

## Synthesis of Acryl Phosphate Antistatic Agent and Its Effect on the Antistatic, Thermal and Mechanical Properties of PMMA

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Received June 16, 2007; Revised August 8, 2007

**Abstract:** A simple and economic antistatic agent, (2-methacryloyloxyethyl)acid phosphate (acryl phosphate), was synthesized via the reaction of 2-hydroxyethyl methacrylate with phosphorus pentoxide. The acryl phosphate antistatic agent, synthesized in this study, was introduced into poly(methyl methacrylate) (PMMA) resin via copolymerization with MMA. This antistatic agent provides the PMMA matrix with excellent antistatic properties, including surface resistance and electric charge. A comparison of the present antistatic agent with other commercial agents demonstrated the excellence of not only its electrical, but also its thermal and mechanical properties.

**Keywords:** acryl phosphate, (2-methacryloyloxyethyl)acid phosphate, antistatic agent, poly(methyl methacrylate).

### Introduction

Except for a few special conductive polymers, all of the organic polymers produced industrially are not electrically conductive and, thus, are used in various insulating or low dielectric applications to minimize the electrical loss in transmission and telecommunications. Although insulating polymers are very useful materials in electrical applications, there do have some drawbacks, which are mostly associated with their electrostatic properties. The electrostatic phenomena of polymers are usually introduced during their processing and sometimes give a severe electrical impact on the human body, as well as causing defect and explosion of product from the adsorption of impurities.<sup>1-3</sup> Some various methods of reducing this electrostatic problem have been proposed; (i) the control of the humidity in the processing or manufacturing environment, (ii) neutralization of the static electrons of the polymer surface using an air ionizing apparatus, (iii) addition of antistatic agents to the matrix polymer resin, and (iv) incorporation of a polar (more hydrophilic) moiety in the polymer chains by chemical reaction. Among these methods, the third one has been most widely used because of its simplicity and cost effectiveness.<sup>4,5</sup>

Since the molecular structure of antistatic agents requires both electric conductive and matrix polymer-compatible parts, many surfactants possessing both hydrophilic and hydrophobic groups have been investigated for this purpose. Electro-conducting materials such as metals, carbon blacks, carbon fibers, aniline, and pyrrole polymers are also

used as antistatic agents, especially when composite materials are preferentially prepared for the manufacture of electrodes and semiconductors. Since these antistatic agents are usually added in large amounts, the inherent properties of the polymer matrix, such as its thermal, mechanical, and optical properties, are considerably affected. While the introduction of a small amount of surfactant solves this problem, its main drawback is the long-term instability associated with its leakage.<sup>6-10</sup>

Poly(methyl methacrylate) (PMMA) resin has been widely used for light illuminating devices, signboards, construction, and accessories, because of its high transparency, high surface gloss, and good thermal and mechanical properties.<sup>11,12</sup> However, the surface of PMMA can be readily damaged by the adsorption of environmental dirt and impurities, as it is easily charged electrically due to its high surface resistance.

The traditional and most widely used method of blocking the electrification of a polymer resin is to incorporate into it or spray a surfactant-type agent onto its surface. The most important factor to consider in using a small amount of antistatic agent with a polymeric material is to maintain its antistatic performance for a long time, while retaining the other bulk properties of the matrix polymer.<sup>13</sup> In this contribution, a simple and economic antistatic agent, (2-methacryloyloxyethyl)acid phosphate (acryl phosphate), was synthesized through the reaction of 2-hydroxyethyl methacrylate with phosphorus pentoxide, and then it was copolymerized with methyl methacrylate, which provides long-term antistatic properties without losing the PMMA bulk properties significantly.<sup>14-18</sup>

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## Experimental

**Raw Materials.** 2-Hydroxyethyl methacrylate (2-HEMA, Aldrich) and phosphorus pentoxide ( $P_2O_5$ , Aldrich) were used as reactants to synthesize mono(2-methacryloyloxyethyl)acid phosphate (acryl phosphate). Monomethylether hydroquinone (MEHQ, Aldrich) was used as an inhibitor for this reaction. Methyl methacrylate (MMA, Aldrich) was used as a monomer, and azobis isobutyronitrile (AIBN, Aldrich) as an initiator. Two commercial antistatic agents, poly(ethylene glycol acrylate) (PEGDA, Nano Chemical) and glycerin monostearate (GMS) (Ilsin Chemical, Korea), were used as purchased to compare their performance with the present one.

