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Research Article

Mechanical and Electrical Properties of Polylactic Acid with Aliphatic-Aromatic Polyester

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Assuming an application where polylactic acid (PLA), a hard bioplastic, is used to sheath electrical wire, the author added 20 wt% of aliphatic-aromatic polyester or polybutyrate adipate terephthalate (PBAT), a soft resin, to PLA and then investigated the softened PLA's mechanical and electrical properties. As a result of adding PBAT to PLA, T_g shifted to about 10°C lower than PLA. In addition, adding PBAT to PLA made the PLA softer and even more so at temperatures above 40°C. Furthermore, adding PBAT to PLA decreased the electric breakdown strength (E_B) of the PLA by about 1 MV/cm over the temperature range of 0°C to 50°C, and E_B was slightly higher than that of PVC over the temperature range of −10 to 60°C.

1. Introduction

The number of research papers on the electrical properties of bioplastics [1–5] is relatively small. Polylactic acid (PLA) is a kind of bioplastic (plant derived material made of cornstarch and other vegetable products). This is a carbon-neutral material: when buried in the ground for disposal, it is decomposed into hydrogen and carbon dioxide by microorganisms, and these products are then reused for plant photosynthesis. These features have brought PLA increased attention recently as a resource-circulation material. The author is pursuing the possibility of using PLA as an electrically insulating material and has already found that it has excellent electrically insulating properties at temperatures that range from normal room temperature to 60°C [6, 7]. However, it is known that PLA becomes a poor electrical insulator over 60°C. The authors added a nucleating agent made of β-crystalline chitin particles, extracted from squid gladii, to PLA and found that this moderates the decrease in electrical insulation of PLA at temperatures over 60°C [8]. As PLA is a hard resin, it has to be softened before it can be used as electrical wire sheathing. Although the addition of a liquid plasticizer can also soften PLA [9], it has a problem where it tends to bleed out as the amount used increases. In this paper, instead of a plasticizer, polybutylene adipate terephthalate (PBAT), which is a solid soft resin and is much more flexible than PLA, was chosen and the mechanical and electrical properties of PLA with PBAT added were investigated.

2. Specimen and Experimental Method

2.1. Samples. Samples were made by adding BASF Japan-made PBAT (Ecoflex), a soft resin, to Mitsui Chemicals-made PLA (LACEA H-400). As an organic solvent, chloroform of Kanto Chemical Co., Inc. was used for blending PLA and PBAT. The added amount of PBAT was set to 20 wt%, which is almost equal to the break elongation rate of LDPE at room temperature. After adding 20 wt% PBAT to PLA, drying treatment was carried out for 1 hour or more. It was then hot pressed at 180°C into a film before it was rapidly cooled to room temperature. Here, PLA denotes a sample that does not contain any PBAT, and PLA/PBAT denotes a sample of PBAT-added PLA. As reference samples, low-density polyethylene (LDPE) and polyvinylchloride (PVC) were used.

2.2. Thermal Analysis. A differential scanning calorimetry (DSC) instrument (Shimadzu, DSC-60) was used for thermal analysis. α-Alumina was used as a reference material, and

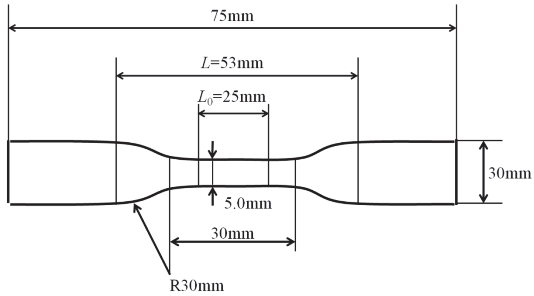


FIGURE 1: Dimensions of the sample used in the tensile test.

the DSC spectrum for PLA was observed over a rise in temperature from 30°C to 200°C at a rate of 10°C/min in a nitrogen atmosphere.

2.3. Mechanical Properties. Figure 1 shows the dimensions of a sample used for tensile testing. Samples were half of the size specified in the Japanese Industrial Standards (JIS K7113-1995) with a width of 10 mm, an elongated part width of 5 mm, and a length of 75 mm. Two parallel marked lines that were 25 mm apart were made at the center of the sample. The sample was measured at a speed of 20 mm/min and a temperature range of −25°C to 60°C.

2.4. Dielectric Properties. A precision LCR meter (Agilent Technologies, 4284A) was used to determine dielectric properties. To obtain the dielectric properties, the capacity (C) and the dielectric dissipation factor ($\tan\delta$) of a specimen were measured simultaneously while heating the specimen at a rate of 1°C per minute from −30°C to 150°C, and the relative permittivity (ε_r') and relative dielectric loss factor (ε_r''), the real part and the imaginary part of complex relative permittivity ($\varepsilon_r{}^*$), respectively, were obtained. A voltage of 1 Vrms was applied to measure C and $\tan\delta$. A frequency (f) of 1 kHz was used to examine the temperature dependency of ε_r' and ε_r''.

2.5. Dielectric Breakdown Properties. Figure 2 shows the experimental system for measuring dielectric breakdown strength. The samples were cut into 50 × 50 mm squares. The side at high voltage was made into a ball electrode with ϕ 10 mm, and the earthed side was made into a disk electrode with rounded edges with ϕ 25 mm. To prevent creeping discharge, epoxy resin guard insulation was placed on the contacts surrounding the high voltage electrode and the sample. The sample and the electrode system were soaked in silicone oil, and a positive high voltage direct current was applied at a rate of increase of 1 kV/sec. The temperature of the sample changed from −20°C to 80°C, and the specific conditions were measured at least ten times.

