



A novel stiffener skeleton strategy in catalytic carbonization system with enhanced carbon layer structure and improved fire retardancy

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ABSTRACT

Catalyzing carbonization of polymer itself to form a protective carbonaceous layer has been proven to be an effective way to improve polymer's flame retardancy, but there is still a great challenge to achieve synchronous enhancement in traditional test standards (such as LOI and UL-94 testing). In this study, a stiffener skeleton strategy combined with catalyzing carbonization was proposed to improve the flame retardancy of polycarbonate (PC). The synergistic effect of nanosized carbon black (CB)/Ni₂O₃ on carbon yield and combustion properties of PC were investigated. An improvement with 31.4% in LOI, V0 in UL-94, and 50% reduction for PHRR in cone calorimeter test was achieved. According to char morphology and structure analysis, the flame retardancy mechanism was attributed to the enhanced barrier effect of carbon layer with interconnected structure and self-supporting capacity, which was promoted by the formation of carbon skeleton framework from PC and the catalytic carbonization from combined catalysts.

1. Introduction

In recent years, there is a growing tendency on developing novel strategy to improve the fire retardancy of polymer materials [1–10]. Catalytic carbonization of polymer itself to form protective carbonaceous layer during combustion has been proven to be an effective way, as carbonaceous materials have the properties of less flammability, reflecting energy and generating a barrier between the degradation products of the polymer and the flame. The fire retardancy mechanism of catalytic carbonization is more or less similar to intumescent fire retardants (IFRs), but the carbon sources for their residual chars are quite different: the former is from polymer itself whereas the latter from the added IFRs. Generally, with the incorporation of a small amount of catalysts (less than 10 wt%), polymer chains are selectively degraded into organic compounds with lower carbon numbers, subsequently these degradation products are dehydrogenated (and/or dehydrated) and further aromatized into solid carbon products [11–14]. Therefore, in comparison with other conventional methods, “catalytic carbonization” is considered to be one of the most desirable approaches due to its unique advantages, mainly including low filler loading, high carbon yield, environmental friendliness and long-term stability with no deterioration, as well as no damage (or even improvement) to mechanical

performances of polymer matrix.

To achieve good catalytic carbonization efficiency, the key is to find or synthesize appropriate catalysts for promoting the degradation of polymers as well as the carbonization of the degraded products. In 2005, our group firstly reported that the combination of organically modified clay (OMC) and supported nickel catalysts (Ni-Cat), could effectively catalyze the carbonization of polypropylene (PP) into carbon nanotubes, and dramatically improve PP's fire retardancy [15,16]. Furthermore, a variety of other combined catalysts were explored, such as zeolite/nickel compounds [14], halogenated compound/Ni₂O₃ [17], silica/Ni₂O₃ [18] and activated carbon (or carbon black)/Ni₂O₃ [12,19], which could efficiently enhance the residual char yield of polymer materials during combustion and greatly decrease their heat release rate (HRR) and total heat release (THR) in cone calorimeter test. Up to now, other research groups also have done a mountain of research work on the design and synthesis of novel catalyst or hybrids for the catalytic carbonization [20–28]. Song et al. [21] reported that the addition of 2 wt% Ni(Ac)₂ into PP/functionalized lignin (PN-lignin) composites could increase char residue by ~44%, and improve the LOI value up to 26, as well as reduce the peak heat release rate (PHRR) to 330 kW/m². Xu and co-workers [22] fabricated a multi-component RGO-LDH/Mo hybrid and added it into polyurethane elastomer (PUE)

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system, in which the char yield of PUE was significantly increased, meanwhile the PHRR and the maximum smoke density of the PUE composites drastically decreased. They found that the MoO_3 in-situ formed in the decomposition process of RGO-LDH/Mo promoted the catalytic carbonization and smoke suppression effect. Notably, Hu group [23,24] have done much excellent work on the catalytic carbonization function of two-dimensional nanomaterial hybrids. For example, $\alpha\text{-FeOOH}$ improved the smoke suppression properties of PS; NiAl-LDH reduced the heat release rate, smoke production and CO production of PMMA; layered metal phenylphosphonates showed catalyzing carbonization effect on the degraded products of PS. Besides, Hu group [25] synthesized a novel three-dimensional nanostructure catalyst (3D PZM@ Co_2P @RGO), and found that the addition of this catalyst resulted in a dramatic reduction of the fire hazards of epoxy resin (EP), such as a 47.9% decrease in PHRR, a 29.2% decrease in THR, and lower toxic CO yield. Hu group [26] also synthesized ternary HM-SiO₂@CeO₂/NiO hybrids and incorporated it into EP, in which the obviously improved fire safety properties included the decrease of PHRR and the reduce of toxic effluents' concentration, owing to the catalytic charring effect of CeO₂/NiO. Besides, Wang group prepared Cu-doped graphene [27] and Fe₃O₄-doped sepiolite [28], and found that the presence of these materials could decrease heat release rate, total smoke production and smoke production rate, and obviously improved LOI values of epoxy composites. Based on the above reports, the influence of catalytic carbonization for fire retardancy of polymers is mainly reflected in the remarkable reduction of heat release rate during cone calorimeter testing and a little increasing of the LOI value, but it is still unhelpful to improve the vertical burning grade (UL-94) to V0 rating in most cases. Thus, exploring novel catalytic carbonization system to achieve synchronously improved fire retardancy on different test standards is obviously requisite and attractive.