**Synthesis of (2-Methacryloyloxyethyl) Acid Phosphate (Acryl Phosphate).** 2-HEMA was reacted with phosphorus pentoxide. 260.28 g (2.0 mol) of 2-HEMA and 0.4 g (3.22 mmol) of MEHQ were placed in a 500 mL 3 neck flask equipped with a mechanical agitator, a thermometer, and a condenser. Different amounts of phosphorus pentoxide, viz. 99.372 g (0.7 mol), 141.96 g (1.0 mol), and 184.548 g (1.3 mol), were added to the reactor in which the temperature was kept below 50 °C. The phosphorus pentoxide was added very slowly to prevent the polymerization of 2-HEMA

induced by the exothermic heat of mixing. The reaction was conducted for 4 h under a nitrogen gas environment. Table I summarizes the mole composition of the reactants, and Figure 1 illustrates the synthetic scheme of acryl phosphate.

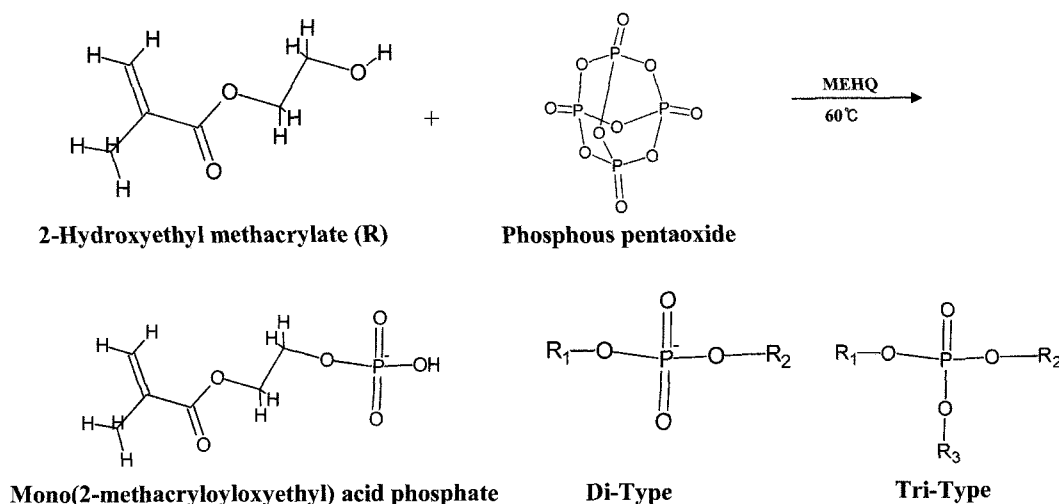
**Copolymerization of Methyl Methacrylate and Acryl Phosphate.** 100 g (1.04 mol) of MMA and a predetermined amount of acryl phosphate were placed in a reactor. After 0.05 g of AIBN was added as an initiator, the reactants were stirred for 30 min before injecting them into a casting mold composed of a reinforced glass pair (10 cm × 10 cm) and a gasket. The cast monomer mixture was maintained at 60 °C for 10 h, and then at 110 °C for 4 h. The product was removed from the glasses and gasket after the completion of the reaction. The PMMAs containing the other antistatic agents (i.e. PEGDA and GMS) were also prepared using the same procedure.

**Analysis of Chemical Structure and Materials Properties.** Fourier transform infrared spectroscopy (FT-IR, IR 4200, JASCO, Japan) and  $^1H$ -Fourier transform nuclear magnetic resonance spectroscopy (FT NMR, 300 MHz, JEOL, USA) were used to identify the chemical structure and purity of the synthesized product.

