

Research Article

Effects of Thermal and Solvent Aging on Breakdown Voltage of TPE, PBT/PET Alloy, and PBT Insulated Low Voltage Electric Wire

Eun-Soo Park

Youngchang Silicone Co., Ltd., 481-7 Gasan-Dong, Kumchun-Gu, Seoul 153-803, Republic of Korea

Correspondence should be addressed to Eun-Soo Park; t2phage1@daum.net

Received 22 March 2013; Revised 14 June 2013; Accepted 17 June 2013

Academic Editor: Changwoon Nah

Copyright © 2013 Eun-Soo Park. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Tests were performed to evaluate the effects of thermal and solvent aging on the mechanical and dielectric breakdown properties of four types of polyester resins, namely, the insulation layer of poly(butylene terephthalat) (PBT)-based thermoplastic elastomer (TPE, TPE1), poly(butylene 2,6-naphthalate)-based TPE (TPE2), PBT/poly(ethylene terephthalate) alloy (Alloy), and PBT extruded onto a copper conductor of low voltage electric wire. The tensile specimens used in this series were prepared from the same extruded resins. The prepared electric wires and tensile specimens were thermally aged in air and in toluene, xylene, TCB, and NMP. When Alloy and PBT were thermally aged in toluene, xylene and TCB at 120°C for 6 h, the tensile properties were significantly decreased compared to TPE1 and TPE2 at the same condition. The reduction of elongation at break of Alloy was more discernible than that of PBT. This result indicated that Alloy is more affected by thermal and solvent ageing. Among them, TPE2 showed the highest breakdown voltage (BDV), and it has also the highest BDV after thermal and solvent aging.

1. Introduction

The service life of electric wire is determined by the condition of the insulating material. Insulations are commonly used as a flexible polymer coating on electric wire. Defects such as voids, contaminants, and scratches in the insulation structure lead to electrical failure in polymer insulated wires [1–4]. Thermoplastic polyesters, enclosing poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), copolymers, and blends, are widely used for electrical and electronic applications such as switching transformers, inverters, and information and telecommunications equipment due to their good electrical insulation and dielectric properties.

Many manufacturers of transformers get electrical insulating varnishes for secondary insulation and have to apply and transform them using a chemical curing process. The insulating varnish is applied to coils of polyester insulated wire, in the process of which it fills the gaps and micropores, and after curing it forms into a continuous resin film. It is important for mechanical stability and protection of coiled wire against dust, moisture, and chemicals which might cause insulation deterioration. Thereby, leakage currents or short

circuits can be avoided so that safe and reliable electrical products can be produced [5].

However, the insulating varnishes, which are provided for this purpose, are highly reactive materials. They are usually included in one or more solvents, such as toluene, xylene, isophorone, naphtha, 1,2,4-trichlorobenzene (TCB), and 1-methyl-2-pyrrolidinone (NMP). Varnishes for impregnation of electrical coils have until lately been diluted by solvents to lower the viscosity so as to permit full penetration of the windings. The varnish is generally applied by dip process. In this method, preheated winding wire is slowly dipped in the varnish, preferably with the slots in vertical direction. After certain time, the winding is removed from the varnish tank and excess varnish is allowed to drip and cured. Depending upon the type used, the winding is cured at elevated temperature (~160°C) for ~6 h in an oven. When the coils are baked, the varnish dries and the solvent is driven off. The drying leaves very small holes through which moisture can penetrate and in which corona may form.

Ribnick et al. [6] reported that a number of organic solvents (toluene, acetonitrile, dimethylformamide (DMF),

trichloroethylene, perchloroethylene, and tetrachloroethane) have been causing a high level of shrinkage in oriented semicrystalline polyester. Knox and coworkers [7] observed that aqueous and solvent-treated semicrystalline polyester samples were similar in that there was an increase in structural porosity as a result of crystallization in the swollen state. Weigmann and coworkers [8] found that the formation of void-containing structures by polar solvent treatment depends on the ability of the solvent to swell the polymer and to cause recrystallization in the swollen state. Thereby, the varnish treatment process influences the deterioration of the insulation made from polyester materials and reduces the ability of the wire to withstand short circuits.

In this study, PBT-based thermoplastic elastomer (TPE, TPE1), poly(butylene 2,6-naphthalate)-*b*-poly(tetramethylene ether glycol) [PBN-*b*-PTMG (TPE2)], PBT/PET alloy (Alloy), and PBT resins extruded onto a conductor of low voltage electric wire. The effects of thermal aging of extruded wires in toluene, xylene, TCB, and NMP on dielectric breakdown voltage (BDV) change were investigated. The changes in tensile properties of dumb-bell type specimen after the aging also have been evaluated.

2. Experimental

2.1. Materials. Toluene (Sigma-Aldrich, Inc., St. Louis, MO, USA), xylene (DC chemical Co., Seoul, Republic of Korea), TCB (Sigma-Aldrich, Inc., St. Louis, MO, USA), and NMP (TEDIA company Inc., Fairfield, OH, USA) were of reagent grade and were used without further purification. PBT (TRIBIT 1500, Samyang Co., Jeonju, Republic of Korea), Alloy (KP513 (PBT/PET = 30/70 wt%), Kolon Industries, Inc., Gwacheon, Republic of Korea), polyester type TPE (TPE1, G182D, SK Chemicals, Seoul, Republic of Korea), and PBN-*b*-PTMG type TPE (TPE2, EN5000, Plastech Service Inc., Seoul, Republic of Korea) resins were used as received. All polymer resins were predried in a convection oven for at least 12 h at 80°C to remove any moisture from the pellets before processing. The characteristics of the resins used in this study were summarized in Table 1.

2.2. Instrumentation. Scanning electron microscopy (SEM) observations of the specimens were performed on a Hitachi S-4200 model (Tokyo, Japan). The fractured surfaces of the specimens were prepared by using cryogenic fracturing in liquid nitrogen followed by a coating with gold in an SPI sputter coater. The morphology was determined using an accelerating voltage of 15 kV.

Thermal properties of the polymers were determined by differential scanning calorimetry (DSC, Perkin Elmer DSC 7, Norwalk, CT, USA). Thermal history of the samples was removed by scanning to 300°C with the heating rate of 20°C/min. After cooling down the specimen at the rate of -5°C/min to room temperature, it was reheated from 20 to 300°C with the heating rate of 20°C/min, and the DSC curves were obtained.

Thermal stability of samples was determined by thermogravimetry (TG, TGA-Q50, TA instrument, USA). The TG

TABLE 1: Characteristics of the insulation materials.