To achieve good fire retardancy of polymers via catalytic carbonization, the barrier effect of carbon layer is very important, so the quality of carbon layer plays a crucial role, and more specifically, it is much more important than the amount of residual char (carbon conversion). In our previous work [19,29], the carbon conversion from polymers is beyond 50%, but it is still no-ratting in UL-94 vertical burning test. As shown in Scheme 1a, a large amount of carbon products (amorphous and graphitized carbon) is formed due to the high catalytic efficiency of combined catalysts, but actually the char is loose and infirm structure with lack of self-supporting capacity. Therefore, it is a key issue to improve char structure with higher strength. Inspired from reinforcement structures by metal stiffeners in building construction, here a novel stiffener skeleton strategy is proposed (Scheme

1b). If a skeleton structure as the stiffener of carbonized products is firstly formed on the surfaces of polymers during combustion, then the newly generated carbon products are catalytically carbonized and quickly deposited on the carbon skeleton, finally an interconnected carbon layer with good supporting capacity and improved structural strength will be established. In this case, the fire retardancy of polymers will probably be improved due to enhanced barrier effect of carbon layer.

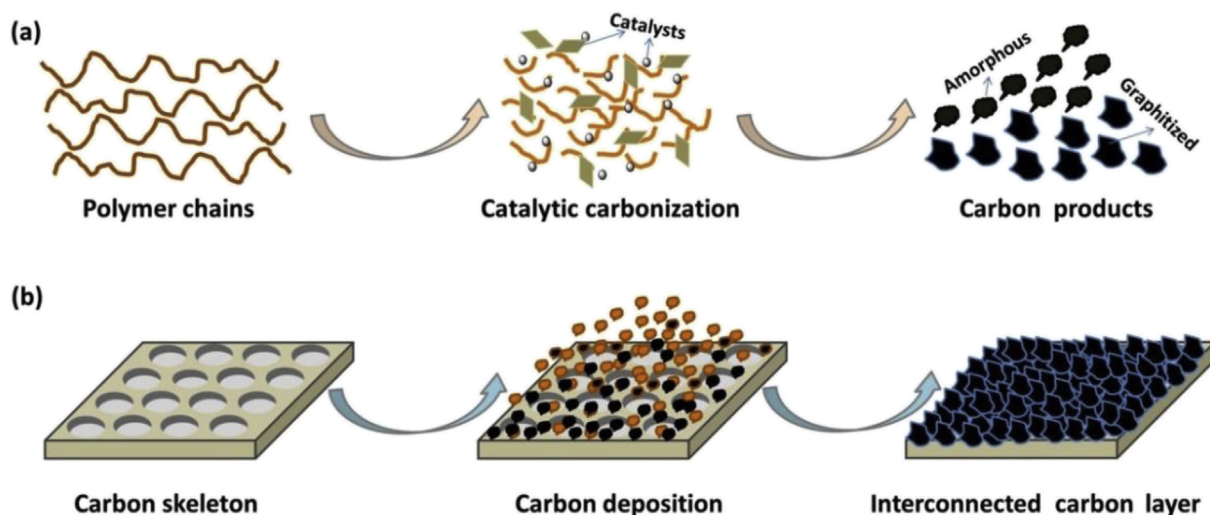
In order to achieve the carbon layer with good strength and stiffness, the interface fuse between in-situ formed carbon products via catalytic carbonization and stiffener skeleton is decisive during material burning (Only when they are syncretic, the carbon products can be adsorbed and further deposited on the skeleton), so it is better to form a carbon skeleton with similar compositions to in-situ formed carbon products. Considering the convenience of operation, it is more attractive that the polymer matrix itself can produce a carbon skeleton during combustion. It is well-known that polycarbonate (PC) possesses characteristic char capability [30] due to its benzene ring structure in its molecular backbone, so it is a proper candidate as carbon skeleton materials. Our previous reports demonstrated that the combination between nanosized carbon black and Ni₂O₃ as a “universal” catalysts [11,12], displayed high-efficiency on catalyzing carbonization of various polymers. To demonstrate the feasibility of our stiffener skeleton strategy, in this work, we selected PC both as carbon skeleton material and carbon sources of residual chars, nanosized carbon black and Ni₂O₃ as combined catalysts, to investigate their synergistic effect on improving the fire retardancy of PC composites and their catalyzing carbonization effect on PC. Moreover, the char morphology and structure were analyzed in detail to discuss the enhancement mechanism.

2. Experiments

2.1. Materials and preparation of PC composites

2.1.1. Materials

Polycarbonate (PC 2805, melt flow rate, 10.0 g/10 min) purchased from Bayer Chemicals (Germany). Nanosized carbon black (CB, purity: > 99.9%) was purchased from Linzi Qishun Chemical Co., Shandong, China, with an original particle diameter of 17 nm Ni₂O₃ was from Lingfeng Chemical Company of Shanghai, China, with an average diameter of 250–300 nm. PC and all catalysts were dried under vacuum at 120 °C for 6 h before usage.



Scheme 1. Schematic diagrams of a) the catalytic carbonization process for polymers and b) the possible forming process for interconnected carbon layer.

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