The cast film was stored in a chamber with a relative humidity of 65% at 23 °C. The washing process of the cast

**Table I. Composition of Reactants for the Synthesis of Acryl Phosphate**

	2-HEMA/ $P_2O_5$ Mole Ratio = 1/0.7	2-HEMA/ $P_2O_5$ Mole Ratio = 1/1	2-HEMA/ $P_2O_5$ Mole Ratio = 1/1.3
Acid Value (mg/KOH)	387.3	429.6	446.3
Viscosity (cps/25 °C)	1960	2160	2760
Moisture (%)	1.0	2.5	4.0
2-HEMA (wt%)	22.67	10.78	4.05
Mono-type (wt%)	50.47	53.35	55.12
Di-type (wt%)	20.19	26.06	27.33
Free $P_2O_5$ (wt%)	5.67	7.31	9.75



**Figure 1.** Reaction scheme for the synthesis of acryl phosphate.

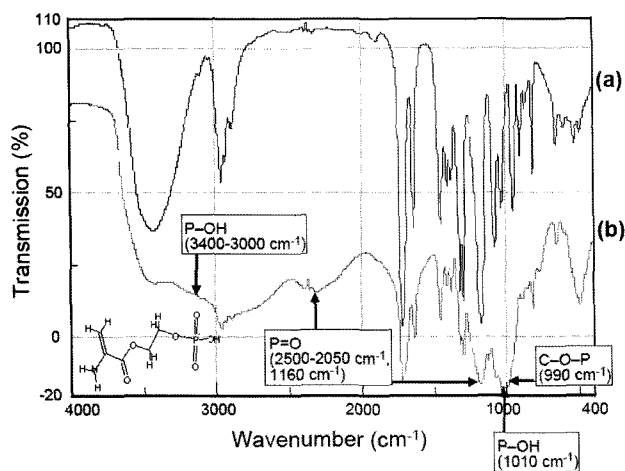
film was conducted in ultrasonic water for 30 min at 30 °C. A mega-ohm meter (TR-8601, Takeda Riken, Japan) was used to measure the surface resistance of the cast film. The surface resistance ( $\Omega$ ) was measured 1 min after applying 500 Volts at 23 °C and 65% relative humidity. A static honest meter (Sisido-shokai, Japan) was used to measure the half decay time of the electric charge. It was measured by applying 10,000 V to the sample for 30 s at room temperature and 65% relative humidity. The half decay time of the electric charge is defined as the elapsed time (s) required for reaching one half of the initial potential. A haze meter (SEP-H-SS, Nippon Seimitu-Gocaku, Japan) was used to measure the extent of the haze of the sample.

Differential scanning calorimetry (DSC7, Perkin-Elmer, Norwalk, CT) was used to measure the heat deflection temperature of the sample in the scanning range from 30 to 200 °C. Samples were loaded into aluminum alloy pans. Each sample was first heated from 30 to 200 °C at a heating rate of 10 °C/min. After thermal stabilization, the sample was cooled down to 30 °C at the same rate using liquid nitrogen and then heated again at 10 °C/min to 200 °C. An empty pan was used as a reference. The tensile strength was measured using a universal tensile machine (Instron 5565, Lloyd, UK) at a constant cross-head speed of 20 mm/min. The Young's modulus and stress at break were computed from the load-time curve.