Material	Density (g/cm ³)	Hardness (°C)	T_m (°C)	Melt flow index (MI) (g/10 min)
PBT	1.31	112	221	4 (230°C/2.16 kg)
Alloy	1.40	116	251	5 (265°C/2.16 kg)
TPE1	1.27	77	217	8 (230°C/2.16 kg)
TPE2	1.24	75	226	11 (235°C/2.16 kg)

curves were obtained under an N₂ atmosphere at a flow rate of 4 mL/min and a scanning from 20 to 800°C with the heating rate of 20°C/min.

The surface appearance of the wire after solvent aging was measured by a video microscope (Inf-500TM, charge-coupled device (CCD) video microscope, Moritex Corp., Tokyo, Japan) with a PC that contained video capture software (i-Solution Lite, Image & Microscope Technology, Daejeon, Republic of Korea).

Fourier transform infrared (FTIR) absorption spectra of the samples were measured with a Perkin Elmer infrared spectrometer (Spectrum 2000, Shelton, CT, USA) in the wave number range from 4000 to 400 cm⁻¹ and analyzed using commercial software.

2.3. Extrusion Weight (g/10 min) Measurements. Extrusion weight (g) of the polymer samples was measured for 10 min using an extruder (φ20 Extruder, Flontec Co., Ltd., Republic of Korea) equipped with resin bypass (8 mm inner diameter and 10 mm length orifice). The extruder was preheated from room temperature to 265°C, and then the pellets of polymer sample were fed into the extruder and allowed to melt. The polymer stays in the molten form inside the extruder for approximately 10 min and then the molten polymer is vented at a screw rotation speed of 200 rpm out from the exit valve.

2.4. Tensile Test Procedure. Polymer sheets (around 0.3 mm) were prepared on a hot press at 265°C for 5 min under ca. 5 atm, followed by quenching in water. The sheet thus formed was free from any distortion problems.

Dumb-bell specimens for tensile tests were prepared in accordance with IEC 60811-1-1 specification. The test specimens were preconditioned to 20% relative humidity and 20 ± 1°C in order to standardize test conditions. Tensile properties of samples were determined with a universal test machine (UTM, Model DECMC00, Dawha test machine, Republic of Korea) at a cross head speed of 250 mm/min according to IEC 60811-1-1. The mean value of at least five specimens of each sample was taken, although specimens that broke in an unusual manner were disregarded.

2.5. Extrusion of Electric Wire. Polymers were dried in a hopper equipped with a dehumidifying dryer at least 24 hr at 80°C to remove any moisture from the pellets before extruding. The electric wire was composed of conductor and 1st and 2nd insulation layers. The 1st insulation layer was applied to the annealed copper conductor by extrusion with TPE1, TPE2, Alloy, or PBT (thickness: 30 μm). The 2nd layer

was applied to the 1st extruded layer by extrusion with the same material and the thickness of 1st layer. All insulation layers were extruded (temperature setting of rear zone: 235°C, second zone: 255°C, forward zone: 260°C, adapter: 265°C, and die: 265°C) at a speed of 200 rpm using an extruder (ϕ 20 Extruder, Flontec Co. Ltd., Seoul, Republic of Korea) equipped with a 1:3 compression ratio screw. Extruded samples were quenched by passage through a water-cooling zone at a rate of 200 m/min.

2.6. Breakdown Voltage (BDV) Measurement. The measurements of BDV were carried out at 60 Hz AC voltage by using a high voltage tester (SM-40PT08, Sungmin Instruments, Republic of Korea) with a rate of 0.5 kV/s according to UL 758 standard. The test sample consists of copper conductor (diameter of 0.3 mm) and insulation (thickness: 60 μ m). The voltage was applied between the conductor and aluminum foil wrapped intimate contact with the center 152 mm of the wire. Ten samples are tested and the average voltage is calculated.

2.7. Solvent Immersion of Extrude Wire. Solvent immersion test was performed to determine the ability of wire to resist degradation when exposed to toluene, xylene, TCB, and NMP according to the modified MIL-STD-2223 method 1001. Five specimens of 600 mm extruded wires were immersed to within 150 mm of each end in a 200 mm tall test tube containing 80 mL of solvent for 6 h at $20 \pm 2^\circ\text{C}$ ($60 \pm 2^\circ\text{C}$ or $120 \pm 2^\circ\text{C}$). After the predetermined time, specimens were removed from the glass tube, cleaned with methanol, and dried in an oven at 60°C until constant weight. The insulation was removed for a distance of 12 mm from each end of wire sample, and the specimens were subjected to the BDV measurement.

2.8. Solvent Immersion of Tensile Test Specimen. Ten dumb-bell specimens for tensile tests were immersed to a 200 mm tall test tube containing 80 mL of solvent (toluene, xylene, TCB, and NMP) for 6 h at $20 \pm 1^\circ\text{C}$ ($60 \pm 1^\circ\text{C}$ or $120 \pm 2^\circ\text{C}$). After the predetermined time, specimens were removed from the glass tube, cleaned with methanol, and dried in an oven at 60°C until constant weight. The specimens were subjected to the tensile test in accordance with the IEC 60811-1-1 specification.

3. Results and Discussion

3.1. Extrusion Conditions of TPE1, TPE2, PBT, and Alloy. Extrusion weight of TPE1, TPE2, Alloy, and PBT was measured in an extruder equipped with 8 mm diameter orifice at 265°C for 10 min, and the results are summarized in Table 2. For the thin film extrusion process, melt viscosity is an important property since it affects the flow of the molten polymer. They have good melt flow in processing temperature range and they are adequate for thin layer extrusion (>80 g/10 min). The extruding weight of samples increased in the order of Alloy $<$ TPE2 $<$ PBT $<$ TPE1 at the same conditions due to the mobility of the polymer molecules

being more restricted as the melt is contained with PET and PBN unit.

Four types of polymers were extruded onto 3 mm diameter copper conductor at die temperature of 270°C with a speed of 200 rpm using a single screw extruder. The most common extrusion fault is operating at an incorrect temperature. Too low extrusion temperature will result in a nonhomogeneous mixture while too high temperature will lead to voids or micropores being formed. The presence of voids on the insulation can significantly reduce the dielectric properties [4, 9]. SEM micrograph of the cryogenically fractured surface of the extruded TPE1, TPE2, PBT, and Alloy insulations was demonstrated in Figure 1. SEM photographs showed that the TPE1 exhibited a rough structure with numerous spikes, whereas TPE2, Alloy, and PBT have a relatively smooth fracture surface without the formation of necking indicating weak resistance to crack propagation. TPE2 shows a phase separation like structure with dispersed droplets. It is shown that the extrusion process does not cause any significant voids or areas of stress concentrations, which might affect the overall mechanical and electrical properties of the material.

