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Synthesis and Properties of Water-soluble Polyamine Phosphate Type Durable Antistatic Agent

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Abstract : Water-soluble polyamines (PEG-DETs) were obtained by reacting PEG 600-diglycidyl ether with tetraethylenepentamine, which is a highly conductive aliphatic amine and curing agent. Then water-soluble polyamine phosphates (PEG-DETPs) were synthesized by cationization of PEG-DETs with phosphoric acid to prevent gelation and enhance solution stability. Antistatic agents were prepared by adding water to these PEG-DETs and PEG-DETPs. Several antistatic tests were carried out after applying the prepared antistatic agents to PET textile with and without resin. Tests showed that PEG-DETPs possessed the durability along with antistatic properties and washability.

1. Introduction

The concept of the generation of static electricity on synthetic fibers has been known since Hersh and Montgomery revealed the theory of friction triboelectric series on all kinds of synthetic fibers in 1955[1]. As a result, in our daily lives their static electricity hazard has stood out considerably with the development of synthetic fibers.

In order to prevent static electricity hazard, temperature and humidity were controlled or corona electric discharge and others have been used etc. But antistatic agent[2,3] has usually been applied as an coating in the case of synthetic fibers. Antistatic agent is usually applied on the molded polymetric surface as a thin film by coating an electroconductive material (surfactant) aqueous or organic solution. In this method, surfactant has been often utilized.

To control the static electricity the following things are considered; one is the generation of friction electric charge related to the structure of surfactant and the other is how to eliminate surface charge related to

adsorption-amount and hygroscopicity of surfactant. The former is explained by electron transfer among substances on the surface, and the latter by charge transfer or ion transfer through absorbed moisture as an medium[4].

A few non-durable antistatic agents have been synthesized and applied as a surface coating by Henshall[3] and Marshall[5] et al. But most of them are water-soluble and highly hygroscopic so that they are easily lost by washing or arrangement reversion in the continuous layers of hydrophilic group. This is the case for spray antistatics, which is in sale at a market now and static electricity will generate again after repeated washing.

Therefore, the development of polymeric surfactant has been accelerated because it has excellent adhesion and better durability by forming a tough uniform thin film. It does not have any migration upon heating. Kimura[6] treated polyamide textile with poly (oxyethylene) diglycolic acid, and Maity et al.[7] applied a durable copolymer of acrylamide and diallyldimethylammonium chloride to polyethylene

terephthalate (PET) textile. But on the whole the materials are unstable and did not have semi-permanent property. And Park et al.[8-10] synthesized a durable antistatic agent by converting 2-dimethylaminoethyl methacrylate to quaternary ammonium salt such as acetic acid or dimethyl sulfate and then by copolymerizing N-methylolacrylamide. They treated it on PET textile and investigated the various changes in properties.

In this study, epichlorohydrin and polyethylene glycol (PEG) 600[11], which is known for having hygroscopicity, softness and antistatic effect, were reacted to PEG 600-diglycidyl ether using BF_3 as a catalyst. Next this product was reacted with highly electroconductive tetraethylenepentamine[12] to obtain polyamine intermediate which has water-soluble long chain. And then in order to prevent its gelation and to raise its stability of aqueous solution this intermediate was cationated with phosphoric acid, so that water-soluble quaternary ammonium polyamine was prepared as an antistatic agent.

Both the prepared antistatic agent and the commercial antistatic were applied with and without resin on PET textile. Surface resistivity and half-life [13] by static honestmeter were compared and examined before and after washing and wash cycles.

2. Experimental

2.1 Materials

Tetraethylenepentamine (TEPA, first grade reagent, Junsei Chemical Co.) was used and complexed BF_3 -ether (special grade reagent, Tokyo Kasei Kogyo Co.) was used as a catalyst. Polyethylene (PEG) 600 (Dai-ichi Kogyo Seiyaku Co.) was used as received and epichlorohydrin (EH, Hayashi Pure Chemical Co.) was vacuum distilled to obtain fraction with boiling point of $28\sim 29^\circ\text{C}$ at 20 mmHg.

