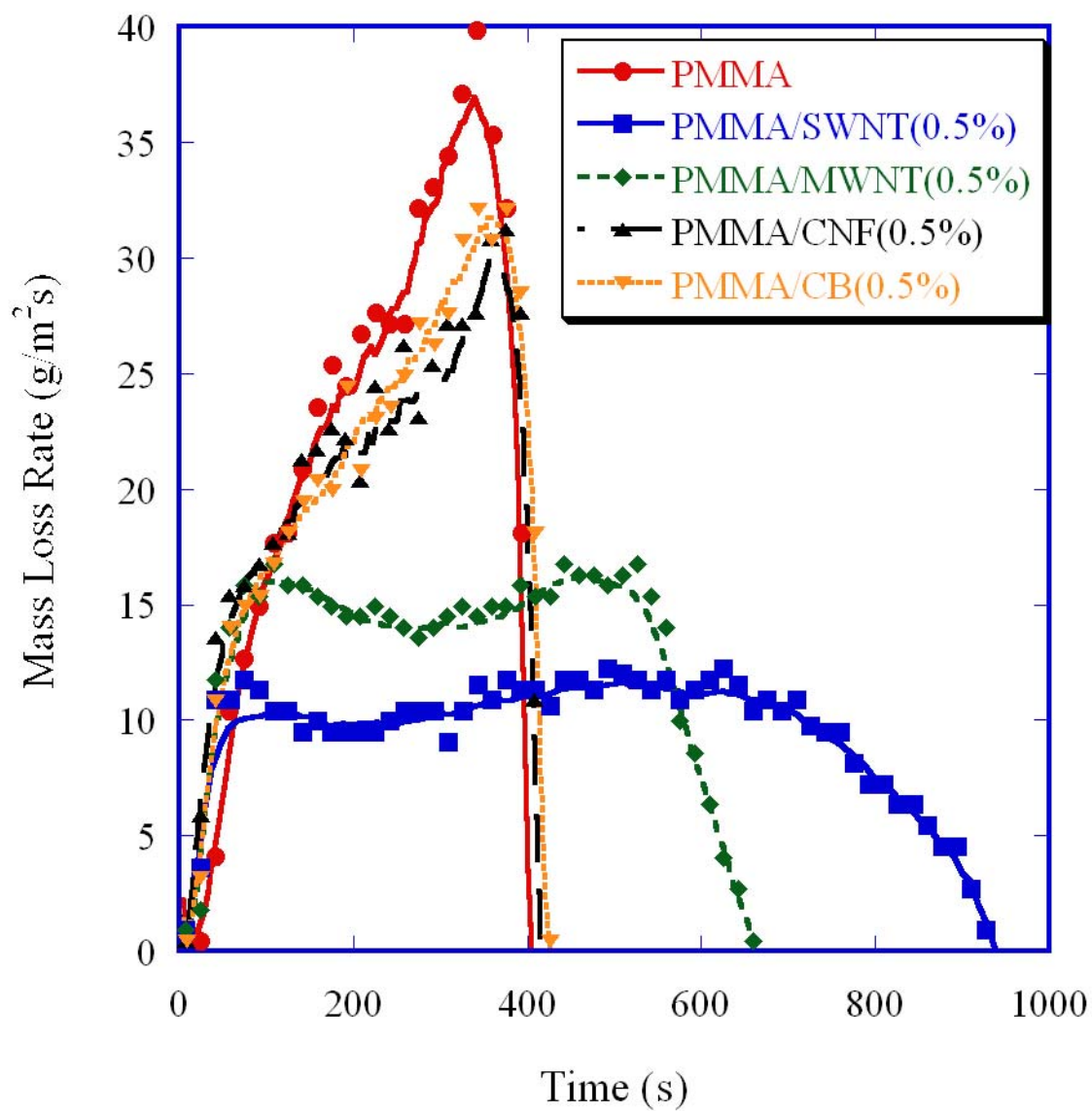


Figure 2.

