난연성 고충격 폴리스티렌의 합성 및 특성해석

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Preparation and Characterization of Flame Retardant High Impact Polystyrene

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초록: 난연성 고충격 폴리스티렌(HIPS)의 합성을 위하여 라디칼계 부가반응을 통해 트리페닐포스페이트(TPP)를 그래프트하였다. FTIR과 ^{1}H NMR 분석을 통하여 TPP의 부가반응이 성공적으로 이루어졌음과 HIPS를 구성하는 폴리부타디엔(PB)의 이중결합이 감소하였음을 확인하였다. 또한 TPP의 부가에 따른 이중결합의 감소는 Izod 충격강도의 감소를 통해 확인하였다. 그래프트된 TPP가 TPP@HIPS의 비결정영역에 존재하고 있음은 ^{31}P NMR 분석을 통해 확인하였다. TGA 분석의 잔존 char yield로부터 TPP@HIPS의 열안정성이 향상되었음을 유추할 수 있었다. TPP@HIPS의 잔존 char yield는 600 °C 이상에서 16.65 wt%를 보였으며, 미처리 HIPS(pHIPS)의 경우에는 잔존하는 char가 존재하지 않았다. 한계산소지수(LOI) 수치는 pHIPS와 TPP@HIPS에 있어 유의미한 차이를 나타내지 않았으나, UL94 수직시험법을 통해 TPP@HIPS가 V-1 등급의 우수한 난연성을 나타냄을 확인하였다.

Abstract: A triphenyl phosphate (TPP) graft high impact polystyrene (HIPS) (TPP@HIPS) is synthesized to prepare flame retarding HIPS *via* radical addition reaction of TPP. From FTIR and ^{1}H NMR analyses, successful addition reaction of the TPP and decreases of the amount of double bond of polybutadiene parts in HIPS were confirmed. Reduction of the amount of double bond by addition of TPP can also be confirmed through comparison of Izod impact strength values. From ^{31}P NMR characterization, it can be supposed that the TPP exists as amorphous phase in TPP@HIPS. Thermal stability of the TPP@HIPS is improved, which is deduced by increasing residual char yield observed from TGA analyses. Residual char content of the TPP@HIPS at over 600 °C was 16.65 wt%, whereas there was no residue for pure HIPS (pHIPS). There are not significant differences in limited oxygen index (LOI) values of pHIPS and TPP@HIPS. However, the TPP@HIPS showed superior flame retardancy of V-1 rating in UL94 vertical test.

Keywords: high impact polystyrene, triphenyl phosphate, flame retardant, residual char content, UL94 vertical test.

Introduction

Polystyrene (PS) has an excellent processability over a wide range of temperatures and pressures, and an unusually good dimension stability, rigidity, and low moisture absorption.[1] These superior properties enabled it to be used in various fields. However, it has a defect of poor impact strength. So, high impact polystyrene (HIPS) has developed to improve that defects of PS. This HIPS is prepared through adding around 3-8 mol% polybutadiene (PB) rubber parts.[2] HIPS has been applied to various fields because it has excellent toughness, suitable electric property, and satisfactory performances.[3] However, application of HIPS has been gradually restricted because of defects such as combustibility, fire hazard, and mass loss features by heat.[4,5] Until now, flame retardant HIPS has been achieved by introduction of a halogen based flame retardant.[6] Application of halogen based flame retardant, unfortunately, has led to another problems including risk of suffocation and environmental pollution. Therefore non-halogen flame retardants such as phosphorus or silicon based compounds have been magnified.[7] Conventional flame retardant HIPS has been prepared through simple blending of halogen based flame retardants, metal hydroxide, and red phosphorus, which cause various defects including toxicities in