Sumitex resin M-3(M-3) (melamine type, control resin, Sumitomo Chemical Co.) and Sumitex accelerator ACX (ACX) (amine salt type) were used as a fiber finishing resin and as a catalyst, respectively.

2.2 Synthesis of PEG 600-Diglycidyl Ether

PEG 600 114.5g (0.191mol) and BF_3 0.15g as a strong Lewis acid catalyst were put into 250mL 4-necked flask, and under N_2 gas EH 35.3g (0.381mol) was dropped slowly at 75°C and for 70 mins. The reaction product was kept at 80°C for additional 60 min.

This reaction was exothermic so that it was cooled enough. The product was obtained by putting the reaction product into xylene to remove unreacted materials and light-yellow viscose PEG 600-diglycidyl ether (PEG-DE) was obtained.

Table 1 Reaction Conditions and Physical Properties of PEG-DET

Exp. No.	$\frac{[\text{PEG-DE}]^a)}{[\text{TEPA}]}$	Solvent		Reaction conditions		Yield (%)	Stability ^{b)}
		DMF (mL)	Water (mL)	Temp. ($^\circ\text{C}$)	Time (min)		
PEG-DET-1	1.0	150	—	70	100	—	gelated
PEG-DET-2	2.0	150	—	75	150	80	not gelated
PEG-DET-3	3.0	150	—	75	150	80	not gelated
PEG-DET-4	2.0	—	140	75	150	—	gelated
PEG-DET-5	2.0	—	140	65	120	43	not gelated
PEG-DET-6	2.0	—	140	75	100	64	not gelated
PEG-DET-7	2.0	—	140	84	80	—	gelated

^{a)}[PEG-DE]/[TEPA]: Ratio of molar concentration

TEPA : Tetraethylenepentamine

PEG-DE : PEG 600-diglycidyl ether

^{b)}Stability against to gelation

Table 2 Reaction Conditions and Physical Properties of PEG-DETP

Exp. No.	$\frac{[\text{H}_3\text{PO}_4]^{\text{a)}}}{[\text{PEG-DET-2}]}$	$\frac{[\text{H}_3\text{PO}_4]^{\text{a)}}}{[\text{PEG-DET-3}]}$	Water (mL)	Reaction conditions		Yield (%)	Stability ^{b)}
				Temp. (°C)	Time (min)		
PEG-DETP-1	1.0	—	240	85	100	—	gelated
PEG-DETP-2	2.0	—	240	85	100	91	not gelated
PEG-DETP-3	3.0	—	240	85	100	85	not gelated
PEG-DETP-4	—	2.0	240	85	100	90	not gelated

^{a)}PEG-DET-2 and PEG-DET-3 : Water-soluble polyamine^{b)}Stability against to gelation

2.3 Synthesis of Water-soluble Polyamine

The typical method of synthesis is as follows: (Table 1)

Synthesized PEG-DE 98.3g (0.14mol) was put in 500mL 4-necked flask, and then DMF 150mL was added to dissolve it with agitation. After that, under N₂ gas TEPA 13.2g (0.07mol) was dropped slowly and was allowed to undergo additional reaction at 75°C and for 150 min.

This reaction was a exothermic. The obtained product was precipitated in a excess of xylene to remove un-reacted materials. As a result, water-soluble yellow transparent viscose liquid polyamine (PEG-DET) was obtained.

2.4 Synthesis of Water-soluble Polyamine Phosphate

The typical synthesis is as follows: (Table 2)

PEG-DET 161.3g (0.1mol) was put in 500mL 4-necked flask and was dissolved in 240mL distilled water. After that, under N₂ gas, the temperature was raised to 75°C. And then phosphoric acid 19.6g (0.2mol) was dropped at the same temperature during 30 min and was kept at 85°C and for 100 min.