3.2. Thermal Stability of TPE1, TPE2, PBT, and Alloy. Thermal degradation of extruded TPE1, TPE2, PBT, and Alloy insulations is shown in Figure 2. TPE1 shows an initial degradation temperature at 320°C which is the lowest of all investigated samples. Polyester type TPE is usually a linear segmented block copolymer composed of PBT as hard segments and flexible oligomeric polyester as soft segments. Therefore the thermal stability of TPE1 was lower than that of PBT.

In sharp contrast, TPE2 shows similar thermal degradation behavior to PBT. To improve the heat resistance of TPE, a more rigid aromatic diester monomer is needed for the hard segment [10]. The chemical structure of PBN is equivalent to that of PBT except that the benzene ring is replaced by the naphthalene ring. Wholly aromatic and multiaromatic ring structures produced high thermal stability resistance due to their rigid, rod-like aromatic chain. Incorporation of this structure in a polymer dramatically improves thermal properties [11]. The TGA traces of Alloy also show a significant shift of the weight loss towards higher temperature with stabilization 20°C higher than PBT.

As listed in Table 2, it can be seen that the Alloy exhibits a higher thermal-oxidative stability in terms of $T_{-5\%}$ (a mass loss of 5% during degradation occurs) than that of TPE1, TPE2, and PBT. With elevating temperature, the carbonaceous residues are oxidized to produce volatiles. The residues at 400°C are 64.2, 69.3, 71.4, and 88.2% for TPE1, TPE2, PBT, and Alloy, respectively, which confirms that the TPE1 easier to happen thermal degradation. The residues at 500°C show the same tendency as those at 400°C . The TG curves also show that all the samples nearly crumble at about 500°C (char yield around 8%) indicating that all the polymer mass turns into gaseous product. The decomposition pathways of a polyester composed of glycol and diacid are described in the literature as a three stage process. The first stage is elimination of terephthalic acid. The second stage, around 350°C , is possibly caused by the release of styrene and a complex mixture of

TABLE 2: Thermal properties of the TPE1, TPE2, PBT, and Alloy.

Sample code	Extrusion weight (g/10 min)	TGA thermal properties			DSC thermal properties				
		$T_{-5\%}$ (°C)	Residues at 400°C (%)	Residues at 500°C (%)	1st scan		2nd scan		T_c (°C)
					T_{m11} (°C)	T_{m12} (°C)	T_{m21} (°C)	T_{m22} (°C)	
TPE1	110	343.4	64.2	6.4	—	217	—	218	193
TPE2	98	376.0	69.3	6.7	—	226	217	226	202
PBT	100	379.7	71.4	6.8		221	215	222	195
Alloy	95	389.3	88.2	9.0	216	251	—	230	148

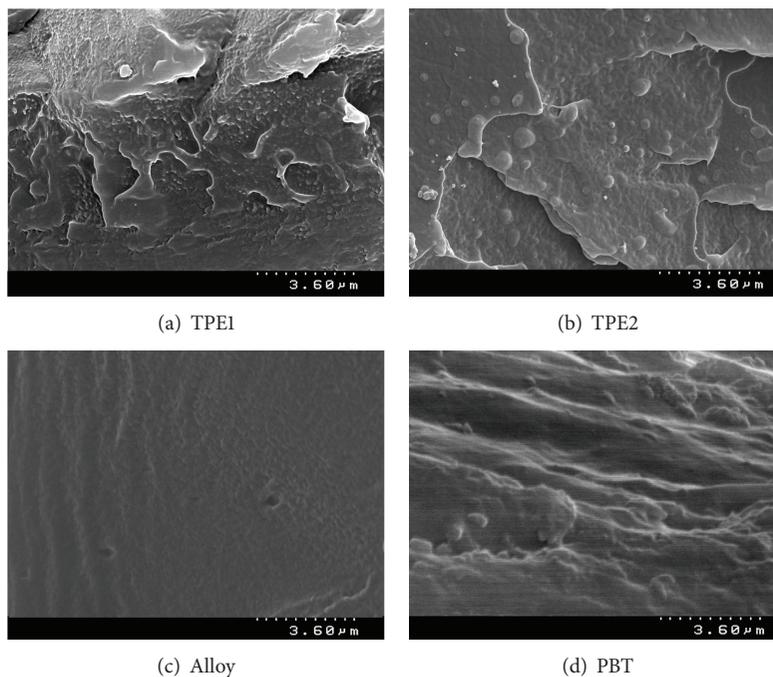


FIGURE 1: SEM micrographs of the fractured surface of extruded insulation layer.

other materials, while the third stage, above 500°C, is related to the loss of high boiling tars and oxidation of the char formed [12].

3.3. DSC Thermal Properties of the Extruded TPE1, TPE2, PBT, and Alloy. The melting and the crystallization behaviors of the extruded insulations were studied by using DSC. The 1st scan DSC data of Table 2 were collected by a heating rate of 20°C/min from 20 to 300°C. When PBT melt was slowly cooled at a rate of -5°C/min and remelted, the one melting peak of 1st scan DSC thermogram was divided into two peaks (Figure 3). PBT exists in two crystalline structures, α and β forms, and the transition between two forms takes place reversibly by crystallization, mechanical deformation, and relaxation [13, 14]. The melting peak of PBN-*b*-PTMG type TPE shows similar behavior to PBT. PBN also has two crystal forms, A and B forms, and four methylene groups in the B form are more extended than those in the A form as in the case of PBT [15, 16]. In the absence of mechanical deformation, both the crystal structures of PBT and PBN

favor the α form and A form, respectively. In contrast, melting temperature (T_m) of TPE1 did not show any changes.

The quenched Alloy sample has two melting peaks, which are associated with PET and PBT separate phase (Figure 3). Escala and Stein [17] found that, upon crystallization, PET and PBT did not cocrystallize. Avramova [18] also reported that, although PET and PBT formed their own crystalline phase upon crystallization of PET/PBT blend, both components could crystallize concurrently at all compositions of the blends, and the presence of one crystalline phase did not affect the crystallization rates of the other. When the Alloy melt was slowly cooled at a rate of -5°C/min and remelted, the two melting peaks of 1st scan DSC thermogram were merged into one peak and shifted to lower temperature. Alloy resin was produced with transesterification reactions occurring in the melt resulting in the formation of block copolymers with a random microstructure. These random copolymers have more irregular homopolymer sequences and have the single melting temperature when fully crystallized [9, 19]. It can be also seen that Alloy had the broad crystallization exotherm.