health and environment.[8-11] Generally, flame retardant can be classified as reactive and additive types according to their application method. Additive type flame retardants are generally incorporated into resin by physical blending. This obviously provides the most economical and expeditious way of promoting flame retardancy for commercial polymers. Nevertheless, various problems including poor compatibility, leaching, and a reduction in mechanical properties, weaken the attraction. The application of reactive flame retardants involves either the design of new molecular structures, intrinsically flame retarding polymers or modification of existing polymers through copolymerisation with a flame retarding unit either in the chain or as a pendent group.[7] In our previous study, flame retardant acrylonitrile-butadiene-styrene (ABS) has been prepared by graft reaction of phosphorus based flame retardant on diene parts of PB moieties.[8] In this study, triphenyl phosphate (TPP) graft HIPS (TPP@HIPS) is synthesized through graft reaction of TPP on polybutadiene (PB) back bone in HIPS resin.[8-10] Physical analyses and flame retardant test concerning TPP@HIPS are also performed.

Experimental

Commercial grade HIPS (Polystyrol 576H) was supported from BASF (Korea) and dried at 90 °C prior to use. 1,1,1-Trichloroethane (TCE) and benzoyl peroxide (BPO) were obtained from Aldrich Chemical (USA) and were used as solvent and initiator, respectively. TPP was received from Junsei Pure Chemical (Japan) and was used as flame retardant. All the other chemicals were used of reagent grade and used as received in our study. Grafting of TPP on PB moieties of HIPS was carried out *via* radical addition reaction according to our previous report.[12] A four neck round flask equipped with reflux condenser, mechanical stirrer, temperature controller, and nitrogen gas inlet was used. 30 g of HIPS was dissolved in 400 mL of TCE at 80 °C under nitrogen atmosphere for 1.5 h, followed by addition of BPO and TPP of 3.0 and 30 g, respectively. After then the reaction proceeded at 80 °C for 8 h. Prepared TPP@HIPS was purified through repeating dissolution-precipitation cycle for 3 times and dried under vacuum at 65 °C for 2 days. TPP@HIPS and pure HIPS (pHIPS) were dried so as to remove residual moisture under vacuum at 90 °C for 24 h for extruding and injection molding procedure. Extrusion was performed by using a twin-screw extruder BA-19 (Bautek, Korea), which was set die-to-hopper temperature of 210-154 °C.[15,16] Injection of test specimens was carried out by

using an injection molder BA-915A (BAUTEK, Korea) with temperature range of 210-160 °C.[17] Fourier transformed infrared (FTIR) spectra were obtained by using a Galaxy 7020A FTIR spectrometer (Mattson, USA) with KBr method. Structural changes were evaluated by ^{1}H and ^{31}P NMR measurements by using DSX-400 solid state 400 MHz NMR (Bruker, Germany). Izod impact strength test was performed by using a cantilever beam impact testing machine according to ASTM D256 test method.[18] Thermal properties including char yield were measured by Q 600 thermogravimetry analyzer (TGA) (TA instrument, Japan) in nitrogen atmosphere. Limited oxygen index (LOI) and UL94 vertical tests were performed by using LOI 2005 (Festec, Korea) and flammability tester QM500VA (Qmesys, Korea) equipped with bunsen burner, respectively.[19,20]