After being precipitated with a excess of THF and removing unreacted materials, water-soluble yellowish viscose polyamine phosphate (PEG-DETP) was obtained.

2.5 Preparation of Antistatic Agent

Either 10g of PEG-DET -2, -5, -6 (Table 1) or 10g of PEG-DETP -2, -4 (Table 2) were put in 300mL beaker, and then were heated to 60°C. Under agitation 200mL

of hot water at 60°C was slowly added into the beaker for 30 min. As a result, water-soluble colorless transparent viscose antistatic agents were prepared.

The products are called PEG-DET -2B, -5B, -6B and PEG-DETP -2B, -4B, corresponding to PEG-DET -2, -5, -6 and PEG-DETP -2, -4.

2.6 Instrumental Analyses

IR analysis was performed on the products using IR spectrophotometer (JASCO A-100). The samples were coated on NaCl cell with THF as a solvent.

NMR analysis was performed using NMR spectrometer (Varian Gemini 200, 200MHz) with DMSO-d₆ as a solvent.

2.7 Experiment of Antistatic Finish

To examine the function, 100% PET textured yarn (warp 75d/35f, filling 75d/36f, density 195×95T, weight 115g/yd²) were treated with PEG-DETs and PEG-DETPs, respectively as follows:

2.7.1 Composition and Treatment Conditions

In independent treatment, 2g antistatic sample which had been already produced was added into 98mL water. And in conjunct treatment, 2g sample, 0.6g M-3 as resin and 0.06g ACX as resin catalyst were added into 97mL water.

100% PET textured yarn was made by padding 2 times with 1 dip, 1 nip padder at 30°C for 2 min. Padding was made to be wet pick-up [14] of 80% with pneumatic heavy padder (Uenoyama Kiko Co., air compression type).

It was dried at 110°C for 2 min. with a hot-wind cycle dryer (Lewis Co.) and then cured at 160°C for 2 min. with

Fig. 1 IR spectra of (a) PEG-DE, (b) PEG-DET-2, and (c) PEG-DETP-2.

Fig. 2 NMR spectra of (a) PEG-DE, (b) PEG-DET-2, and (c) PEG-DETP-2.

show at $\delta 2.7 \sim 2.9$ ppm. That is, it means that the coreaction by polyamine curing agent took place.

3.2 Synthesis and Identification of Water-soluble Polyamine Phosphate

The synthesis of PEG-DETP by phosphoric acid was carried out according to Kim's reaction mechanism^[23] where fatty carbamide was converted to quaternary ammonium salt in acetic acid. The reaction condition and structural formula of PEG-DETP were given in Table 2 and Scheme 1. Nitrogen atom of polyamine was cationated by phosphoric acid to be quaternary ammonium phosphate and consequently cationic polyamine was obtained.

In Table 2, the reaction temperature and time of PEG-DETP-1 to -3 were fixed, and the molar ratio of $[H_3PO_4]/[PEG-DET-2]$ was varied. In the case of PEG-DETP-1 gelation occurred after 13 hours. The gelation can be explained as follows: polyamine in PEG-DETP had 5 nitrogen atoms and one acetic acid molecule reacted with one of 5 nitrogen atoms so that quaternary ammonium phosphate which didn't gel was formed. But the rest of 4 nitrogen atoms had high reactivity, and at last by putting water the epoxy ring of PEG-DETP end group opened and resultant sec-OH attacked 4 nitrogen atoms. So at room temperature the phenomenon of gel was considered to occur slowly.

In the case of PEG-DETP-2 where 2 mol phosphoric acid was introduced for 1 mol of PEG-DET-2, gel was not formed at room temperature with it left alone. By considering the structural formula of PEG-DETP-2 as in Scheme 1, 2 phosphoric acid molecule was thought to be cationated at both end groups of 5 nitrogen atoms. This means that sec-OH around nitrogen atoms of both end groups of PEG-DETP could give strong basic property to nearby nitrogen atoms because sec-OH acts as an electron donor. This explains the fact that 2 phosphoric acid molecule attacked end groups of nitrogen atoms earlier than 3 nitrogens in the middle.

