



# Preparation of epoxy-modified polyethylene by graft extrusion and its applications to polyphenylene sulfide alloys as a compatibilizer

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## ABSTRACT

Epoxy-modified polyethylene (PE-g-GMA) was successfully synthesized from glycidyl methacrylate (GMA) and low-density polyethylene (LDPE) via the grafting reaction of extrusion. The mechanism of grafting reaction and the rapid determination for the percentage of grafting are also reported. Experimental results demonstrated that the PE-g-GMA is a good compatibilizer in polyphenylene sulfide/poly(ethylene terephthalate) (PPS/PET) as well as PPS/nylon 6,6/glass fiber alloys and the addition of PE-g-GMA into PPS alloys may effectively improve the mechanical properties of composites.

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## 1. Introduction

Polyethylene (PE) is a versatile polymer [1,2] and its chemical reactivity can be modified by means of grafting various functionalized monomers onto its backbone without substantial loss of its physical properties. The grafting process may be carried out in solution or molten PE with copolymerization of methyl methacrylate, maleic anhydride, styrene, acrylic acid, and trimethoxysilane [1–4]. The chemically modified PE has extensive applications especially as a compatibilizer for polymer alloys [5]. Although the grafting reaction of PE can be executed by conventional reactors, the process takes several hours for completion and is batch-producing [6–8]. However, the extrusion procedure is fast and continuous, being more suitable for industrial mass production.

In this work, glycidyl methacrylate (GMA) was grafted to low-density polyethylene (LDPE) with initiators by reactive extrusion procedure in a twin screw extruder. The grafted product (PE-g-GMA) was subsequently analyzed by means of FTIR spectra as well as the element analysis. The linear

calibration curve was drawn for a rapid estimation of the percentage of grafting. Moreover, the dependence of the percentage of grafting on processing parameters was also investigated in detail. Finally, the PE-g-GMA was added in polyphenylene sulfide/poly(ethylene terephthalate) (PPS/PET) and the PPS/nylon 6,6/glass fiber alloys to serve as a compatibilizer and a successful enhancement on their mechanical properties was obtained.

## 2. Experimental

### 2.1. Materials

The LDPE pellet (NA 20766), whose density and melt index are 0.923 g/cm<sup>3</sup> and 8 g/10 min, respectively, was supplied by USI Far East Co. of Taiwan. The GMA, PET, PPS (P-4), nylon 6,6, and PE-g-Acrylic acid (PB1009), whose chemical structures were shown in Fig. 1, were obtained from Japanese Oil and Fat Co., Shinkong Synthetic Fibers Co., Du Pont Co., Phillips Petroleum Co., and BP Performance Polymer Inc., respectively. The initiator (2,5-dimethyl-2,5-bis(*t*-butyl-peroxy)hexane (TX 101) as shown in Fig. 1) with a half-life of approximately 6 min at 160 °C was purchased from the Akzo Chemie Co.