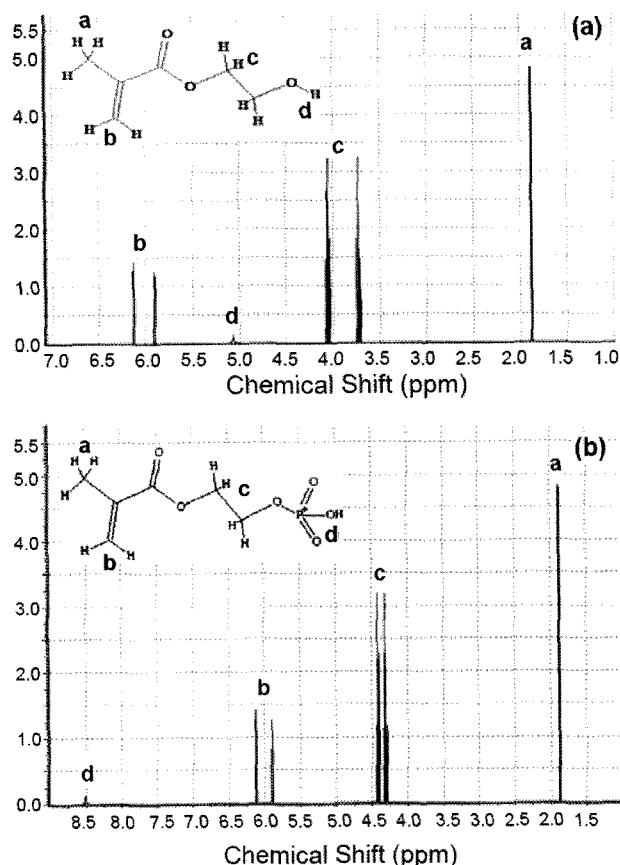
## Results and Discussion

**Chemical Structure Identification.** Figure 2 shows the FT-IR spectra of the homo 2-HEMA and acryl phosphate synthesized from the reaction of 2-HEMA and phosphorus pentoxide at a ratio of 1 to 1.3. The acryl phosphate was characterized by a strong peak at around 990  $\text{cm}^{-1}$  which originated from the formation of the COP bond.

Figures 3(a) and 3(b) show the  $^1\text{H}$ -FT NMR spectra of 2-



**Figure 2.** FT-IR spectra of (a) 2-HEMA and (b) acryl phosphate.

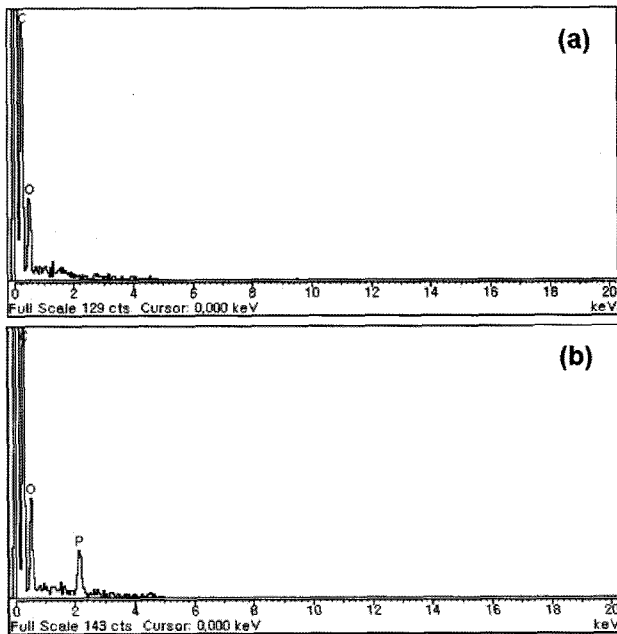


**Figure 3.**  $^1\text{H}$ -NMR spectra of (a) 2-HEMA and (b) acryl phosphate produced from the reaction of 2-HEMA and  $\text{P}_2\text{O}_5$  at a weight ratio of 1 to 1.3.

HEMA and acryl phosphate (2-HEMA : phosphorus pentoxide = 1 : 1.3), respectively. The comparison of the two spectra reveals that the proton peak from the -OH group (around 4.8 ppm in Figure 3(a)) disappears, however, a new peak appears at around 8.5 ppm in Figure 3(b) resulting from the proton in the hydroxyl group bonded to phosphate. The other protons in the two chemical species are assigned to the corresponding peaks, as shown in Figures 3(a) and 3(b).

Figures 4(a) and 4(b) show the EDX spectra of the two chemical species, 2-HEMA and acryl phosphate, respectively. In Figure 4(b), the peak corresponding to the phosphorous atoms, as well as those corresponding to carbon and oxygen, are clearly observed for acryl phosphate, while only those corresponding to the carbon and oxygen atoms of 2-HEMA are observed in Figure 4(a).

**Surface Resistance.** Figure 5(a) shows the surface resistance of the PMMA cast films containing the different types of antistatic agents (i.e. acryl phosphate, PEGDA, and GMS). The concentration of the antistatic agent ranged from 0.1 to 1 wt%. The surface resistance decreased with increasing content of antistatic agent, and the addition of acryl phos-

