



# Effect of trimethylolpropane triacrylate cross-linkages on the thermal stability and char yield of poly (methyl methacrylate) nanocomposites

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## ABSTRACT

Using an *in-situ* polymerization method, poly (methyl methacrylate) (PMMA) cross-linked by trimethylolpropane triacrylate (TMPTA) was embedded with nanosilica, aluminum oxide, or modified montmorillonite to produce various cross-linked nanocomposites. The same three nanofillers were also embedded into PMMA without TMPTA cross-linkages to quantify the effect of TMPTA cross-linkages on the thermal stability and char yield of nanocomposites. Data from Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric Analysis (DTG) were used to show that cross-linking and nanofiller content act synergistically to improve the thermal stability of PMMA, increasing the on-set of degradation by nearly 100 °C. The increase in thermal stability was attributed to the elimination of low temperature end initiated polymer unzipping by TMPTA cross-linkages and simultaneous stabilization of remaining degradation reactions due to nanofiller content. Char formed during a fire accumulates on the surface of the nanocomposite, forming a barrier that protects any unburned material below the surface. The DTG data showed nanocomposites containing 1 wt% silica in PMMA cross-linked by TMPTA produced 14.1% char residues, while nanocomposites without TMPTA cross-linkages required five times the mass of nanofiller to achieve similar yields.

## 1. Introduction

From 1977 to 2014, the total number of fire-related incidents in the United States dropped from 3,264,500 to 1,298,000, indicating significant progress in the ongoing effort to reduce fire losses [1]. Despite this decreasing trend, the total cost due to fire damage in the US was estimated to be \$329 billion in 2011, suggesting that there is still significant room for improvement [2]. The development and implementation of flame-retardants for combustible and flammable materials is one step in minimizing total fire losses.

One active area in flame-retardant research is in polymeric materials. The lightweight, low cost, and high performance properties of polymers make them an ideal candidate for many industrial and household products. However, since polymers are generally composed of energy-dense hydrocarbons, their widespread application has the potential to increase the risk of fire if left unmitigated. It is important to address the flammability of polymeric materials through flame-retardants.

Many polymeric flame-retardants increase the final char yield of a burned polymer [3]. During a fire, the burning polymer produces char, which accumulates as a layer on the surface of the material. This layer

serves as a barrier between the unburned polymer and the fire, reducing heat transfer. Furthermore, the presence of char also indicates incomplete combustion. In a fire, the polymer first undergoes pyrolysis, breaking down into smaller, more volatile compounds that diffuse away from the polymer surface and burn in the vapor phase. By enhancing char yield, more mass is retained in the condensed phase where it cannot burn, reducing the total heat released in the fire. Not only can these flame-retardant polymers be used to produce inherently safer bulk plastics, they can also be applied as protective coatings, producing a sacrificial barrier in the event of a fire.

While polymeric flame-retardants have reduced the consequences associated with polymer flammability, many of these flame-retardants have received criticism over their toxicity and environmental impact. One common flame-retardant, tris (1,3-dichloroisopropyl) phosphate (TDCPP) is a known neurotoxin and mutagen in animals, while other flame-retardants, such as a group of flame-retardants called pentaBDE's, are environmentally persistent pollutants [4–7]. To make matters more complicated, the United States and Europe have prompted the creation of country-specific standards which require the implementation of flame-retardant materials in synthetic furniture, fabrics, and other products [8]. These regulations have led to an

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increase in the use of flame-retardants, highlighting the need for nontoxic and non-persistent flame-retardant alternatives [9,10].

In the last three decades, polymeric nanocomposites, generally consisting of inorganic nanoparticles embedded in a polymer matrix, have gained significant attention in literature as potential replacements for antiquated toxic flame-retardants. When burned, flame-retardant nanocomposites produce a physical barrier on the surface of the burning material, similar to charring flame-retardants. However, unlike traditional charring polymers, much of the char is produced by a catalytic mechanism on the surface of the nanofiller leading to the formation of an insulating physical barrier composed of carbonaceous char and agglomerated nanoparticles [11–17]. In addition, unlike conventional flame-retardants, nanocomposites are generally more thermally stable when compared to neat polymers due to reduced polymer mobility, free-radical trapping by the nanofiller, and the replacement of combustible polymer with thermally stable nanofiller [11]. Since the composition of nanocomposites can be fine tuned with different fillers and polymers, nanocomposites are a good candidate to replace antiquated toxic flame-retardants.

Previous research has been conducted utilizing polymeric nanocomposites in conjunction with traditional flame-retardants with some success. Common flame-retardants such as ammonium polyphosphate (APP) were combined with nanoparticles in a polymeric matrix to produce synergistic flame-retardant systems with enhanced char yields and increased thermal stability [18–20]. Similar to APP and other flame-retardants, cross-linking has been previously shown to increase the char-yield of polymers, but the thermal stability effects of common cross-linking agents in conjunction with nanofillers have not been adequately studied [21].

In this work, the thermal stability and char yield of cross-linked polymer nanocomposites is studied using poly (methyl methacrylate) (PMMA) cross-linked with trimethylolpropane triacrylate (TMPTA). Three different nanofillers, montmorillonite (MMT), aluminum oxide (AO), and nanosilica, are used to observe the effect nanofiller composition has on thermal stability and char yield of TMPTA cross-linked PMMA. In addition, linear (not cross-linked) nanocomposites were produced to compare with the cross-linked materials.

