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# Radiation grafting of glycidyl methacrylate and divinylbenzene onto polyethylene terephthalate fabrics for improving anti-dripping performance

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## HIGHLIGHTS

- Anti-dripping PET fabric was prepared by radiation grafting GMA and DVB.
- Tensile strength and elongation of PET were improved after radiation grafting.
- The anti-dripping performance of PET was improved remarkably after radiation grafting.

## ARTICLE INFO

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## ABSTRACT

A new kind of anti-dripping polyethylene terephthalate (PET) fabric was successfully prepared by simultaneous gamma radiation-induced grafting polymerization of glycidyl methacrylate (GMA) and divinylbenzene (DVB) onto the surface of PET fabrics. The grafting yield (GY) and anti-dripping effect were optimized by changing the total absorbed dose, dose rate, concentration and the feed ratio of GMA and DVB. The grafting yield increased with the increase of absorbed dose and GMA monomer concentration, and decreased with the dose rate. It is confirmed that PET fabrics had been modified by Fourier transform infrared spectroscopy analysis. The tensile strength and elongation at break of modified PET fabrics were improved compared with original PET fabrics. The limiting oxygen index (LOI) of modified PET fabrics with the GY of 23–25% was 21.5, which was similar to that of unmodified PET fabrics. However, the anti-dripping performance of PET fabrics was improved remarkably after radiation modification due to the crosslinking of the sidechains grafted on the PET surface. This anti-dripping fabric may be promising for fire protective clothing.



## 1. Introduction

Polyethylene terephthalate (PET) has excellent performance such as outstanding mechanical properties, heat resistance, good dyeing ability and chemical stability. Therefore, it is widely used in clothing, bedding, furniture textiles, curtains and industrial textiles, its excellent performance such as outstanding mechanical properties, heat resistance, good dyeing ability and chemical stability (Asrar et al., 1999; Atkinson et al., 2000; Callander, 1985; Marcincin, 2002; Molto et al., 2007; Vlad-Bubulac et al., 2006). However, the limiting oxygen index (LOI) of PET is only 20–22% and PET is combustible in the air. Droplets form during the combustion. Cooling and curing droplets cause the skin burned for their releasing latent heat, and removing the droplets sticking to the skin cause second damage. These drawbacks greatly limit its application in infant clothing, uniforms and protective clothing.

Three methods have been exploited to improve the flame retardancy and anti-dripping performance. Flame retardants are incorporated into PET by melt blending, flame-retardant monomers are imported into PET chains or grafted onto PET chains, and fabrics are finished in a solution containing flame retardants (Carosio et al., 2011; Chen et al., 2014; Li et al., 2011a, 2011b).

Zhang et al. (2015) synthesized a monomer containing ionic groups and phosphorus, the potassium salt of 10-hydroxy-10-*oxo*-10 h-phenoxaphosphine-2,8-dicarboxylic acid (DHPPO-K). The flame retardant copolymer which was prepared by melt copolycondensation improved the flame retardancy and reduced melt dripping. Yu et al. (2010) grafted GMA onto PET by photo-induced

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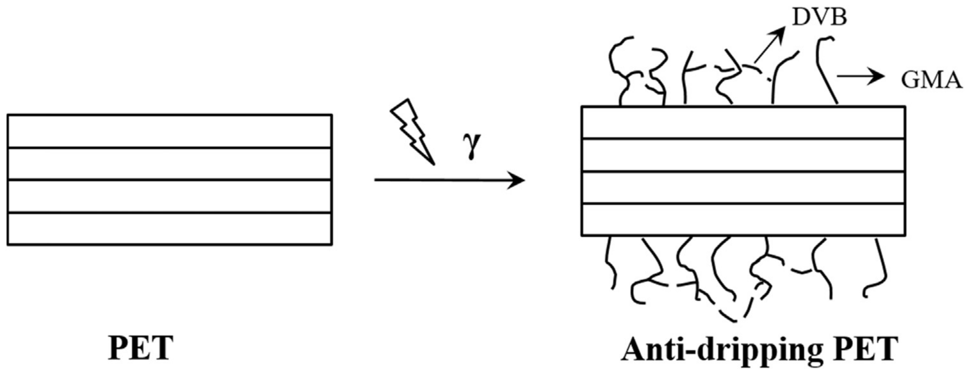