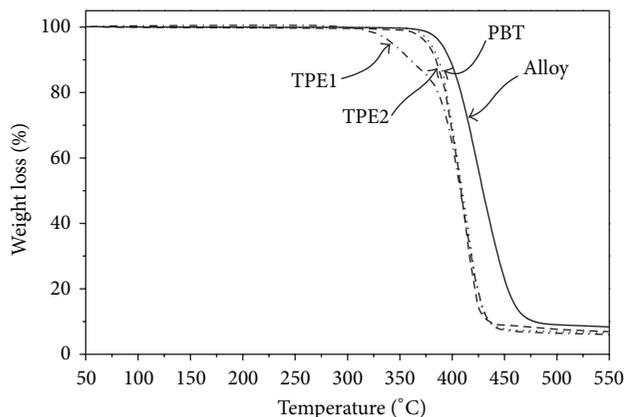


FIGURE 2: TGA thermograms of the TPE1, TPE2, PBT, and Alloy.

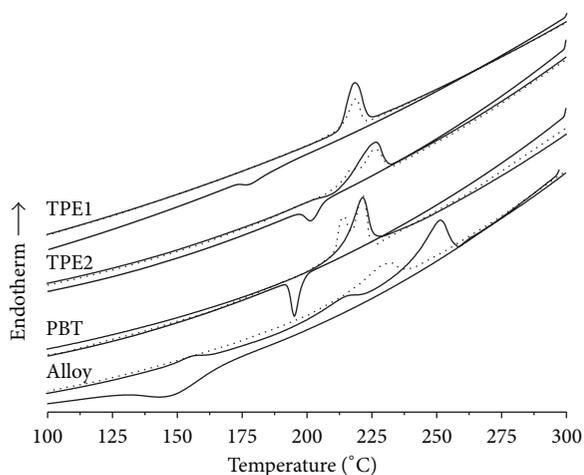


FIGURE 3: DSC thermograms of the TPE1, TPE2, PBT, and Alloy.

This broad peak may arise from concurrent crystallization of two different crystals at nearly the same crystallization temperature (T_c).

3.4. Tensile Properties of TPE1, TPE2, PBT, and Alloy after Thermal and Solvent Aging. Table 3 compared the effect of thermal and solvent aging on the tensile properties of TPE1, TPE2 Alloy, and PBT. The abbreviation of the sample code in Table 2, PBT-120°C-6 h, for example, means that the PBT was thermally aged at 120°C for 6 h. For TPE1, Alloy, and PBT, tensile strength and elongation at break of dumb-bell specimens were significantly decreased with increasing thermal aging temperature. In case of Alloy-180°C-6 h, an approximately 65% and 98% decrease in the tensile strength and elongation at break of 16 MPa and 6% were observed, respectively. The decrease in tensile properties after thermal aging can be related to the increase in brittleness of specimens driven by reduction of molecular weight. Thermal degradation follows the free radicals mechanism, initiated by oxygen or oxidative contamination in the material or other stresses. In the initial stages of thermal degradation of

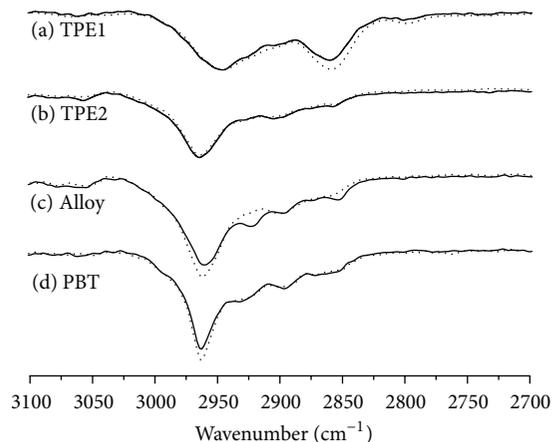


FIGURE 4: FTIR spectra of the insulation samples before (.....) and after (—) thermal aging at 180°C.

polymer, chain scission often prevails, which reduces molecular weight. Shorter polymer chains are more mobile and are thus able to crystallize more readily. In contrast, tensile properties of TPE2 were not changed compared to other samples. Incorporation of naphthalate structure in a polymer improves thermal and mechanical properties [18]. The hard PBN segment serves as a thermally reversible physical cross-linking between molecular domains, contributing thermal stability, mechanical strength, and dimensional stability to the TPE2. Thereby, TPE2 is a little more affected by the thermal aging than TPE1, Alloy, and PBT at the same temperature.

FTIR is an effective measurement for structure characterization. Figure 4 shows the FTIR spectra comparison of before and after thermal aging at 180°C. The peak at 2966–2855 cm^{-1} range is attributed to the vibration of $-\text{C}-\text{H}$ bonds. The most characteristic peaks are those in the region of 1720, 1600–1500, and 1100 cm^{-1} for $-\text{C}=\text{O}$ stretching vibration of the ester carbonyl group, stretching vibration of backbone of benzene, and $-\text{C}-\text{O}-$ stretching vibration, respectively. For Alloy (Figure 4(c)), after thermal aging at 180°C for 6 h, new adjacent bands at 2922 and 2850 cm^{-1} can be identified, and the intensity of the band at 2964 cm^{-1} decreased significantly. In the TPE1 (Figure 4(a)), small adjacent bands at 2924 and 2905 cm^{-1} can be identified and the intensity of the band at 2985 cm^{-1} decreased. In case of PBT, the intensity of the band at 2964 cm^{-1} decreases significantly (Figure 4(d)). These could be an indication of formation of polymeric scission products and cleavage of $-\text{C}-\text{H}$ bonds. In sharp contrast, as depicted in Figure 4(b), no chemical changes were observed by FTIR in the TPE2 specimens after thermal aging. These results are very well agreeing with tensile test.

To examine the effect of solvent aging on the tensile properties, dumb-bell specimens of TPE1, TPE2, Alloy, and PBT were immersed in toluene, xylene, TCB, and NMP at room temperature, 60°C, and 120°C for 6 h. When TPE1 and TPE2 were solvent-immersed for 6 h, the tensile properties were slightly decreased with increasing solvent immersing temperature. In sharp contrast, for Alloy and PBT, both tensile

strength and elongation at break were more rapidly decreased with increasing immersing temperature. This resembles the tensile behavior of thermally aged samples. After solvent-immersing at 120°C, the reduction of tensile properties of Alloy was more discernible than those of other samples. In case of Alloy-120°C-6 h-TCB, an approximately 45% and 98% decrease in the tensile strength and elongation at break of 24 MPa and 29% were observed, respectively. PBT has a faster rate of crystallization most probably due to longer and flexible chains, whereas PET has a slower rate of crystallization because of more rigid molecules in structure that hinder movement of chains. Because the tensile specimens were hot-pressed and quenched in cold water, PET region of Alloy may not be fully crystallized. As shown in Figure 3, Alloy had the broad crystallization range from 110 to 175°C and was able to crystallize more readily in thermal aging temperature range than TPE1, TPE2, and PBT. PET tends to become brittle upon thermally induced crystallization. Despite its high thermal stability, Alloy resin loses its ductility and reduces the tensile properties significantly after thermal treatment [9].