## 2. Methods

### 2.1. Materials

The monomer, methyl methacrylate (MMA), and the initiator, 1,1'-azobis(cyclohexanecarbonitrile) (ABCN), is supplied by Polysciences. The nanofillers, which include montmorillonite nanoclay sheets organically modified with aminopropyltriethoxysilane (MMT, nanoscale thickness, < 20  $\mu\text{m}$  width), spherical aluminum oxide nanoparticles (AO, 13 nm primary particle size), and spherical nanosilica (10–20 nm primary particle size), are purchased from Sigma-Aldrich. The cross-linking agent, trimethylolpropane triacrylate (TMPTA) is also supplied by Sigma-Aldrich. X-Ray Diffraction was conducted using a Bruker D8 power diffractometer and Cu k- $\alpha$  radiation source to initially observe the dispersion of nanocomposite samples. However, tested samples appeared similar to their polymeric counterparts.

### 2.2. Nanocomposite synthesis

Nanocomposites are produced using an *in-situ* method. One of the three nanofillers (MMT, AO, or silica) is massed and added to the MMA monomer in a sealed glass vessel so that concentration of nanofiller in the final nanocomposite is 1 wt%, 3 wt%, or 5 wt%. For cross-linked samples, the cross-linking agent, TMPTA, is added to the solution in a 1:60 M ratio of TMPTA:MMA. No TMPTA is added for linear samples. This solution is mixed using a magnetic stirring bar for 30 min, followed by ultrasonication at 20  $^{\circ}\text{C}$  for an additional 30 min. After ultrasonication, ABCN initiator is massed and added to the solution so

that the initiator concentration is equal to 0.5% of the total monomer and cross-linker mass (0.5% of the mass of MMA and TMPTA combined). A magnetic stirring bar is also added to the vessel before it is sealed tightly using a lid with a silicone septum. Two needles are punctured through the silicone septum to begin inerting. One needle bubbles nitrogen through the solution, while the second prevents overpressurization of the glass vessel. The vessel is then transferred to an oil bath which maintains the polymerization temperature at 70  $^{\circ}\text{C}$ . A hot plate with a magnetic stirrer is used to continually stir both the glass reaction vessel and the oil bath simultaneously. Polymerization proceeds until approximately five minutes before the solution gels, at which point the partially polymerized solution is transferred to small polypropylene vials. Polyethylene insulation foam is used to keep the small polypropylene vials buoyant as they float in the oil bath for an addition 48 h to complete curing, after which the materials are removed from their molds and tested.

### 2.3. Nanocomposite characterization

Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric (DTG) studies was conducted using a Mettler Toledo TGA/DSC 1. TGA was used to measure mass loss with respect to temperature while DTG was used to measure mass loss rate with respect to temperature. This was done under a nitrogen atmosphere and at a ramp rate of 10  $^{\circ}\text{C}/\text{min}$ . Samples were roughly 5 mg in mass and roughly spherical in shape and repeated tests show reproducible results. These data are used to measure the onset of degradation, the char yield, and the general degradation behavior of the nanocomposites produced.

## 3. Results and discussions

Nanocomposites cross-linked by TMPTA with Silica, MMT, and AO nanofillers were tested using TGA and compared with the results from linear nanocomposites to quantify how PMMA cross-linking and nanofiller content interact to affect thermal stability and char yields. In general the low loading (1 wt% nanofiller) samples are homogenous, with increasing levels of agglomeration visually apparent at higher loadings. The results for each nanofiller will be discussed separately and then compared to understand how differences in nanoparticle structure and chemistry may affect degradation.

### 3.1. Thermal stability and char yield of silica nanocomposites

Fig. 1(A) presents the TGA data for linear 1 wt% silica nanocomposites and 1 wt% silica nanocomposites cross-linked by TMPTA, while Fig. 2 shows the corresponding DTG curves. The TGA data for linear PMMA without nanofiller and PMMA cross-linked by TMPTA without nanofiller are also included in Fig. 1(A). The degradation of linear PMMA and 1 wt% silica in linear PMMA occurs in a two-step process, indicated in Fig. 1(A) by two sudden drops in the mass as temperature increases or equivalently in Fig. 2 as two mass loss peaks. The first mass loss begins near 200  $^{\circ}\text{C}$ , and corresponds to unsaturated-end initiated polymer unzipping, while the second mass loss begins near 300  $^{\circ}\text{C}$ , and corresponds to random depolymerization, shown in previous studies [22].

In contrast, cross-linked PMMA and 1 wt% silica nanocomposites cross-linked by TMPTA only have one major degradation region, shown in Fig. 1(A) as a single drop in mass as temperature increases and in Fig. 2 as a single mass loss peak. The DTG for linear and cross-linked 1 wt% silica nanocomposites in Fig. 2 clearly shows the low temperature mass loss peak centered at 250  $^{\circ}\text{C}$  is absent in the cross-linked nanocomposite. This indicates that the presence of TMPTA cross-linkages stabilize unsaturated-end initiated polymer unzipping, shown in previous studies [21]. In addition, the remaining high temperature mass loss peak centered near 370  $^{\circ}\text{C}$  in Fig. 2 is shifted

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