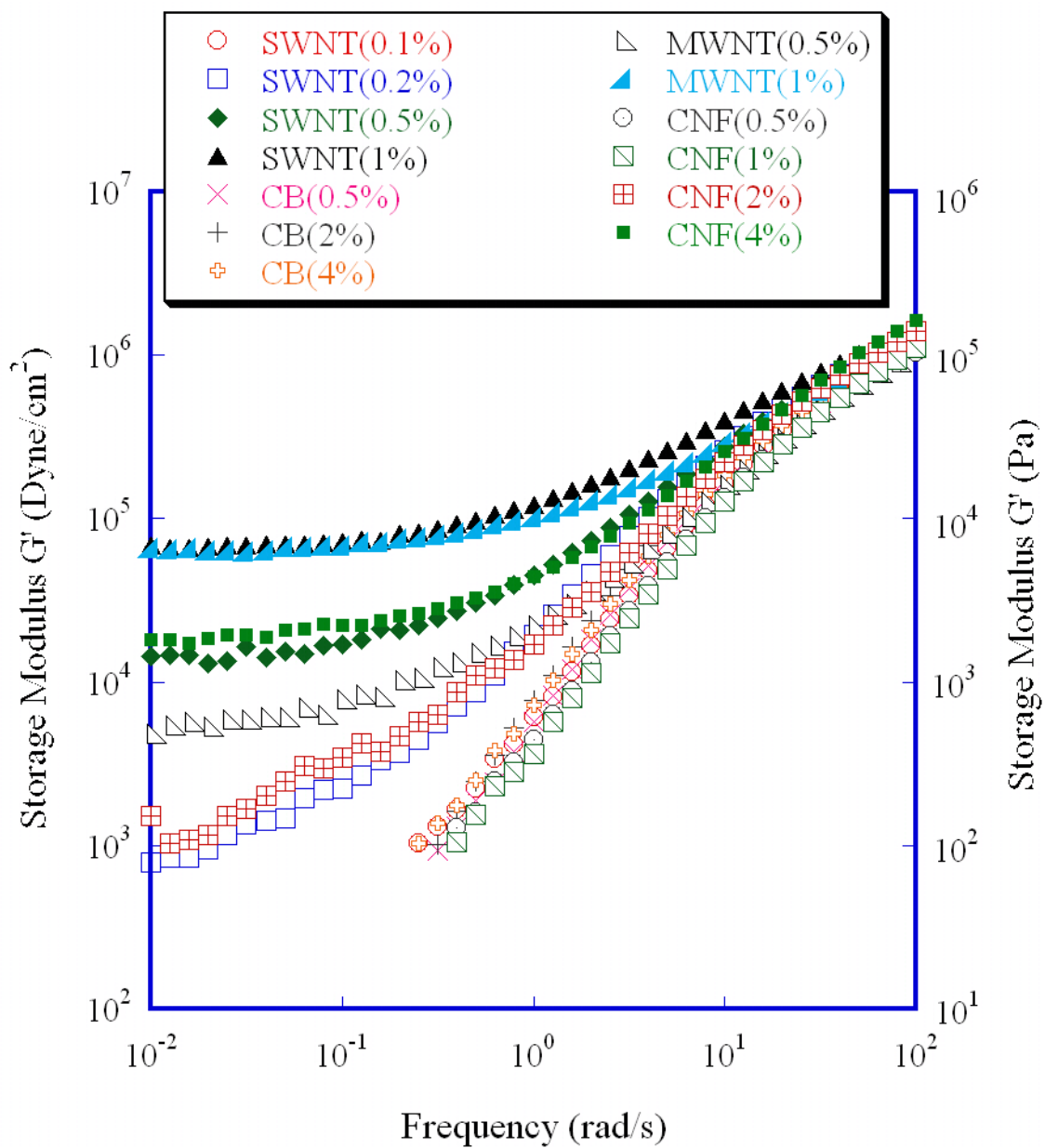


Figure 3.