Results and Discussion

Figure 1 shows the FTIR spectra of TPP@HIPS and pHIPS. When compared with pHIPS, the distinctive peaks of TPP@HIPS can be found at 3477, 2771, and 1253 cm^{-1}. Sohn *et al.*[12] reported that there is a distinct peak for hydroxyl groups
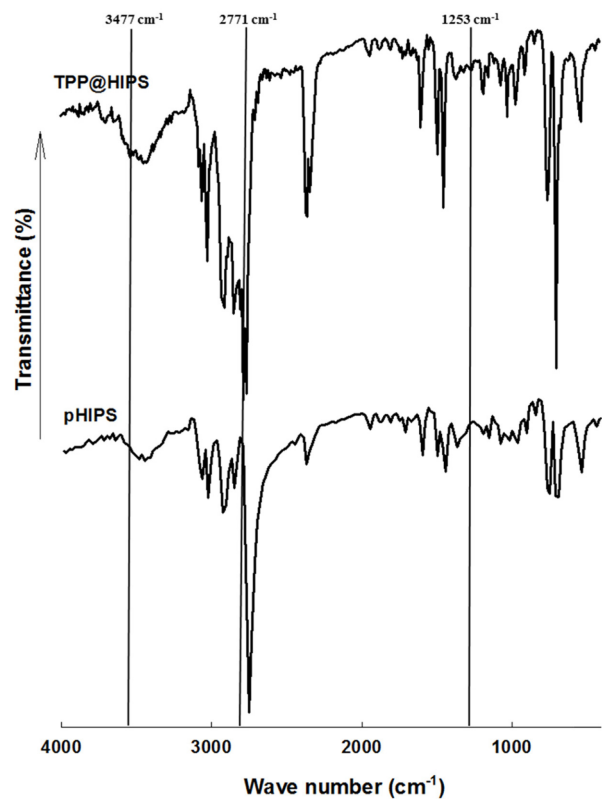

Figure 1. FTIR spectra of pHIPS and TPP@HIPS.

at 3300-3400 cm^{-1} for TPP graft polybutadiene, which cannot be observed for PB. According to Socrates,[21] medium intensity peaks of hydroxyl groups are found at 2725-2525 cm^{-1} region for P-O-H vibrations. Also the P-O-C stretching vibration peak of aryl phosphate is typically observed at 1180-1250 cm^{-1} region. Guo et al.[22] introduced that a weak peak of P=O stretching vibration peak is appeared at 1280 cm^{-1} for phosphates. Moreover they reported that a strong peak of P-O-C (C belongs to aromatic compounds) is observed at 1140 cm^{-1}. Based on these reports, peaks at 3477 and 2771 cm^{-1} can be assigned to O-H stretching vibration for P-O-H structure of TPP. A weak peak appearing at 1253 cm^{-1} is corresponded to P-O-C stretching vibration peak. From these results, it can be deduced that the TPP@HIPS is successively synthesized through graft reaction.

The solid state ^{1}H NMR spectrum of pHIPS and TPP@HIPS are presented in Figure 2. The peak appearing at around 7.0 ppm of TPP@HIPS spectra cannot be observed in pHIPS spectra. The P-O-phenyl structure peaks of grafted TPP on PB are commonly observed between 7.0 and 7.5 ppm region, as reported in our previous study.[12] Furthermore, Zhang et al.[23] have reported that distinctive peaks of TPP are presented around at 7.2-7.6 ppm region. Therefore the peak appearing at around 7.0 ppm can be ascribed to the covalent bond between TPP and polymer backbone. The peak intensities for double bond moieties of TPP@HIPS observed at 1.6~1.9 ppm and 5.2~5.7 ppm are remarkably decreased when compared with those of pHIPS. Aimin et al.[13] and Brydon et al.[14] have reported that the BPO radicals may function an addition on PB
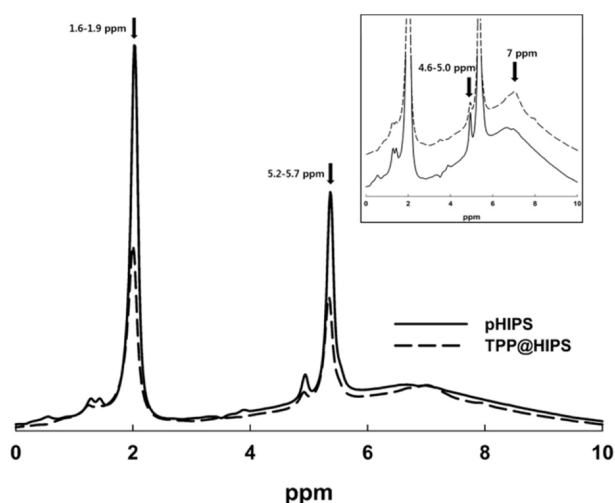