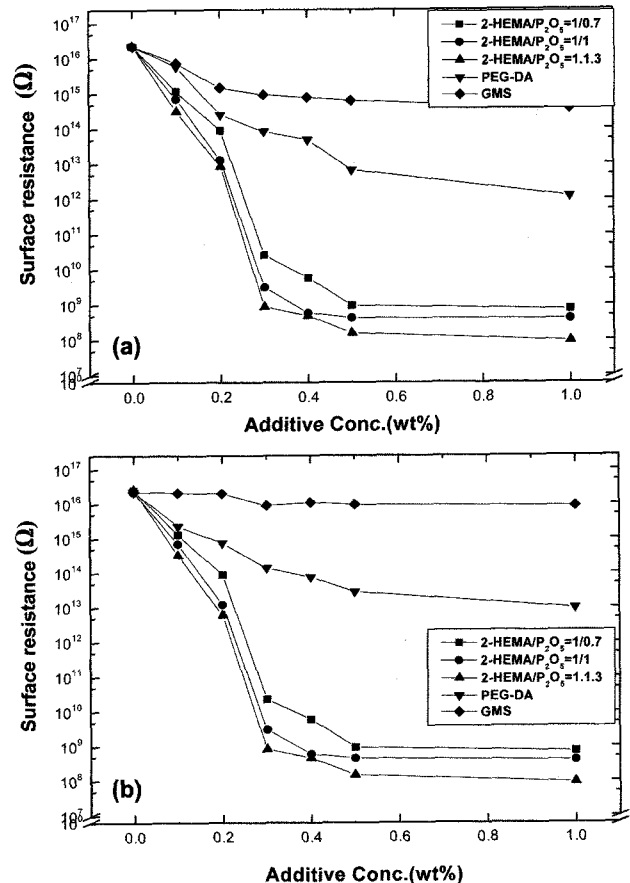


**Figure 4.** SEM-EDX spectra of (a) 2-HEMA and (b) acryl phosphate produced from the reaction of 2-HEMA and  $P_2O_5$  at a weight ratio of 1 to 1.3.

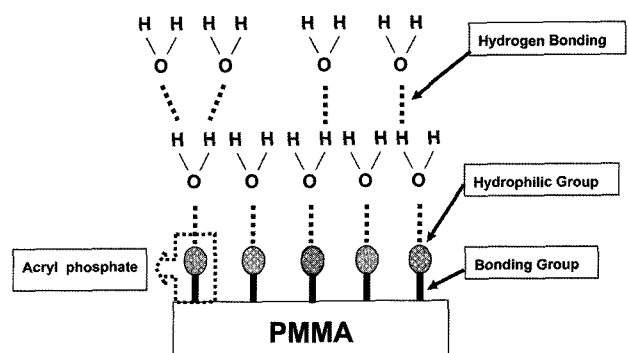
phate was the most effective in reducing the surface resistance. The antistatic effect was prominently observed up to a concentration of 3 wt%, as the surface resistance was not much affected at a higher concentration of the antistatic agent. It was thought that the electrically conducting layer is formed mostly at a concentration of antistatic agent below 3 wt%, which strengthens the molecular polarization.

Figure 5(b) shows the surface resistance of the PMMA cast films containing the antistatic agent which were treated with ultrasonic water. The surface resistance of the GMS containing PMMA cast films became much higher after being treated with water. It is thought to be due to the change of the surface resistance caused by the leakage of the GMS from the film during the water treatment process. Neither the acryl phosphate- nor the PEGDA-containing polymer films showed any difference in the surface resistance before and after the washing processes, which demonstrates that these antistatic agents are very stable in the matrix polymer due to the formation of covalent bonds between the agents and MMA (Figure 6).

**Half Decay Time of Electric Charge.** Figure 7 shows the half decay time of the electric charge for the antistatic agent containing PMMA cast films that were washed in ultrasonic water at 30°C for 30 min. The half decay time indicates how fast the electric charge is eliminated from the sample. As shown in Figure 7, the half decay time considerably increased after washing the GMS containing polymer film as it leaked out of the polymer matrix. The half decay time of the acryl phosphate or PEGDA containing film was