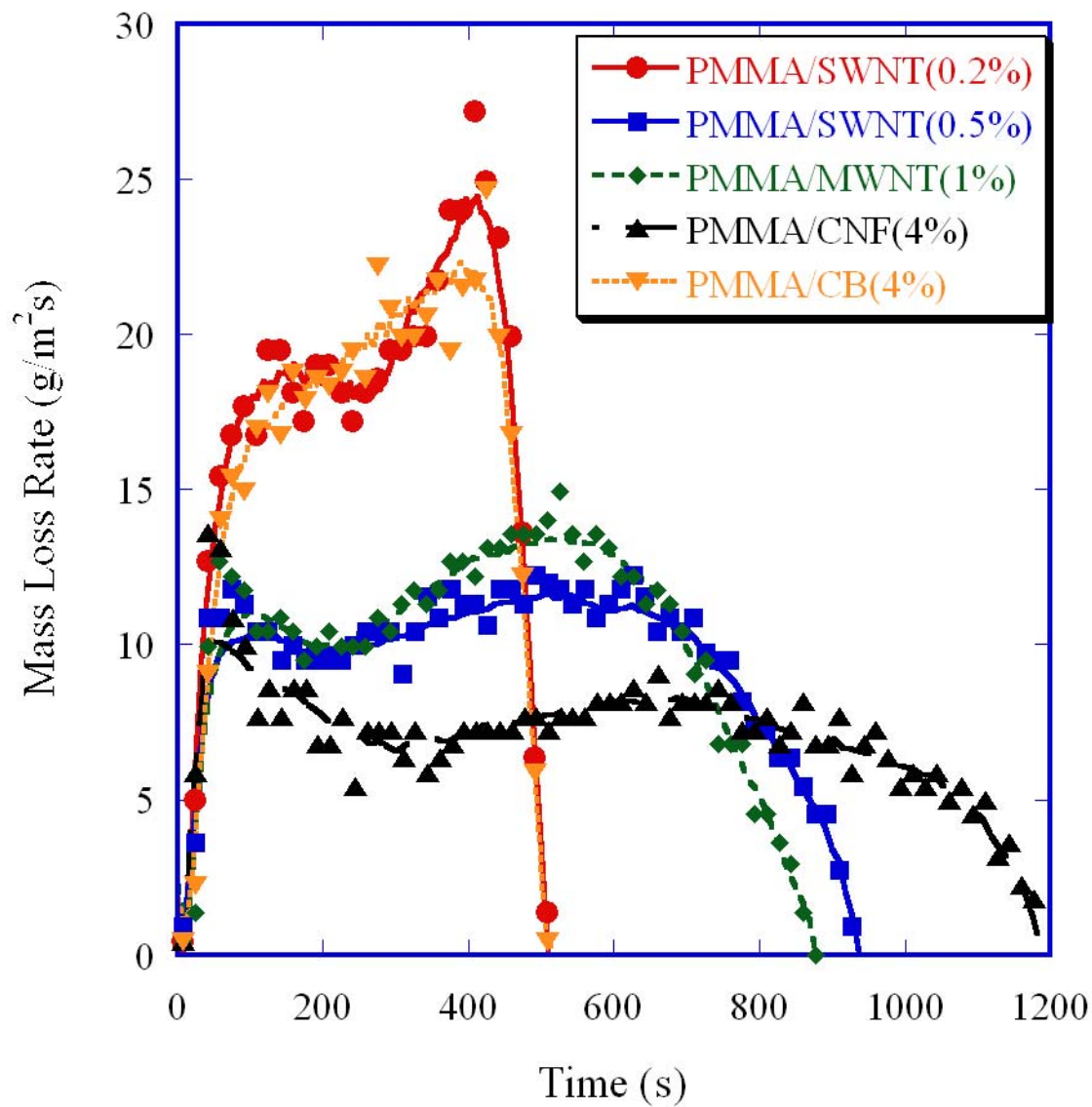


Figure 4a.

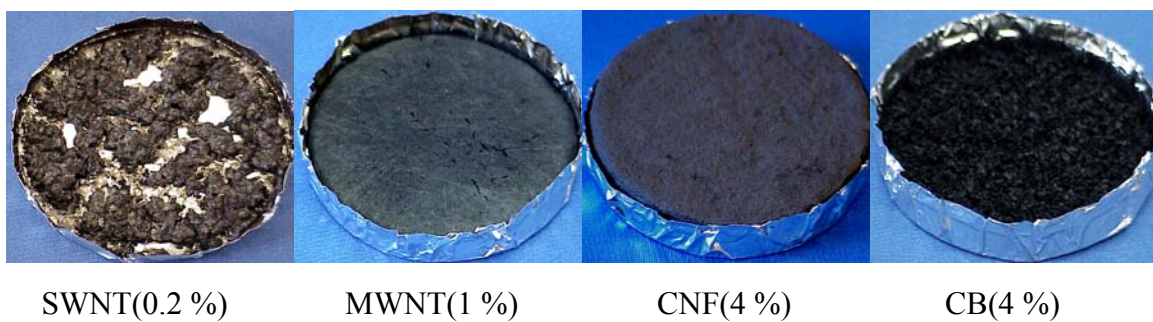


Figure 4 b.