It is interesting to note that the tensile properties of Alloy were increased significantly even after solvent immersion at room temperature than neat Alloy. After immersion in NMP at room temperature for 6 h, the tensile strength of Alloy increased by 32.5%, whereas this immersion in toluene, xylene, and TCB increased it by 13.8, 11.6, and 15.6%, respectively. A minimum 34.6% overall increase in the elongation at break from 451 to 499% was observed after solvent immersion at room temperature. This improvement of the tensile properties was attributed to an increase in the degree of crystallinity and an improvement in crystal perfection without thermal effect. Ribnick et al. [6] suggested that, even at room temperature, strong interactions could be observed between some solvents and the polyester fibers. Moore and Shelden [20] reported that the polar aromatic hydrocarbons such as benzene, toluene, and benzyl alcohol enhance the crystallization of polyester. Acceleration of the crystallization in an organic solvent might be attributed to the fact that the T_g was lowered in the organic solvent.

After immersion test in NMP at 120°C for 6 h, the tensile properties of all samples were significantly decreased compared to other solvents. NMP is a noncorrosive high boiler with excellent solvent power and dissolves polymers, such as cellulose derivatives, polyamides, polyesters, and many copolymers, at higher temperature. As a result, the specimens swell and deform significantly in NMP at 120°C, and this leads to undesirable tensile properties.

3.5. BDV Measurement after Solvent and Thermal Aging. To investigate the electric breakdown properties after solvent and thermal aging of polymer samples, TPE1, TPE2, Alloy, and PBT were extruded on the conductor and quenched at a rate of 200 m/min. Table 4 summarizes dielectric BDV of extruded wire before and after thermal treatment and solvent immersion. The BDV of all samples was gradually decreased with increasing thermal aging temperature. After thermal aging at 180°C, BDV of TPE1, TPE2, Alloy, and PBT insulated wire was decreased by 50.4, 31.1, 26.3, and 34.3%, respectively,

compared to corresponding unaged ones. Dielectric breakdown causes a high-temperature arc to propagate through a dielectric medium and this can lead to ignition of the medium or of surrounding objects. The thermal aging is manifested in two ways by causing formation of polymer radicals [21] and microvoids [22] in the polymer materials due to increasing chain scission and volatility of degradation products.

The morphology and microstructure changes in the insulation layer after thermal aging at 180°C for 6 h are shown in Figure 5. After aging, microvoids were formed near the fracture surfaces indicating that the cavitation was not only a surface phenomenon, but characteristic of internal damage. They usually create a weakened pathway within the material by creating permanent molecular or physical changes. Some of such microvoids can coalesce into larger voids. As soon as sufficiently large voids are formed, from them a crack can start that ultimately breaks insulation.

The dielectric breakdown causes a high-temperature arc to propagate through a dielectric medium and this can lead to ignition of the medium or of the surrounding objects. Figure 6 demonstrates the breakdown points after dielectric breakdown test. As the thermal aging temperature increased, the char formation and size of breakdown point of all wires were decreased significantly. This means that the breakdown of thermally aged wire is determined by the electrical field at the tip of the defect [23].

After the extruded wire was exposed to the solvent immersion in toluene, xylene, and TCB, the BDV of TPE2 and PBT samples is not changed significantly compared to thermally aged ones. In case of PBT, the BDV reduction was more discernible after immersion in TCB than that of toluene and xylene. In sharp contrast, TPE1 was approximately 30% of the overall decrease in the BDV from 3.0 to 6.2 kV that was observed. When the extruded wire was immersed in NMP at 120°C for 6 h, the BDV of all samples decreased significantly. An approximately over 90% overall decrease in the BDV was observed. It can be seen that the BDV of TPE2 is higher than of other samples, and it has also the highest BDV after solvent aging. The voltage required for an electrical insulation to breakdown is a function of its thickness so that the BDV increases linearly with the insulator's thickness. Weigmann and coworkers [8] found that the formation of void-containing structures by organic solvent treatment depends on the ability of the solvent to swell the polymer and to cause recrystallization in the swollen state. While crystallization could occur during thermal shrinkage at higher temperatures, the crystallization of solvated polymer chains required a dissociation of the solvate and the exclusion of the solvent molecules. Park [24] reported that chemical etching of polyester filaments has revealed a complex stress cracking behavior which varied with orientation and thermal crystallization conditions.

The images in Figure 7 demonstrate the extruded wire surface after thermal treatment and xylene and NMP immersion at 120°C for 6 h. The surface images of xylene-immersed samples were similar to those of thermally aged ones except for the weak surface crack phenomenon of TPE1 and Alloy. In sharp contrast, the surface of NMP-immersed samples had many voids and eroded much more than that of thermally

TABLE 4: BDV changes of the TPE1, TPE2, PBT, and Alloy in various solvents.

Sample code	Breakdown voltage (kV)				
	Thermally aged	Thermally aged in solvent			
		Toluene	Xylene	TCB	NMP
TPE1	11.7 ± 0.8	6.2 ± 0.2	4.0 ± 0.3	4.6 ± 0.5	4.5 ± 0.8
TPE1-60°C-6 h	11.9 ± 0.7	5.6 ± 0.6	3.7 ± 0.5	4.7 ± 1.5	3.1 ± 0.5
TPE1-120°C-6 h	7.8 ± 1.4	5.2 ± 0.8	3.0 ± 0.5	4.3 ± 0.9	0.5 ± 0.1
TPE1-180°C-6 h	5.8 ± 1.5	—	—	—	—
TPE2	14.8 ± 1.2	14.2 ± 1.2	13.1 ± 1.1	13.9 ± 1.2	12.1 ± 1.1
TPE2-60°C-6 h	13.6 ± 0.8	13.2 ± 1.0	12.6 ± 1.2	11.7 ± 0.9	8.5 ± 0.2
TPE2-120°C-6 h	11.0 ± 1.1	12.8 ± 1.4	11.9 ± 0.8	11.3 ± 1.2	1.2 ± 0.1
TPE2-180°C-6 h	10.2 ± 1.3	—	—	—	—
PBT	13.7 ± 1.7	13.0 ± 1.7	12.4 ± 1.5	12.4 ± 0.8	11.8 ± 1.1
PBT-60°C-6 h	12.1 ± 1.3	12.2 ± 0.8	12.2 ± 1.0	11.0 ± 2.7	8.3 ± 0.1
PBT-120°C-6 h	10.5 ± 1.4	11.8 ± 1.9	11.0 ± 1.5	10.9 ± 1.6	0.7 ± 0.1
PBT-180°C-6 h	9.0 ± 1.5	—	—	—	—
Alloy	12.9 ± 1.2	12.3 ± 2.1	11.0 ± 1.9	8.1 ± 1.2	6.1 ± 0.4
Alloy-60°C-6 h	11.9 ± 1.3	9.4 ± 1.2	8.3 ± 0.9	6.1 ± 0.7	3.7 ± 0.1
Alloy-120°C-6 h	9.1 ± 3.0	9.0 ± 1.8	8.9 ± 2.6	4.7 ± 0.6	0.5 ± 0.1
Alloy-180°C-6 h	9.5 ± 1.8	—	—	—	—