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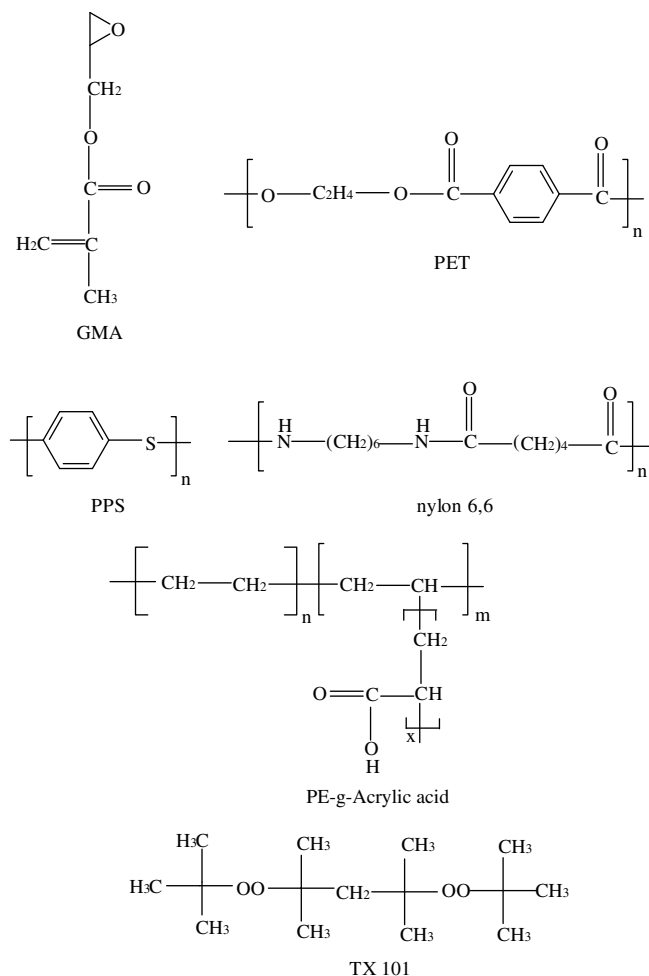


Fig. 1. The chemical structures of GMA, PET, PPS, nylon 6,6, PE-g-Acrylic acid, and TX 101.

## 2.2. Grafting process of GMA and LDPE

The grafting reaction was manifested in Scheme 1 and carried out by using a twin screw extruder (W&P, ZSK 25). The LDPE pellets were fed at 40 g/min into the hopper and the GMA/TX 101 solution was injected into the twin screw extruder from the injection nozzle via a liquid chromatography pump. The extrudate was pelletized and then dried prior to analysis. The crude polymer was dissolved in hot toluene, precipitated the product with methanol, and then dried in reduced pressure at 50 °C for 24 h. The element analyzer (Heraeus CHN-0-Rapid F002) was used to analyze the contents of oxygen of the dried polymer. Thin film samples for Fourier-transform infrared (FTIR) analysis were prepared by pressing the precipitated resin between two mylar sheets at 120 °C and 5000 kg/cm<sup>2</sup> for 1 min. FTIR measurements were performed by using a Bio-Rad Digitlab Division UMA 300/FTS-40 spectrometer. The thermogravimetric analysis (TGA) was carried out by using a Perkin-Elmer TGA7 and in temperatures ranging from room temperature to 470 °C at a heating rate of 10 °C/min in nitrogen ambient.

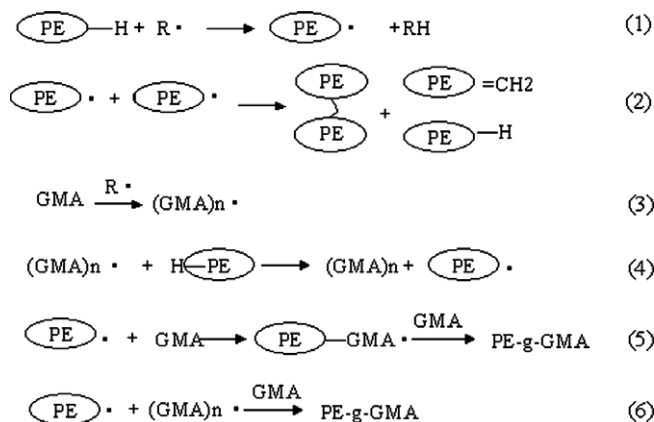
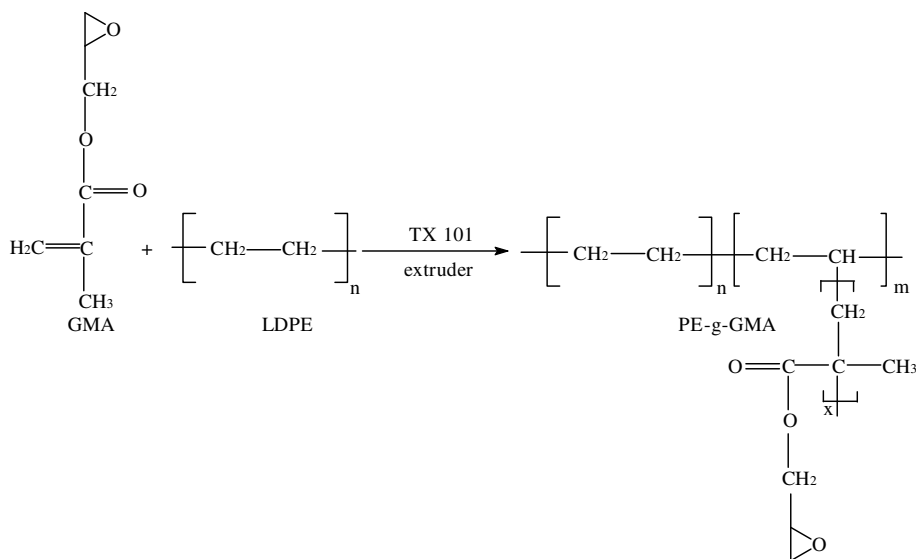
## 2.3. Preparation and characterizations of PPS alloys