**Fig. 1.** The preparation process of anti-dripping PET fabric.

grafting method in association with a pad-curing treatment by using a flame retardant solution containing 1-hydroxy ethylidene-1,1-diphosphonic acid and sulfonic acid. The highest LOI of their samples could reach up to 25.9 and the dripping tendency of PET fabrics was reduced. Tang et al. (Tang et al., 2010) incorporated benzoguanamine (BG) into PET with a melt spinning extrusion, and the UL-94 flame rating was V-0 and no dripping was formed during the LOI measurement when the content of BG being 10%. Li et al. (2009) found that the intumescent flame retardant system containing ammonium polyphosphate, melamine and pentaerythritol could improve flame retardancy and the highest LOI could reach up to 27.9. Sonnier et al. (2015) grafted two phosphorus-based molecules – dimethyl (methacryloxy) methyl phosphonate (MAPC1) and dimethylvinyl phosphonate (DMVP) onto flax fabrics using electron beam irradiation to impart flame retardancy to fabrics, respectively. Improving the flame retardancy attracted more attention, while improving anti-dripping performance of fabrics attracted less attention. Even if some methods could reduce dripping tendency, dripping behavior was characterized through LOI measurement in which these samples were ignited from the top down. Droplets usually did not appear when samples were ignited from the top down, but appeared when samples were ignited from the bottom up. Moreover, flame-retardant monomers imported into PET chains changed the nature of PET, and the flame retardant performance were not stable by physical blending and retardant finishing.

The radiation grafting specific monomers on polymer backbones is an effective strategy to modify polymers, for it may change the surface activity of polymers without causing serious detriment to their mechanical properties (Anjum et al., 2006; Bozzi and Chapiro, 1988; Curti et al., 2005). Radiation-induced grafting allows the substrates to maintain their intrinsic characteristics, such as mechanical strength, dyeing property and thermal stability (Enomoto et al., 2012). The main advantage of γ-ray radiation induced grafting copolymerization is the extensive penetration in the polymer matrix to form uniform radicals rapidly to initiate the graft polymerization, and the reaction can be conducted at room temperature and in gaseous, liquid, or even solid-state phase (Dilli and Garnett, 1967; Fukada et al., 1960; Gupta et al., 1996; Wellons and Stannett, 1965).

We synthesized a kind of anti-dripping PET fabrics by gamma-ray radiation-induced grafting glycidyl methacrylate (GMA) and divinylbenzene (DVB) onto the surface of PET fabrics to reduce the dripping tendency of PET fabric. Three key factors of affecting grafting polymerization were investigated: the monomer concentration, absorbed dose and absorbed dose rate. The flame retardancy and anti-dripping performance were evaluated by LOI and the vertical flammability tests, respectively. The structure of residual char was observed by SEM to elucidate the possible reason.

## 2. Experiment

### 2.1. Materials

Polyethylene terephthalate (PET) fabrics (85 g/m$^2$) were supplied by Wujiang Fei Silk Textile Co., Ltd (Jiangsu, China). Glycidyl methacrylate (GMA) and divinylbenzene (*m*- and *p*-mixture) were purchased from J&K Chemical Reagents Co., Ltd. Acetone and dichloromethane were purchased from Beijing Chemical Works. Other chemical reagents were analytical-grade and used as received without any further purification.

### 2.2. Preparation of PET-g-PGMA and PET-g-PGMA/DVB

The preparation process of anti-dripping PET is illustrated in Fig. 1.

The PET fabrics were ultrasonic cleaned with methanol (3 × 150 ml) for 30 min. The same procedure was performed with deionized water. Then the fabrics were dried to constant weight in oven at 80 °C. The grafting solution was prepared by adding GMA into dichloromethane with the coexistence of DVB at various concentrations. The dried fabrics were immersed into the solution. Purified nitrogen was bubbled through the monomer solution at room temperature for about 30 min to get rid of oxygen, followed by the tube being sealed.

The samples were irradiated to the required total dose at corresponding dose rate at ambient temperature by using Co-60 γ source (Peking University, China). Dose rate was traced by Fricke dosimeter.

These grafted fabrics were Soxhlet-extracted with acetone for 24 h to remove the residues of GMA monomers and homopolymers.

### 2.3. The grafting yield

The samples were dried at 80 °C to constant weight after extraction. The grafting yield (GY) was determined according to the following Eq. (1):

$$GY(\%)=\frac{(Wg-Wo)}{Wo}\times 100 \quad (1)$$

where $W_o$ and $W_g$ are the weights of original PET fabrics and grafted PET fabrics in dry state, respectively.

### 2.4. Elemental analysis

The element types and contents of the original and modified PET fabrics were measured by an elemental analysis (EA), Elementar Vario EL CUBE (Germany).