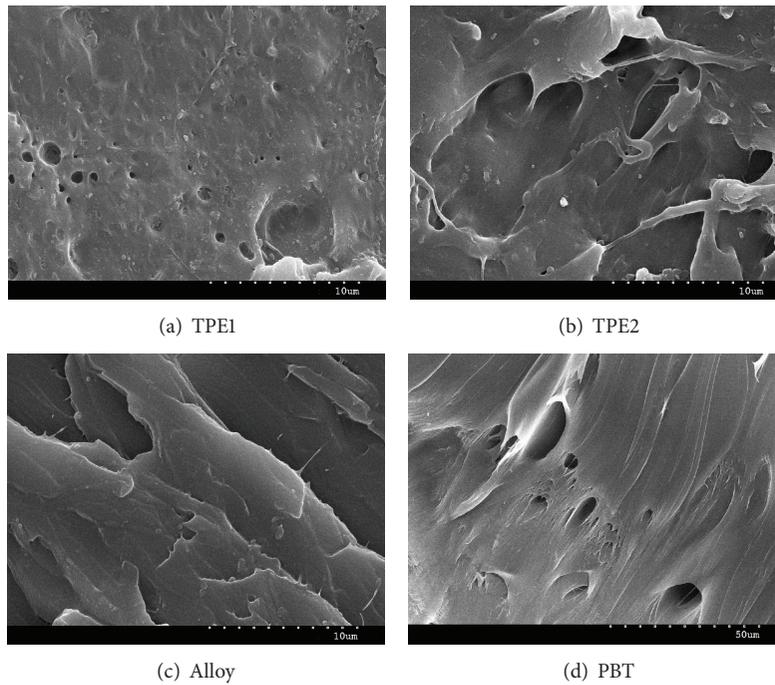


FIGURE 5: SEM micrographs of the fractured insulation layer after thermal aging at 180°C for 6 h.

and xylene-treated samples, and this agreed with the rapid BDV reduction results listed in Table 4. The presence of voids and cracking on the insulation significantly reduces the BDV [20, 22]. This is due to a combination of two factors: (1) air has lower breakdown strength than polymers and (2) presence of a void creates local electric field strength irregularities, with the lower permittivity of air causing an intensification of the electric field at the solid/void interface. Consequently, breakdown that preferentially occurs first at

a solid/void interface has the consequence of disrupting the polymer structure and increasing the void size [21].

4. Conclusions

TPE1, TPE2, PBT, and Alloy were extruded as the insulation layer of low voltage electric wire, and its dielectric BDV changes after thermal and solvent aging were investigated. The presence of voids on the insulation can significantly