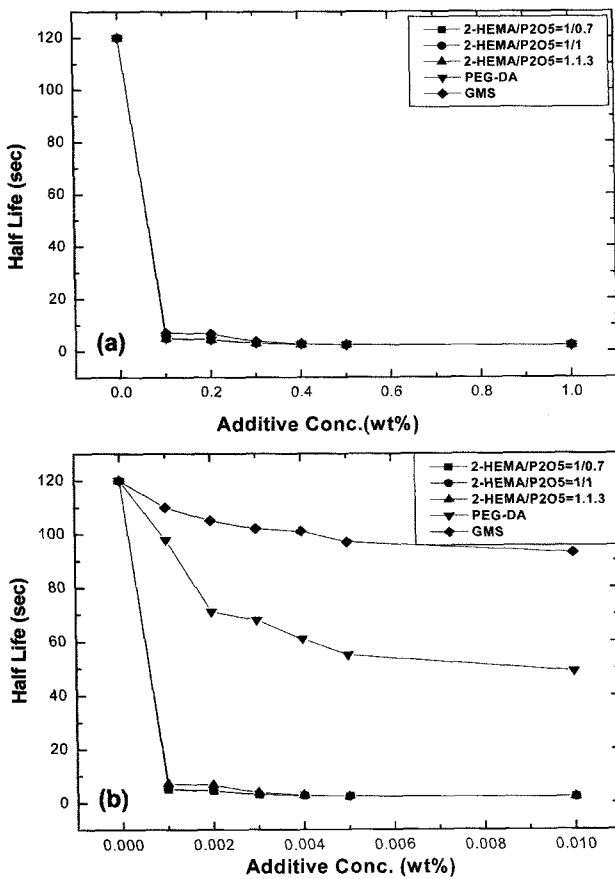
**Figure 5.** Surface resistance of PMMA resins containing acryl phosphate, PEGDA and GMS, according to their composition (a) before and (b) after ultrasonic water treatment.



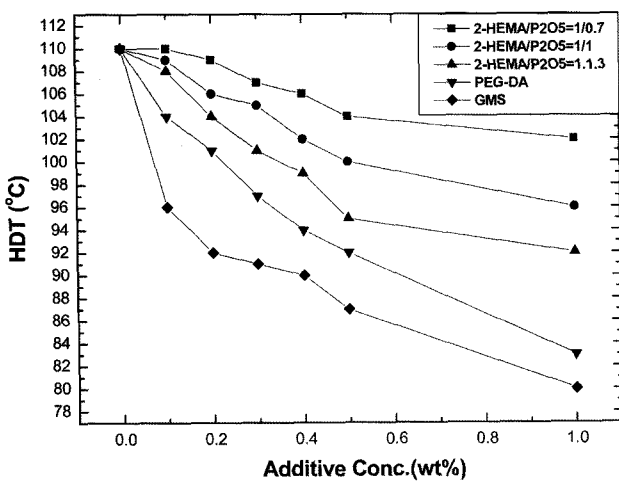
**Figure 6.** Antistatic mechanism of acryl phosphate in PMMA.

not as high as that of the GMS containing one, because of the presence of strong covalent bonding formed via copolymerization with MMA. The effect of the PEGDA system on the half decay time was, however, not as good as that of the acryl phosphate system. This is probably because the presence of the di- or tri- forms of acryl phosphate tightens the covalent bonding with the monomer formed by the

crosslinking reaction, even if its amount was not so high (Table I). In the acryl phosphate systems, however, the



**Figure 7.** Half decay time of electric charge of PMMA resins containing acryl phosphate, PEGDA and GMS, according to their composition (a) before and (b) after ultrasonic water treatment.



**Figure 8.** Heat deflection temperature of PMMA resins containing acryl phosphate, PEGDA and GMS, according to their composition.

weight ratio effect of HEMA/phosphorus pentoxide on the half decay time was not clearly observed in this concentration range.

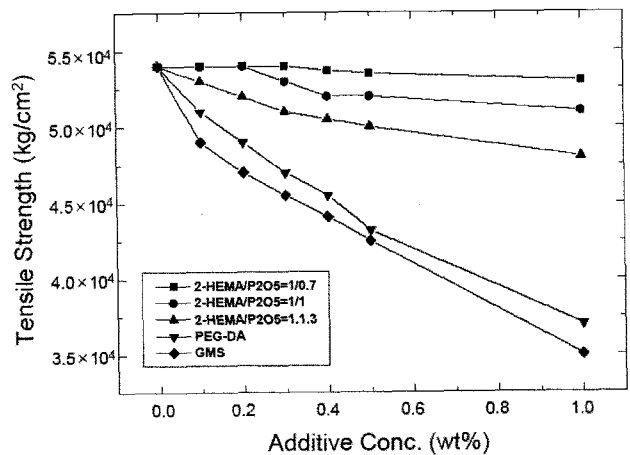
**Heat Deflection Temperature and Tensile Strength.**