In the case of PEG-DETP-3 where 3 mol phosphoric acid was introduced for 1 mol PEG-DET-2, all of phosphoric acid molecule could not react, so that some were precipitated as un-reacted materials. The approach of phosphoric acid was prevented because of screening effect of phosphoric acids present at both end groups. But PEG-DETP-4, whose synthetic condition was same except for the use of 3 mol phosphoric acid,

was similar to PEG-DETP-2. Therefore, PEG-DET-2 and -4 were suitable for antistatic purpose.

Fig. 1(c) is IR spectrum of PEG-DETP-2. Stretching vibration[22] of P-OH newly appears at 2600 cm^{-1} , and at 1100 cm^{-1} stretching vibration[22] of H_2PO_4^- overlaps with existing C-O-C stretching vibration in EO, which confirms that cationation by phosphoric acid was formed. Fig. 2(c) is NMR spectrum of PEG-DETP-2, which shows the same overlapping epoxy ring and EO absorbing peaks at $\delta 3.4\sim 3.7$ ppm. Two other new peaks are also present: one peak at $\delta 2.7\sim 2.9$ ppm is assigned to $\equiv\text{C}-\text{CH}_2-\text{N}=\text{}$ and the other peak at $\delta 7.9$ ppm to H_2PO_4^- . Therefore IR and NMR can identify the structure of PEG-DETP-2.

3.3 Effectiveness of Antistatic

The synthesized antistatic agent and Eletat U-52 (Japan Ipposha Oil Co., polymer of special cation) were tested for comparison. Antistatic agents were applied onto PET textured yarn with and without resin. The reason for the choice of PET textured yarn as a textile was its easy generation of static electricity among all kinds of textiles.

Durability results upto 50 washing cycles are shown in Figs. 3~6. Fig. 3 is the surface electric resistivity of the yarn treated without resin. Compared to Eletat U-52, PEG-DET-2B, -5B, -6B had little antistatic effectiveness because their surface electric resistivities are high. On the other hand, the antistatic effectiveness of PEG-DETP-2B, -4B were better than that of Eletat. The differences in effectiveness among the synthesized antistatic agents may be related to the reaction conditions for PEG-DET and PEG-DETP. The conditions for PEG-DET-5B, -6B were not suitable to prevent them from gelation by water solvent. PEG-DET-2B was not cationated. Therefore, to improve the antistatic effectiveness of PEG-DET the synthesis conditions should be as follows: the reaction medium should be done in organic solvent and PEG-DET be mildly cationated by phosphoric acid.

On the other hand, the washability of the antistatic agents rather decreased after 20 washing cycles because surface resistivity reached almost consistent value. As a consequence it may have durability.

Fig. 4 shows the surface electric resistivity as a function of wash cycle for the yarn treated with resin.

Fig. 3 Changes of surface electrical resistivity vs. wash cycles on the fabrics treated independently with antistatic agents. Antistatic agents : Blank (■), PEG-DET-5B (▲), PEG-DET-6B (●), PEG-DET-2B (▼), Eletat U-52 (□), PEG-DETP-4B (○), and PEG-DETP-2B (△).

But its effectiveness was inferior to the one treated without resin. In treatment of one-bath method, the effectiveness was found to be rather decreased. When the yarns were treated with the synthesized antistatics, the difference in surface resistivity was smaller between independent treatment and conjunct treatment than that of Eletat U-52. This implies that the synthesized ones have a good compatibility with resin for fiber finishing.

In Fig. 5 the relation between voltage and wash cycle for the yarn treated with and without resin is shown. The initial voltage is smaller than that of the resin treated yarn suggesting the better effectiveness. In terms of effectiveness, PEG-DETP-4B, -2B was found out to be best.