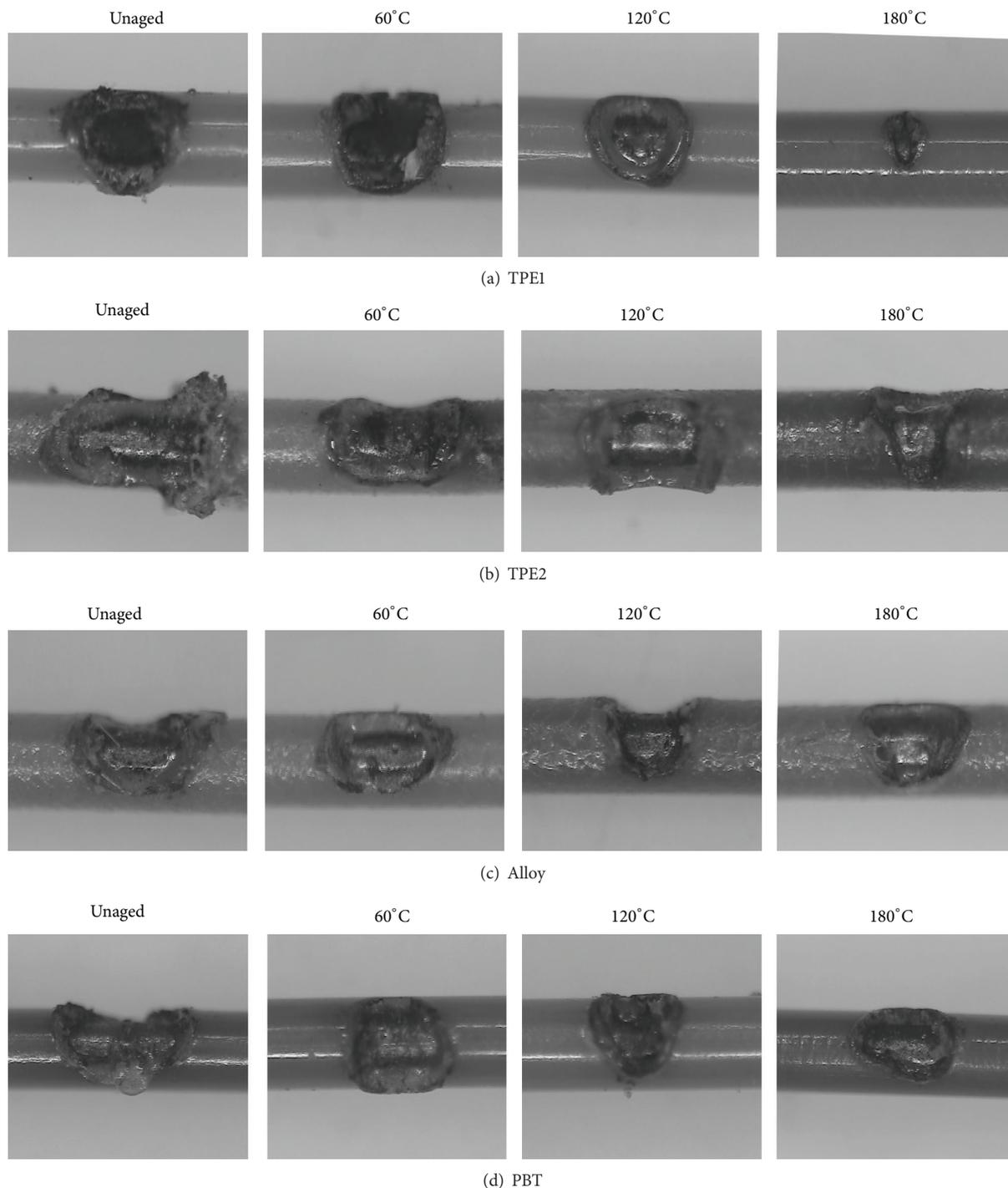


FIGURE 6: Images of the breakdown points after dielectric breakdown test (thermally aged at corresponding temperature for 6 h, 200x).

reduce the dielectric properties. SEM observation confirmed that there are significant voids or pores that were not detected in all extruded samples. In TG analysis, TPE1 shows an initial degradation temperature at 320°C which is the lowest of all investigated samples. In sharp contrast, TPE2 shows similar thermal degradation behavior to PBT because multiaromatic ring structures produced high thermal stability. Among

them, Alloy showed the highest thermal stability. When Alloy and PBT were thermally aged in toluene, xylene, and TCB at 120°C for 6 h, the tensile properties were significantly decreased compared to TPE1 and TPE2. It can be also found that reduction in elongation at break of Alloy was more discernible than that of PBT. DSC traces confirmed that Alloy has the broad crystallization exotherm and it is able to

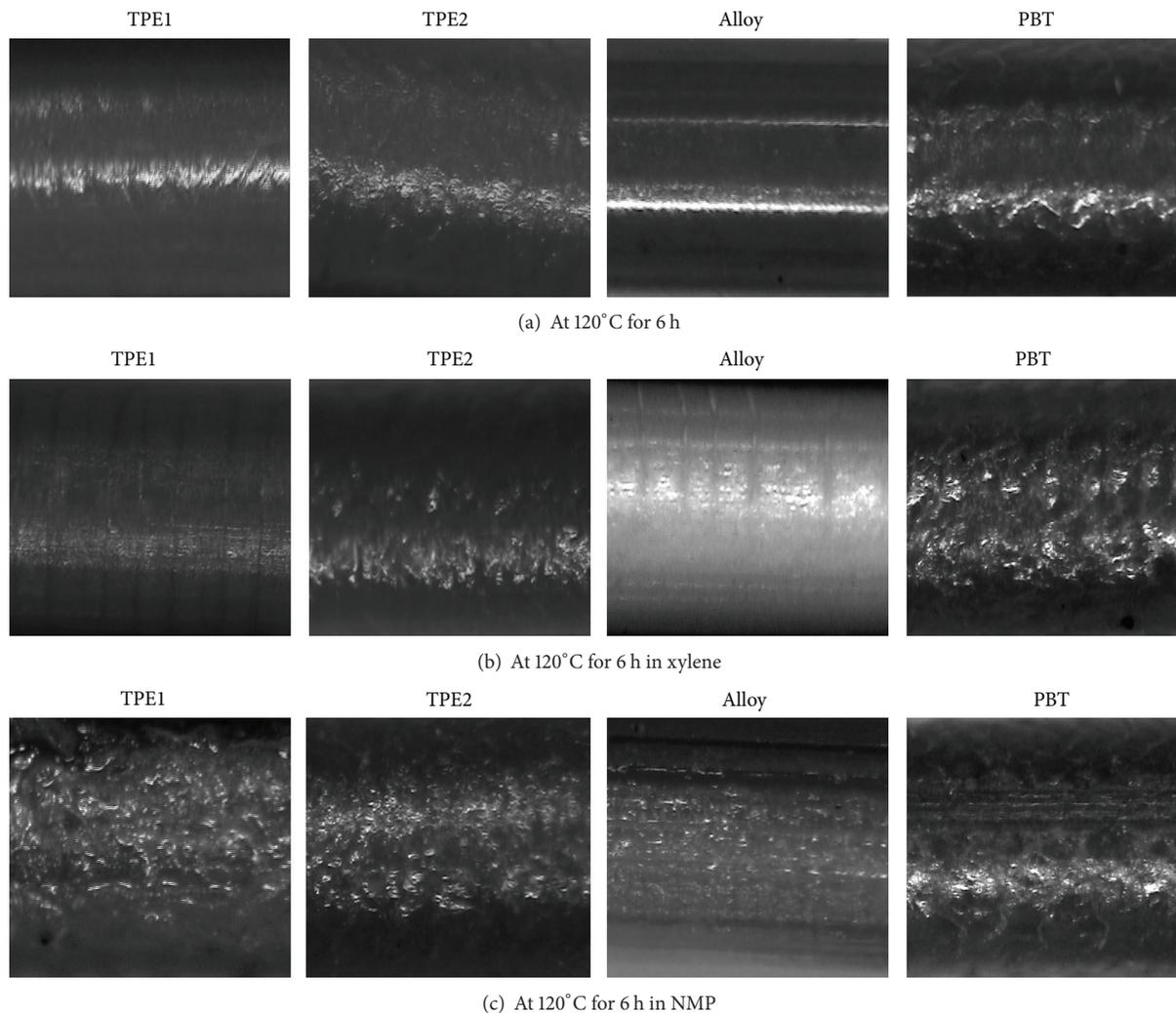


FIGURE 7: Microphotographs (200x) of the surface of extruded insulation layer after solvent aging at 120°C for 6 h.

crystallize more readily in thermal aging temperature range. This is because thermally degraded PET regions in Alloy become brittle upon thermally induced crystallization.

When the extruded wire was exposed the solvent immersion in toluene, xylene, and TCB, the BDV of TPE2 and PBT samples is not changed significantly compared to thermally aged ones. In sharp contrast, for the wire immersed in NMP at 120°C for 6 h, the BDV of all samples decreased significantly. Video microscope observation shows that the surface images of xylene-immersed samples were similar to those of thermally aged ones except for the weak surface crack phenomenon of TPE1 and Alloy. In sharp contrast, the surface of NMP-immersed samples had many voids and eroded much more than that of thermally and xylene-immersed samples and this agreed with the rapid BDV reduction results. Dielectric breakdown that preferentially occurs first at a solid/void interface has the consequence of disrupting the polymer structure and increasing the defects. The thermal and solvent aging process easily corrodes the extruded layer and effectively reduces its thickness causing a lowering in the dielectric properties. Deterioration of the

insulating material reduces the dielectric strength and also reduces the ability of the final products to withstand short-circuit events. Thermal and solvent aging studies of the TPE1, TPE2, PBT, and Alloy showed significant reduction of BDV in accordance with aging temperature and solvent type indicating that selection of curing condition and solvents in varnish is a more important factor for determining life cycle of final products.