PPS powder, PET or nylon 6,6 pellets/glass fiber, and the compatibilizer (PE-g-GMA) were mixed in the twin screw extruder at 280 °C at a screw speed of 300 rpm. The extrudate was then cooled and pelletized. Impact test specimens were prepared by an injection molding machine (Toshiba IS55). Izod impact test was conducted on unnotched specimens at 25 °C according to ASTM D256 test standard. Morphologies of fractured surfaces of PPS/PET alloys were examined by scanning electron microscopy (SEM, Cambridge model S360).

## 3. Results and discussion

### 3.1. The mechanism of grafting reactions

Fig. 2 depicts the possible reactions taking place during grafting procedure [9]. First, the primary R<sup>•</sup> radical produced by thermal decomposition of TX 101 extracts a hydrogen atom from PE chains (reaction (1)). The radicals generated by peroxide decomposition then attack PE,



**Fig. 2.** Overview of the free radical reactions.

preferentially at branch chain, to produce PE $\cdot$ ; which either undergo crosslinking or disproportionation (reaction (2)). Simultaneously, the homopolymerization of GMA occurs, yielding (GMA) $_n\cdot$  which undergoes chain transfer to form PE $\cdot$  (reactions (3) and (4)). These reactive sites of PE backbone either react with GMA or capture (GMA) $_n\cdot$ , and finally result in grafting reactions (reactions (5) and (6)). Among these possible reactions, reaction (5) is the key reaction for the grafting process of LDPE and GMA.

### 3.2. Estimation of the percentage of grafting

The FTIR spectra of pure LDPE and PE-g-GMA are presented in Fig. 3a and b, respectively. As shown in Fig. 3b, the absorption bands at 846, 908, and 995  $\text{cm}^{-1}$  are the characteristic vibrations of epoxy groups [10], indicating the occurrence of grafting reaction (Scheme 1). As to the percentage of grafting (%grafting), it can be directly calculated by the ratio of the absorbance of the carbonyl