In Fig. 6 the change of half-life according to wash cycle in with and without resin treatment are shown. The half life became longer with washing and the effectiveness of PEG-DET-2B was decreased. So it was not suitable for durable antistatic agent. Eletat U-52 had a good durability in independent treatment, but in

Fig. 4 Changes of surface electrical resistivity vs. wash cycles on the fabrics treated conjunctly with antistatic agents. Antistatic agents : Blank (■), PEG-DET-5B (▲), PEG-DET-6B (●), PEG-DET-2B (▼), Eletat U-52 (□), PEG-DETP-4B (○), and PEG-DETP-2B (△).

Fig. 5 Changes of initial voltage vs. wash cycles on the fabrics treated with antistatic agents. Solid line and dotted line refer to independent treatment and conjunct treatment, respectively. Antistatic agents : Blank (■), PEG-DET-2B (▼), Eletat U-52 (□), PEG-DETP-4B (○), and PEG-DETP-2B (△).

conjunct treatment its half-life value was increased rapidly until 20 washing cycles and eventually, its effectiveness was decreased. In the cases of PEG-DETP-4B and -2B there was little change of their half-life value in with and without resin treatment, so they had a good compatibility between antistatic and resin for textile processing. And after 50 times washing their half-life value was 2.2~2.6 seconds, 2.9~3.5 seconds in with and without resin treatment. That is, it proved that they were the antistatics which had considerable durability.

3.4 Effect of Humidity on Antistatic Effectiveness

In 1962, Diemunsch and Chabert[24] insisted that absorbed water in texture should be a necessary factor in the course of protecting antistatic. Sereda and Feldman[25] found the theory that antistatic value was reduced when monolayer of water was formed on the surface of all texture.

Fig. 7 shows the effect of relative humidity on the

Fig. 6 Changes of decay half time vs. wash cycles on the fabrics treated with antistatic agents. Solid line and dotted line refer to independent treatment and conjunct treatment, respectively. Antistatic agents : Blank (■), PEG-DET-2B (▼), Eletat U-52 (□), PEG-DETP-4B (○), and PEG-DETP-2B (△).

surface resistivity for the textile treated with the antistatic agents. The samples were exposed at the relative humidity of 20, 40, 60% for 24 hours prior to the measurement. When the standard condition was set at relative humidity of 40%, the less humidity got, the more surface electric resistivity increased. And as humidity got more, the phenomenon of slow reduction was shown. That is, the more humidity got, the better effectiveness was shown. The reason was considered why when humidity increased on the air, the part of hydrophile property caused by treatment of antistatic on PET texture surface induced and combined monolayer of water.

4. Conclusion

Water-soluble polyamine phosphate (PEG-DETP) was obtained by cationation of polyamine (PEG-DET) with phosphoric acid in order to prevent PEG-DET from gelation and to improve stability of its aqueous solution. Water-soluble PEG-DET was obtained by reacting with tetraethylenepentamine in PEG 600-diglycidyl ether. The suitable condition for PEG-DET synthesis was as follows: the solvent was

DMF and the molar ratio of [PEG-DE]/[TEDA] was 2.0. The reaction temperature and time were 75°C and 150 min., respectively. The reaction condition for PEG-DETP was that the molar ratio of $[H_3PO_4]/[PEG-DET-2]$ was 2.0, at 85°C for 100 min.

Antistatic agents, PEG-DET-2B, -5B, -6B and PEG-DETP-2B, -4B were prepared by adding water to PEG-DETs and PEG-DETPs, and applied onto PET textured yarns with and without resin. PEG-DETP-2B and -4B had a considerable durability by examining their antistatic effectiveness as a function of washing cycles upto 50. Also the results from the surface electric resistivity and half-life proved that they were good candidates for antistatic agents.

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Fig. 7 Changes of electrical resistivity vs. relative humidity on the fabrics treated independently with antistatic agents. Antistatic agents : PEG-DET-5B(▲), PEG-DET-6B(●), PEG-DET-2B(▼), Eletat U-52(□), PEG-DETP-4B(○), and PEG-DETP-2B(△).

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