Conflict of Interests

This paper does not have a direct financial relation with the commercial identities mentioned in it that might lead to a conflict of interests for the author.

Acknowledgment

The author is grateful to the Small and Medium Enterprises (SMEs) Technology Innovation Program, Republic of Korea, for the financial support of this experimental work.

References

- [1] M. T. Shaw and S. H. Shaw, "Water treeing in solid dielectrics," *IEEE Transactions on Electrical Insulation*, vol. 19, no. 5, pp. 419–452, 1984.
- [2] R. J. Densley, "Investigation into the growth of electrical trees in xlpe cable insulation," *IEEE Transactions on Electrical Insulation*, vol. 14, no. 3, pp. 148–158, 1979.
- [3] H. Y. Shin and E. S. Park, "Mechanical and dielectric breakdown properties of PBT/TPE, PBT/PBT/PET, and PBT/antioxidant blends," *Journal of Applied Polymer Science*, vol. 114, no. 5, pp. 3008–3015, 2009.
- [4] E. S. Park, "Processibility and mechanical properties of micronized polytetrafluoroethylene reinforced silicone rubber composites," *Journal of Applied Polymer Science*, vol. 107, no. 1, pp. 372–381, 2008.
- [5] A. M. Majdi and H. Günter, "Safety and Environmental Aspects in the Use of Impregnating Materials," in *ELANTAS Technical Presentations, Inductica Conference*, Berlin, Germany, 2008.
- [6] A. S. Ribnick, H. D. Weigmann, and L. Rebenfeld, "Interactions of nonaqueous solvent with textile fibers—2. Isothermal shrinkage kinetics of a polyester yarn," *Textile Research Journal*, vol. 43, no. 3, pp. 176–183, 1973.
- [7] B. H. Knox, H. D. Weigmann, M. G. Scott, and L. Rebenfeld, "Effects of an aqueous medium on the structure and physical properties of a polyester yarn," *Textile Research Journal*, vol. 51, no. 8, pp. 549–558, 1981.
- [8] H. D. Weigmann, M. G. Scott, and A. S. Ribnick, "Interactions of nonaqueous solvents with textile fibers part X: effects of thermal history on polyester-solvent interactions," *Textile Research Journal*, vol. 48, no. 1, pp. 4–13, 1978.
- [9] E. S. Park, "Morphology, mechanical, and dielectric breakdown properties of PBT/PET/TPE, PBT/PET/PA66, PBT/PET/LMPE, and PBT/PET/TiO₂ blends," *Polymer Composites*, vol. 29, no. 10, pp. 1111–1118, 2008.
- [10] T. H. Ahn, Y. H. Park, S. H. Kim, and D. H. Baik, "Preparation and characterization of poly(ether ester) thermoplastic elastomers containing the 2,6-naphthalenedicarboxyl group," *Journal of Applied Polymer Science*, vol. 90, no. 13, pp. 3473–3480, 2003.
- [11] Y. G. Jeong, W. H. Jo, and S. C. Lee, "Cocrystallization behavior of poly(butylene terephthalate-co-butylene 2,6-naphthalate) random copolymers," *Macromolecules*, vol. 33, no. 26, pp. 9705–9711, 2000.
- [12] P. A. Atkinson, P. J. Maines, and G. A. Skinner, "Inorganic tin compounds as flame retardants and smoke suppressants for polyester thermosets," *Thermochimica Acta*, vol. 360, no. 1, pp. 29–40, 2000.
- [13] I. H. Hall and M. G. Pass, "Chain conformation of poly(tetramethylene terephthalate) and its change with strain," *Polymer*, vol. 17, no. 9, pp. 807–816, 1976.
- [14] M. Yokouchi, Y. Sakakibara, Y. Chatani, H. Tadokoro, T. Tanaka, and K. Yoda, "Structures of two crystalline forms of poly(butylene terephthalate) and reversible transition between them by mechanical deformation," *Macromolecules*, vol. 9, no. 2, pp. 266–273, 1976.
- [15] H. Watanabe, "Stretching and structure of polybutylene-naphthalene-2,6-dicarboxylate films," *Kobunshi Ronbunshu*, vol. 33, no. 4, pp. 299–237, 1976.
- [16] H. Koyano, Y. Yamamoto, Y. Saito, T. Yamanobe, and T. Komoto, "Crystal structure of poly(butylene-2,6-naphthalate)," *Polymer*, vol. 39, no. 18, pp. 4385–4391, 1998.
- [17] A. Escala and R. S. Stein, "Crystallization studies of blends of polyethylene terephthalate and polybutylene terephthalate," *Advances in Chemistry Series*, vol. 176, pp. 455–487, 1979.
- [18] N. Avramova, "Amorphous poly(ethylene terephthalate)/poly(butylene terephthalate) blends: miscibility and properties," *Polymer*, vol. 36, no. 4, pp. 801–808, 1995.
- [19] G. K. Guenther and D. G. Baird, "Rheology of a textured fluid consisting of poly(ethylene terephthalate) and nylon 6,6," *Journal of Applied Polymer Science*, vol. 59, no. 5, pp. 845–859, 1996.
- [20] W. R. Moore and R. P. Shelden, "The crystallization of polyethylene terephthalate by organic liquids," *Polymer*, vol. 2, pp. 315–321, 1961.
- [21] L. A. Dissado and J. C. Fothergill, *Electrical Degradation and Breakdown in Polymers*, Peter Peregrinus, London, UK, 1992.
- [22] R. Bartnikas and E. J. McMahon, *Engineering Dielectrics*, vol. 2B, ASTM, Philadelphia, Pa, USA, 1987.
- [23] R. S. Chauhan, M. V. S. Rao, and N. E. Dweltz, "Chemical etching of poly(ethylene terephthalate) filaments," *Journal of Applied Polymer Science*, vol. 30, no. 1, pp. 19–33, 1985.
- [24] E. S. Park, "Effects of electron beam irradiation on properties of ETFE insulated electric wire," *Iranian Polymer Journal (English Edition)*, vol. 20, no. 11, pp. 873–885, 2011.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