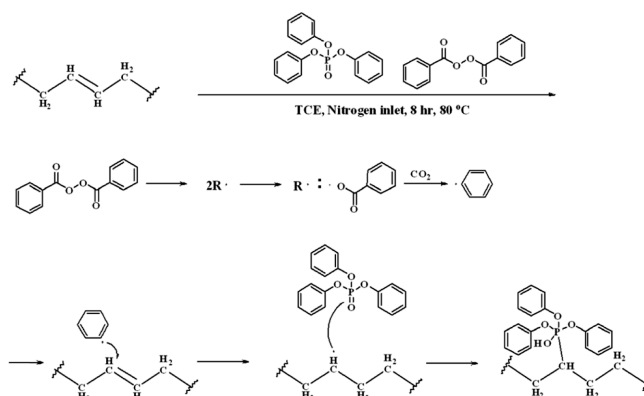Figure 3. Reaction mechanism of TPP@HIPS.

Table 1. Izod Impact Strength of pHIPS and TPP@HIPS

Izod impact strength (unit: kg cm/cm)		
Materials	Average	Standard deviation
pHIPS	8.63	±0.165
TPP@HIPS	1.98	±0.210

double bond and removal of an allylic hydrogen atom for radical reaction. Therefore, it can be supposed that the decreases of peak intensities concerning double bond moieties are able to be attributed to formation of covalent bonds between HIPS main chain and TPP through abstraction of α-hydrogen for alkene bond of butadiene parts and addition of TPP radical (Figure 3).

Izod impact strength test was performed for TPP@HIPS using pHIPS as control. Tests were repeated 3 times for each specimen and impact strength values were averaged. Those results are shown in Table 1. Izod impact strengths of pHIPS and TPP@HIPS were 9.0 and 2.0 kg·cm/cm, respectively. Usually rubber part is added to improve mechanical strength, i.e. impact strength, of PS.[2] Hence, decreased impact strength of TPP@HIPS is corresponded to the reduction of rubber parts confirmed by ^{1}H NMR characterization.

Figure 4 shows the solid state ^{31}P NMR spectra of TPP@HIPS using a cross polarization magic angle spinning probe. The ^{31}P NMR analysis is typically used to determine a presence of phosphorus moiety in inorganic phosphorus and organophosphorus compounds.[24] The solid state ^{31}P NMR resonance band of TPP@HIPS appears between -5 and -35 ppm. It is corresponded to the range of typical phosphate resonance band from 15 to -46 ppm reported by Fichera et al.[25] and Grimmer et al..[26] Therefore this resonance band can be assigned to the phosphorous part derived from grafted TPP
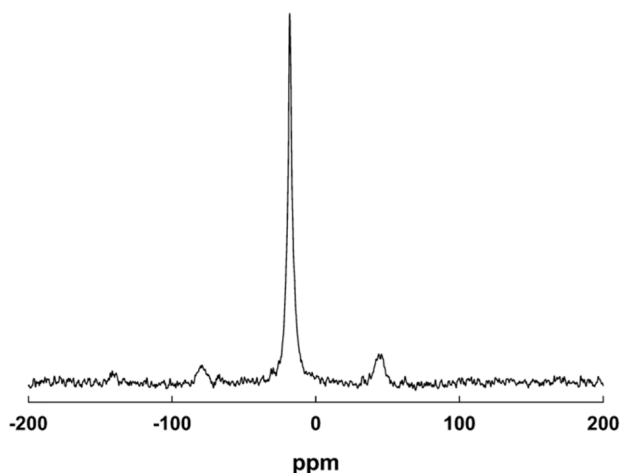

Figure 2. Solid state ^{1}H NMR spectra of pHIPS and TPP@HIPS.

Figure 4. Solid state ^{31}P NMR spectrum of TPP@HIPS.