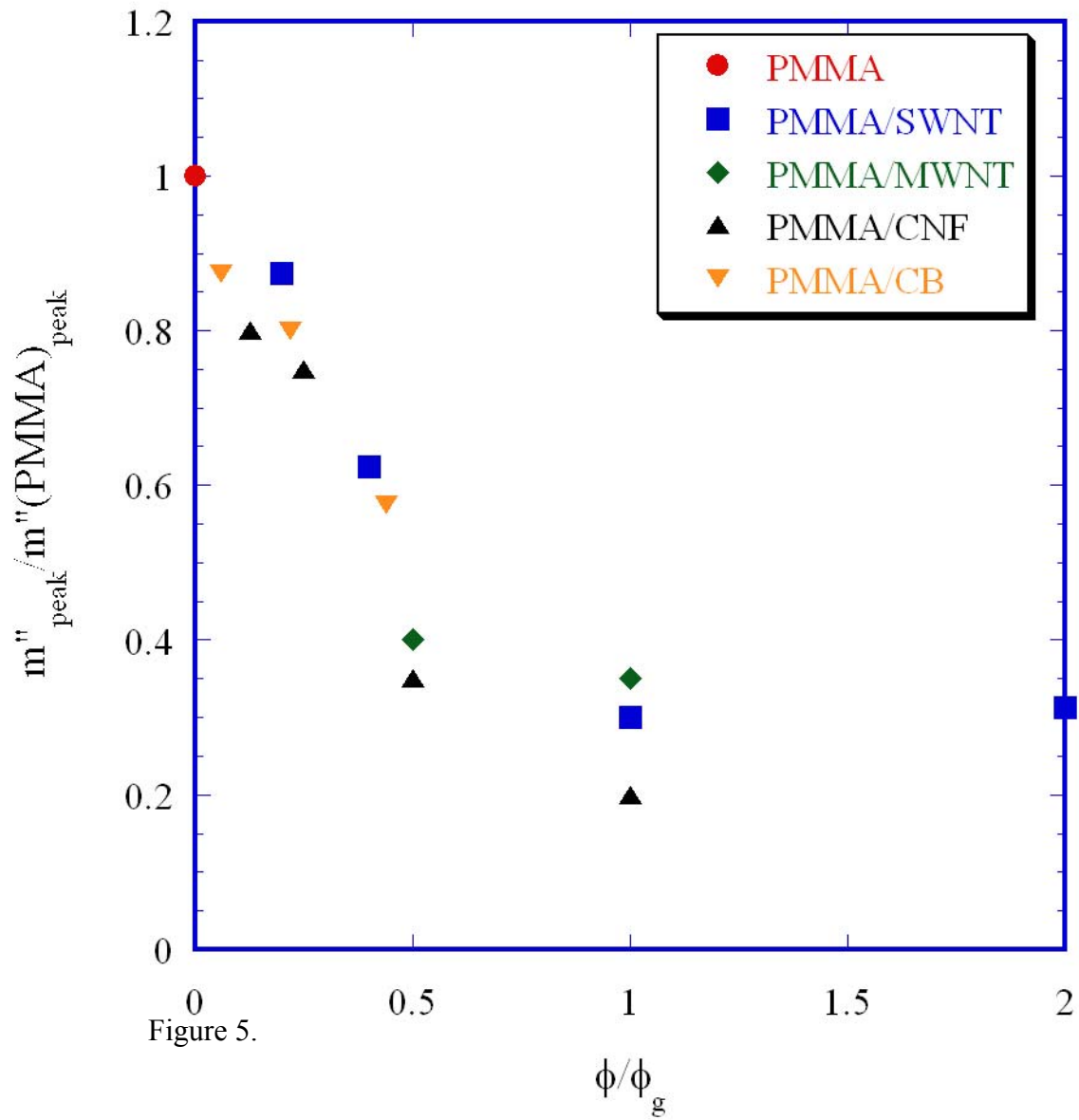


Figure 5.