group for PE-g-GMA to that of the methylene group for pure LDPE. However, this method is tedious. In order to simplify the determination of %grafting, we draw the calibration curve [11] in terms of the experimental results of extrudates **a**, **b**, **c**, and **d** (Table 1) as shown in Fig. 4, whose abscissa is the ratio of carbonyl stretch ( $\nu_{\text{CO}}$ , 1731  $\text{cm}^{-1}$ ) to the methyl stretch ( $\delta_{\text{CH}_3}$ , 1376  $\text{cm}^{-1}$ ) for PE-g-GMA (i.e.,  $\nu_{\text{CO}}/\delta_{\text{CH}_3}$ ) and ordinate is the content of oxygen for PE-g-GMA (%oxygen), respectively. The  $\nu_{\text{CO}}/\delta_{\text{CH}_3}$  and %oxygen are measured by FTIR and element analysis, respectively. Since the linear calibration curve has been successfully established, the %grafting can be rapidly estimated from the %oxygen as shown in Fig. 4, whose acquirement is much easier than  $\nu_{\text{CO}}/\delta_{\text{CH}_3}$ , through fitting of the linear calibration curve. For example, in case of extrudates **e**, we obtain %oxygen (0.16) from the FTIR result and then the %grafting can be determined to be 0.48 by matching the calibration curve (Fig. 4).

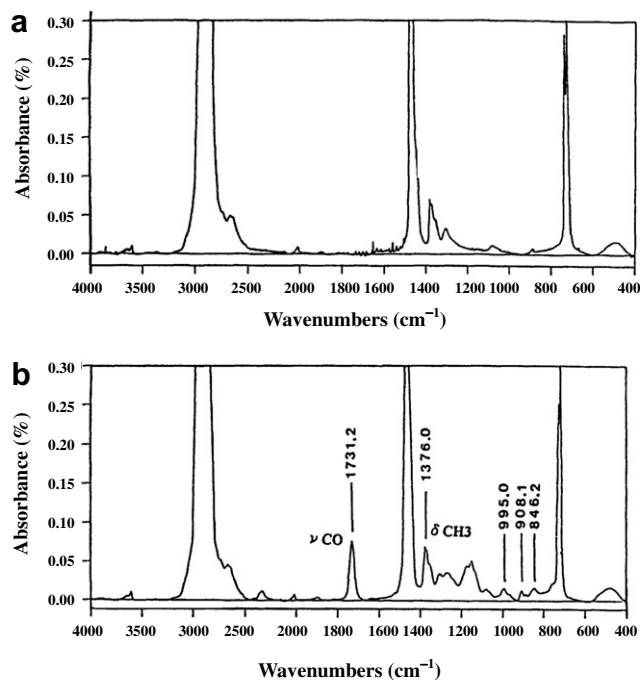


Fig. 3. The FTIR spectra of (a) pure LDPE and (b) PE-g-GMA.

Table 1

Summary of the experimental results of grafting reactions

Extrudate	Composition of LDPE/GMA/TX101 (wt./wt./wt.)	Screw speed (rpm)	Processing temp. (°C)	$\nu\text{CO}/\delta\text{CH}_3$	%Oxygen	%Grafting
a	100/40/0.2	100	120	2.49	1.42	4.20
b	100/20/0.8	200	200	2.44	1.45	4.29
c	100/30/1	300	220	2.98	1.75	5.18
d	100/5/2	100	275	0.96	0.60	1.78
e	100/10/0.27	200	220	–	0.16	0.48
f	100/10/0.53	200	220	–	0.21	0.62
g	100/10/0.80	200	220	–	0.28	0.82
h	100/10/0.53	300	220	–	0.11	0.33
i	100/10/0.53	100	220	–	0.26	0.77
j	100/15/0.27	200	220	–	0.20	0.59
k	100/15/0.27	200	145	–	0.05	0.14
l	100/15/0.27	200	255	–	0.58	1.72

### 3.3. Dependence of processing parameters on grafting reaction of extrusion

As shown in Table 1, the %grafting is strongly dependent on the processing parameters such as concentration of initiator, screw speed, concentration of GMA, and processing temperature. In case of the extrudates e, f, and g, %grafting increases with the rising of concentration of initiator (TX 101), revealing higher concentration of TX 101 promotes the initiation of grafting reaction (reaction (1) of Fig. 2) and raises the %grafting. Furthermore, a comparison of the experimental results of extrudates f, h, and i indicates the %grafting decreases with the increase of screw speed, revealing the faster screw speed shortens the residence time of reactants in the extruder and thus reduces the %grafting. In case of extrudates e and j, %grafting rises with the raising of concentration of reactant (GMA). In addition,