Figure 5. TGA thermograms of pHIPS and TPP@HIPS.

molecule on HIPS. Fichera *et al.*[25] and M. Feike *et al.*[27] have also reported that the crystallinity of phosphorous compounds can be classified by the shape of the resonance. According to their reports, the peak for crystalline phase phosphorous shows sharp shape of *ca.* 1.5 ppm of width. This phosphorous peak is gradually broadened according to the decrease of degree of crystallinity. From those reports, it can be deduced that the introduced phosphorus moieties in TPP@HIPS may form an amorphous phase. Also, it can also be deduced that the introduced TPP is not localized but immobilized in phosphorous amorphous phase of TPP@HIPS.

The thermal degradation behaviors of pHIPS and TPP@HIPS are evaluated by TGA measurement. These results are shown in Figure 5 and Table 2. Usually, the important features of thermal degradation are 10% weight loss temperature (as symbol $T_{0.1}$), 50% weight loss temperature (as symbol $T_{0.5}$), and the amount of non-volatile residue remained at over 600 °C which is called char yield. In here, $T_{0.1}$ is considered as the begin temperature of the thermal degradation. The mid-point temperature of thermal degradation, $T_{0.5}$, is regarded as another important indicator of thermal stability.[28] Typically, there are large differences between $T_{0.1}$ and $T_{0.5}$ because of the continuous development of protective layer on polymer surface during thermal decomposition. Char, the carbonaceous solid residue, plays an important role in protecting surface of polymer from flame and inhibiting a leakage of fuel gas derived from pyrolysis of polymer during combustion.[7] These protecting and inhibiting roles of char residue are the most important mechanism for flame retardant in solid phase flame retardation of polymers on pyrolysis.[29,30] The onset of thermal degradation temperatures, $T_{0.1}$, for pHIPS and
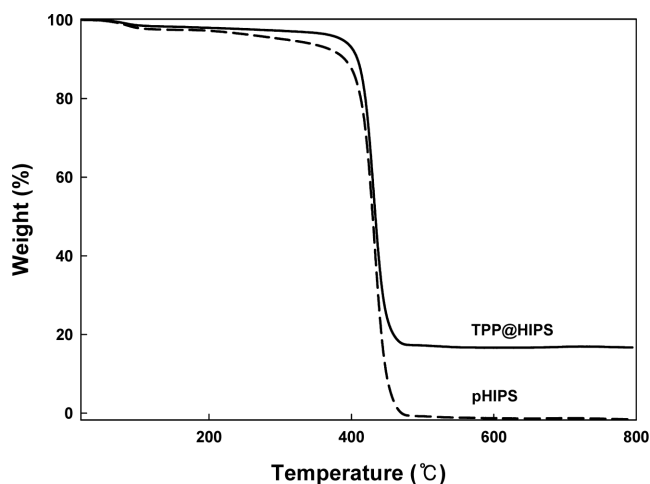
Table 2. TGA Data of pHIPS and TPP@HIPS

	TGA		
Sample	$T_{0.1}$ (°C)	$T_{0.5}$ (°C)	Char yield
pHIPS	390.6	429.9	No residue
TPP@HIPS	408.5	433.7	16.65 wt%

$T_{0.1}$ and $T_{0.5}$ indicate thermal decomposition temperature with weight loss of 10% and 50% on heating, respectively. Char yield means amount of non-volatile residues at over 600 °C.