Figure 8 shows the heat deflection temperatures of the antistatic agent containing PMMA samples. The heat deflection temperature (HDT) decreased with increasing concentration of antistatic agent. The introduction of GMS decreased the HDT the most, as this short molecular weight additive acted like a plasticizer in terms of its effect on the thermal and mechanical behavior of the bulk polymer. Acryl phosphate and PEGDA reduced the HDT less than GMS, as they eventually acted as a comonomer rather than a plasticizer in the PMMA resin. The lower HDT of the PEGDA system than that of the acryl phosphate one was caused by the more hydrophilic nature of poly(ethylene glycol). The longer side chain of the PEGDA system than that of acryl phosphate is another reason for the lower HDT values. Since the molecular weight of the PEG side group (ca. 700 g/mol) was higher than that of acryl phosphate after copolymerization, the molecular mobility of the acryl phosphate side group would be expected to be less.

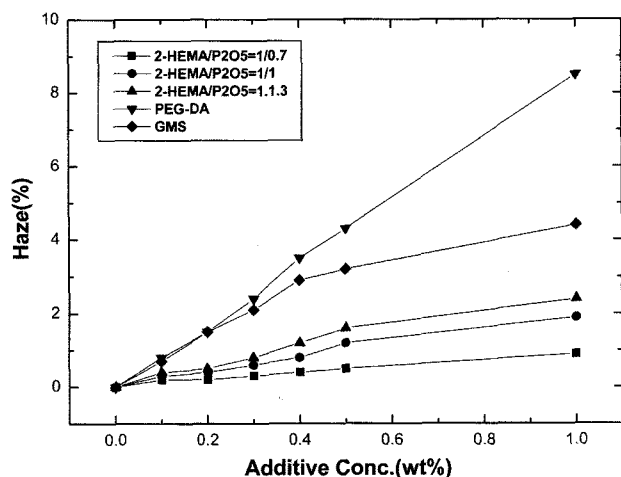
In the acryl phosphate systems, a higher concentration of phosphorus pentoxide resulted in a lower HDT, because the small amount of phosphorus pentoxide residue not involved in the synthesis of acryl phosphate acted as a hygroscopic additive in the polymer matrix, especially at a high concentration.

Figure 9 shows the tensile behavior of the antistatic agent containing PMMA cast films. This mechanical behavior was similar to the HDT behavior for the reasons mentioned above.

**Haze.** The haze behavior of the PMMA cast film is shown in Figure 10. The haze increased with increasing concentration of antistatic agent for all of the systems, but the worst behavior was observed for the GMS system due to



**Figure 9.** Tensile behavior of PMMA resins containing acryl phosphate, PEGDA and GMS, according to their composition.



**Figure 10.** Haze behavior of PMMA resins containing acryl phosphate, PEGDA and GMS, according to their composition.

its poor compatibility with the PMMA matrix. The haze of the PEGDA containing film was not as good as that of the acryl phosphate containing one, because the former is not as compatible with PMMA as the latter one. Unreacted phosphorus pentoxide may be present when a higher content of phosphorus pentoxide than the stoichiometry was introduced. In this case, the residual phosphorus pentoxide acted as an impurity, ruining the transparency of the PMMA matrix. The acryl phosphate synthesized using a lower amount of phosphorus pentoxide (i.e.  $P_2O_5/2$ -HEMA ratio) led to higher transparency in the acryl phosphate systems, because almost all of the phosphorus pentoxide reacted (consumed) during the synthesis.

## Conclusions

Three types of antistatic agents (i.e. the acryl phosphate synthesized in this experiment and commercial PEGDA and GMS) were introduced into PMMA resins either by blending or copolymerization to analyze the antistatic and other physical properties of the polymer samples. Acryl phosphate showed much better performance than the other antistatic agents through the observation and comparison of the

various electrical, thermal, and mechanical properties, such as the surface resistance, half decay time of the electric charge, heat deflection temperature, tensile strength, and haze. The small quantity of residual phosphorous pentoxide existing in the polymer matrix had only a trivial negative effect on the thermal, mechanical, and transparent properties, while maintaining the antistatic properties such as the surface resistance and half decay time, as it acted just as an impurity.

**Acknowledgements.** This work was supported by the Korean Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) (No. R0A-2007-000-10029-0).

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