it was also found that the processing temperature highly influences the %grafting. As shown in the experimental results of extrudates j, k, and l, the %grafting heightens with the increase of the processing temperature; manifesting higher temperature causes higher speed and yield of grafting reaction. Therefore, we can ingeniously manipulate the %grafting by the modulation of processing parameters. In the near future, we will keep on analyzing the influence of the grafting procedure on grafting efficiency by statistical methods to acquire more detailed results.

### 3.4. PE-g-GMA as the compatibilizer of PPS Alloys

#### 3.4.1. Thermal properties of PE-g-GMA

PPS alloys have been produced before with appropriate commercially available compatibilizers (e.g. PE-g-Acrylic acid, PE-g-maleic anhydride, etc.) [12–14]. However, these

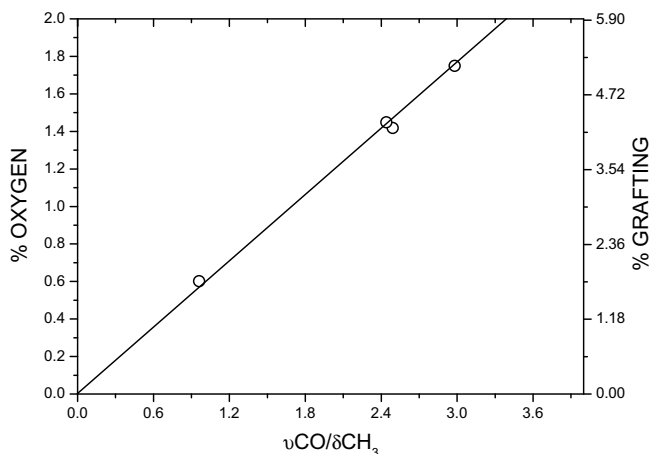


Fig. 4. The calibration curve for PE-g-GMA.

compatibilizers exhibit poor thermal stability, limiting the application of PPS alloys. Fig. 5 illustrates the TGA curve of PE-g-GMA. In case of PE-g-GMA, no degradation occurred until 300 °C in nitrogen ambient and its decomposition temperature could reach 372 °C. In comparison with the commercially available compatibilizer (PE-g-Acrylic acid), PE-g-GMA apparently exhibits a superior thermal stability since the epoxy group in PE-g-GMA can be more effective in resisting the heat than the carboxyl acid group of PE-g-acrylic acid. This result reveals that PE-g-GMA is a better compatibilizer for alloys of high performance engineering plastics, e.g., PPS/PET or PPS/nylon 66, etc., than PE-g-Acrylic acid.

### 3.4.2. PE-g-GMA as a compatibilizer of PPS/PET and PPS/Nylon 6,6/Glass fiber alloys

The PPS, PET and PE-g-GMA were blended in the twin screw extruder and the specimens for subsequent tests were prepared by injection molding. The blend composi-

tions and the mechanical properties of the PPS/PET alloys are tabulated in Table 2. The experimental results illustrate that the unnotched impact strength of PPS/PET alloys with PE-g-GMA (alloy **n**) is higher than that without PE-g-GMA (alloy **m**), indicating the introduction of PE-g-GMA is capable of promoting the mechanical properties. Furthermore, the improvement of compatibility for PPS/PET alloys could be deduced from the results of SEM observation. As shown

Table 2

Summary of the experimental results of PPS/PET alloys

Alloy	Composition of PPS/PET/PE-g-GMA (wt./wt./wt.)	Unnotched impact strength (kg/cm) <sup>a</sup>
<b>m</b>	100/50/0	6.81
<b>n</b>	100/50/12.5	10.0

<sup>a</sup> Measured at 25 °C after aging at 240 °C for 231 h (the standard deviations = ±2%).