TPP@HIPS are observed at 390.6 and 408.5 °C, respectively. On the other hand, the mid-point thermal degradation temperature, $T_{0.5}$, of pHIPS and TPP@HIPS are showed 429.9 and 433.7 °C, respectively. From these results, it can be deduced that the introduction of TPP can increase the thermal stability of TPP@HIPS in early stage of combustion. At mid-point of combustion, there were no significant differences in thermal degradation. It is supposed that this noticeable weight loss difference between pHIPS and TPP@HIPS appearing at $T_{0.1}$ is caused by the enhanced char formation mechanism of TPP@HIPS confirmed by residual char content at over 600 °C, as shown in Table 2. As well known, the thermal decomposition of polymer can be reduced by formation of carbonaceous char layer in condensed phase.[7,31] Both pHIPS and TPP@HIPS appear similar single step thermal degradation behavior without individual decomposition step. However, TPP@HIPS shows noticeable amount of char residue (16.7 wt%) when compared with pHIPS (no residue). This result is significantly distinguished from thermal degradation tendency of general pHIPS which is known as non-charrable polymer.[28,29] Generally, the phenyl phosphate based flame retardants show fire retarding effect both in gas and solid phase

Table 3. UL94 Vertical Test Results

Sample	1st Ignition (sec)	2nd Ignition (sec)	Dripping	Grade
pHIPS	Burn out	Burn out	Yes	No. rating
TPP@HIPS	2	4	Yes	V-1

flame retarding mechanism on burning.[30,32] These aryl phosphate based flame retardants, however, usually show a little char residue and a lot of weight loss because of low evaporation temperature on heating.[32,33] In this study, however, TPP@HIPS shows considerable amount of char residue. It can be attributed to the reduction of thermal evaporation and resulting weight loss of TPP at TPP@HIPS by the formation of covalent bond. This chemical bond enables the formation of enhanced char layer which plays an important role in solid phase flame retardant mechanism in combustion of polymer.[7,34]

As well known, flame retardancy of polymers in solid phase flame retardation mechanism will be enhanced by the increase of char yield.[7] Therefore, flame retardancy of TPP@HIPS was expected to be improved due to its increased char yield. Flame retardancy of TPP@HIPS was evaluated by LOI and UL94 vertical tests. LOI values mean minimal oxygen concentration for staying combustion of materials. Therefore the higher value ensures the better flame retardancy.[35] In this study, LOI values for pHIPS and TPP@HIPS were 20 and 22, respectively. There was not any significant difference in LOI value of TPP@HIPS compared with that of pHIPS. Kreveren[36] has reported that LOI values of polymers are proportional to char yield. However the increment of char yield had little influence on LOI value of TPP@HIPS of this study. Although the LOI is meaningful index for flame retardancy, it cannot be a direct indicator for fire performance of polymer.[30,37] Therefore, it is not enough to evaluate flame retardant performance of TPP@HIPS by LOI value alone. In this study, UL94 vertical test was carried out for direct evaluation of flame retardancy and results were shown in Table 3. All the test specimens of pHIPS and TPP@HIPS were measured three times and averaged. pHIPS shows no rating results due to burning out. TPP@HIPS represents good combustion time of 2 and 4 sec. As well known, UL94 V-1 rating can be addressed for specimen with less than 30 sec of ignition time for the sum of 1st or 2nd tests without second fire by dripping. In this study, TPP@HIPS showed less than 5 sec of total ignition time for 1st or 2nd tests with dripping which do not induce second fire. Therefore, flame retardant performance of TPP@HIPS could be determined as UL94 V-1 rating.

Conclusions

TPP@HIPS is synthesized by radical addition reaction of TPP on HIPS to prepare flame retarding HIPS. The addition of TPP can be confirmed by FTIR, ^{1}H NMR, and ^{31}P NMR analyses. The decrease of double bond moieties of PB parts in HIPS which was observed from ^{1}H NMR characterization, was ascribed to the covalent bond formation between TPP and HIPS. These results can also be confirmed by decreasing of Izod impact strength of TPP@HIPS. The increases of thermal stability and residual char content of TPP@HIPS are clarified by TGA analyses. TPP@HIPS showed superior flame retardancy of V-1 rating in UL94 vertical test whereas pHIPS shows burning out and no flame retardancy rating. Improvement of flame retardancy of TPP@HIPS by adopting anti-dripping agent is undergoing and will be reported elsewhere.

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