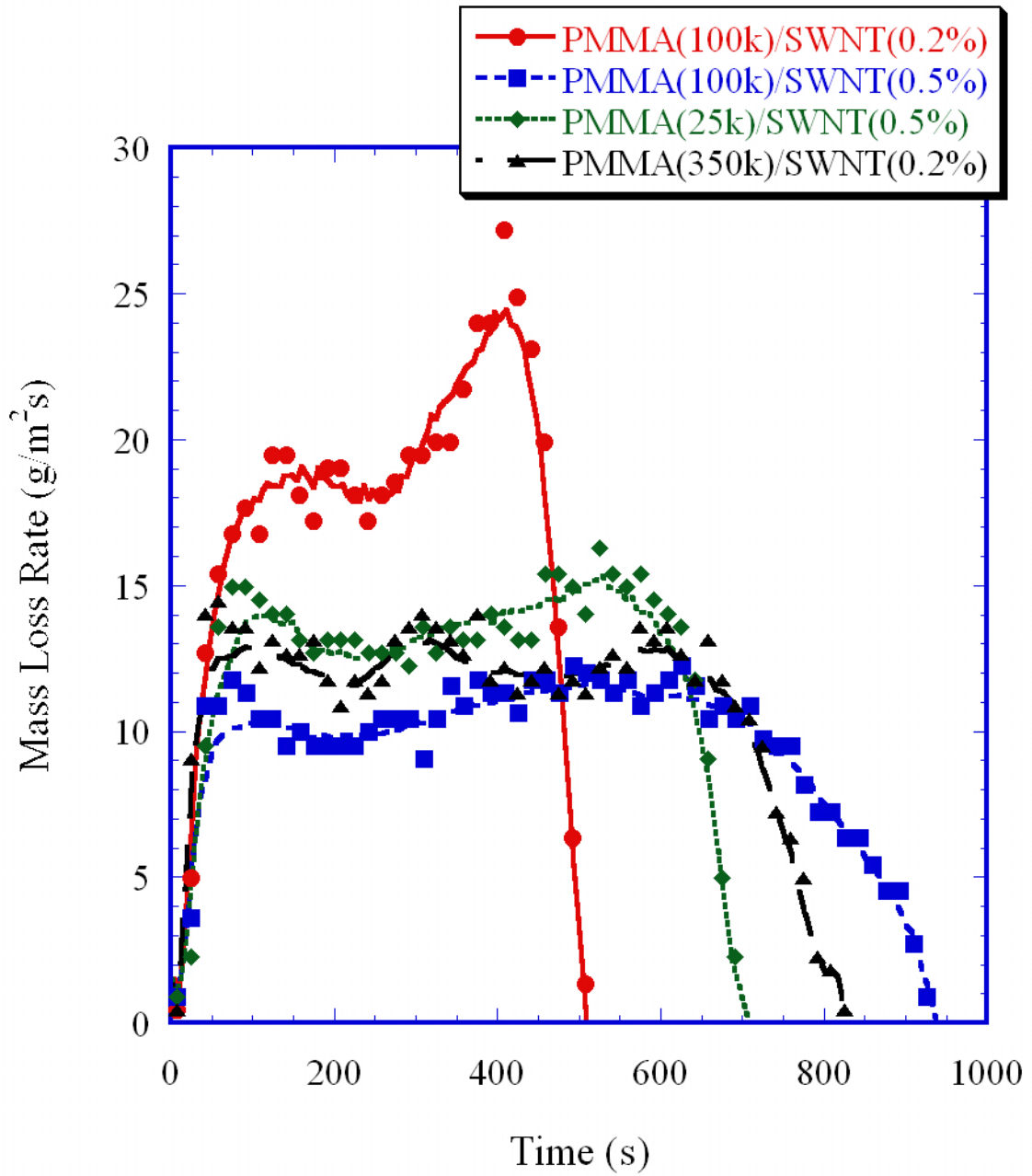


Figure 6.