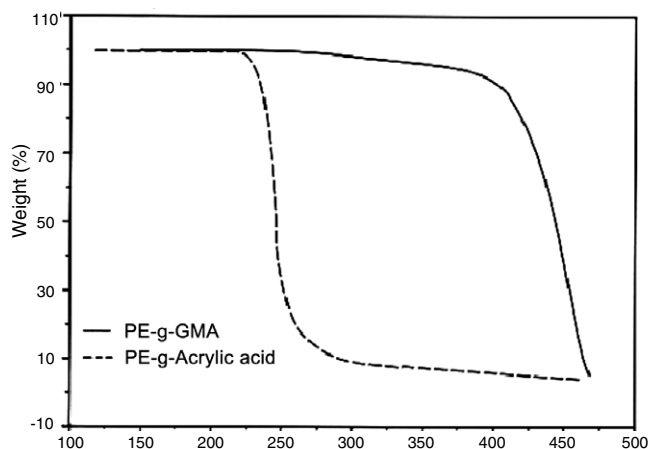
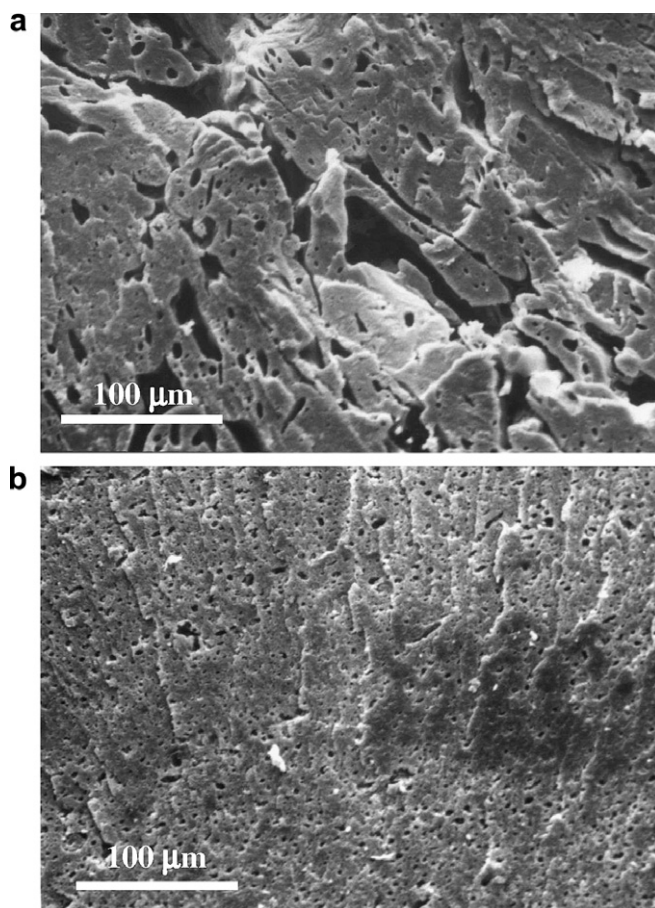


Fig. 5. The TGA curves of PE-g-GMA and PE-g-Acrylic acid in nitrogen ambient.



**Fig. 6.** SEM micrographs of PPS/PET alloys: (a) without PE-g-GMA (b) with the PE-g-GMA.

in Fig. 6a, alloy **m** exhibits the morphology with an incompatible phenomenon, while alloy **n** (Fig. 6b) exhibits the morphology with fine and uniform dispersion, manifesting the enhancement of the compatibility between PPS and PET by PE-g-GMA since the epoxy group of PE-g-GMA may attract with the carboxyl as well as oxygen groups of PET and the sulfide group of PPS *via* strong van der Waal forces.

In order to further raise the mechanical properties of PPS, we also introduced nylon 6,6 and glass fiber into the PPS to form PPS/nylon 6,6/glass fiber alloys *via* the same procedures described above. As shown in Table 3, the PE-g-GMA is an excellent compatibilizer of PPS/nylon 6,6/glass fiber alloys since the impact strength of alloy **p** is higher than alloy **o** due to the generation of strong van der Waal forces in between the epoxy group of PE-g-GMA and the amine group of nylon 6,6 as well as the sulfide group of PPS. Moreover, chemical reaction between the nylon 6,6 and the PE-g-GMA may proceed from the amine addition [15], further promoting the compatibility of PPS/PA6,6 alloys. As shown in Tables 2 and 3, in addition, the impact strength of PPS/nylon 6,6/glass fiber alloys with PE-g-GMA (alloy **p**) is much higher than that of PPS/PET alloys with PE-g-GMA (alloy **n**), revealing that addition of

**Table 3**

Summary of the experimental results of PPS/nylon 6,6/ glass fiber alloys

Alloy	Composition of PPS/nylon 6,6/glass fiber/PE-g-GMA (wt./wt./wt./wt.)	Unnotched impact strength (kg/cm) <sup>a</sup>
<b>o</b>	100/50/45/0	78
<b>p</b>	100/50/45/12.5	>100

<sup>a</sup> Measured at 25 °C after aging at 240 °C for 231 h (the standard deviations = ±2%).

nylon 6,6 and glass fiber can drastically increase the mechanical properties of PPS.

#### 4. Conclusions

In conclusion, grafting extrusion of epoxy-modified polyethylene (PE-g-GMA) was successfully performed and the percentage of grafting could be rapidly estimated by the linear calibration curve. With PE-g-GMA as a compatibilizer, PPS/PET and PPS/nylon 6,6/glass fiber alloys are homogeneously dispersed and their unnotched impact strengths were effectively enhanced due to strong van der Waal forces between the epoxy group of PE-g-GMA and functional groups of polymers (*i.e.* the carboxyl as well

as oxygen groups of PET, the sulfide group of PPS, and the amine group of nylon 6,6).

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### References

- [1] D. Braun, U. Eisenlohr, *Angew. Makromol. Chem.* 55 (1976) 43.
- [2] R.A. Steinkamp, T.J. Grail, U.S. Patent 3,953,655, 1976.
- [3] N.G. Gaylord, M. Mehta, *J. Polym. Sci., A* 26 (1988) 1189.
- [4] M. Tomescu, M. Dimonie, E. Calota, C. Ionescu, *Mater. Plast.* 15 (1978) 10.
- [5] B.E. Spivey, U.S. Patent 3,383,372, 1968.
- [6] T.C. Chung, *Prog. Polym. Sci.* 27 (2002) 39.
- [7] M.F. Diaz, S.E. Barbosa, N.J. Capiati, *Polymer* 43 (2002) 4851.
- [8] D.S. Rosa, C.G.F. Guedes, M.A.G. Bardi, *Polym. Test.* 26 (2007) 209.
- [9] R.R. Gallucci, R.C. Going, *J. Appl. Polym. Sci.* 27 (1982) 425.
- [10] K. Nakanishi, *Infrared Absorption Spectroscopy*, Holden-Day, San Francisco, 1962.
- [11] J.G. Martinez, R. Benavides, C. Guerrero, B.E. Reyes, *Polym. Degrad. Stab.* 86 (2004) 129.
- [12] T. Hisamatsu, S. Nakano, T. Adachi, M. Ishikawa, K. Iwakura, *Polymer* 41 (2000) 4803.
- [13] F.P. Tseng, J.J. Lin, C.R. Tseng, F.C. Chang, *Polymer* 42 (2001) 713.
- [14] N.C. Liu, H.Q. Xie, W.E. Baker, *Polymer* 34 (1993) 4680.
- [15] A.V. Pocius, *Adhesion and Adhesive Technology: An Introduction*, Hanser/Gardner Publications, New York, 1997.