3. Experimental Results and Discussion

3.1. Thermal Analysis. Figure 3 shows the DSC curves of PLA and PLA/PBAT. The spectrum of PLA/PBAT in this figure has been shifted by −7.5 W/g to make the DSC curves more

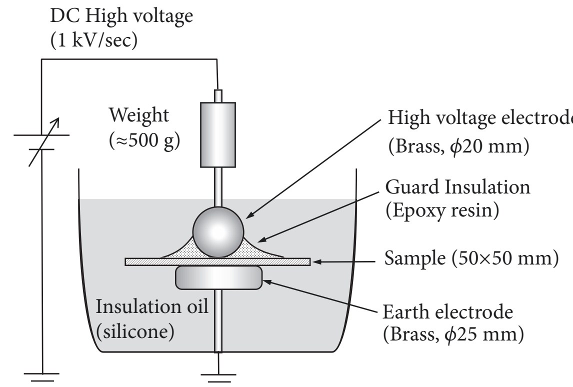


FIGURE 2: Experimental system for measuring dielectric breakdown strength.

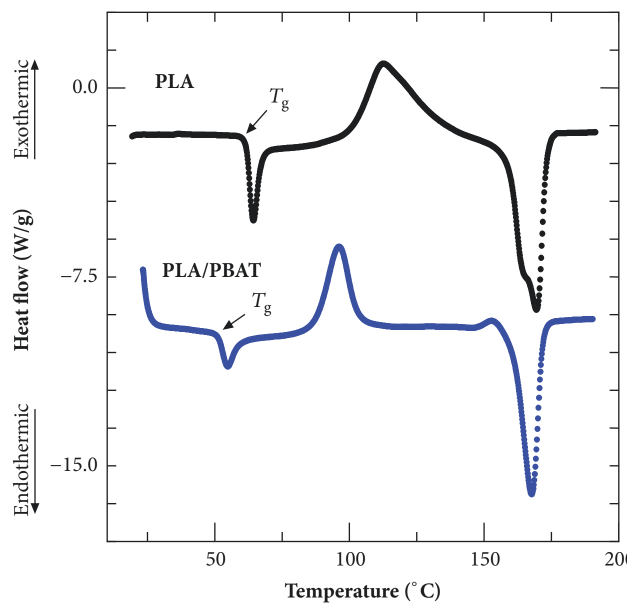
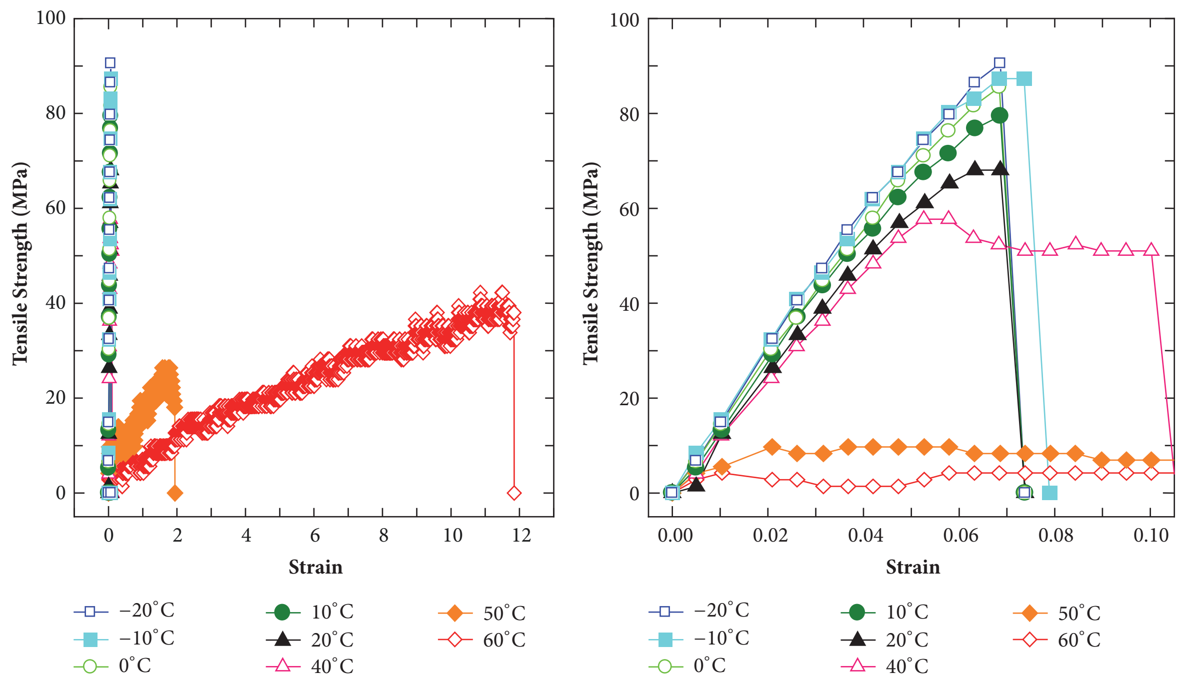


FIGURE 3: DSC curves of PLA and PLA/PBAT.

distinguishable. The glass transition temperature (T_g) of PLA was about 61°C, while that of PLA/PBAT was about 50°C. The addition of PBAT to PLA decreased T_g by about 10°C. This is likely caused by the addition of PBAT to PLA widening the molecular chains of PLA, easing their molecular motions. Meanwhile, the melting points of PLA and PLA/PBAT were about the same, meaning that the addition of PBAT to PLA did not change the melting point.

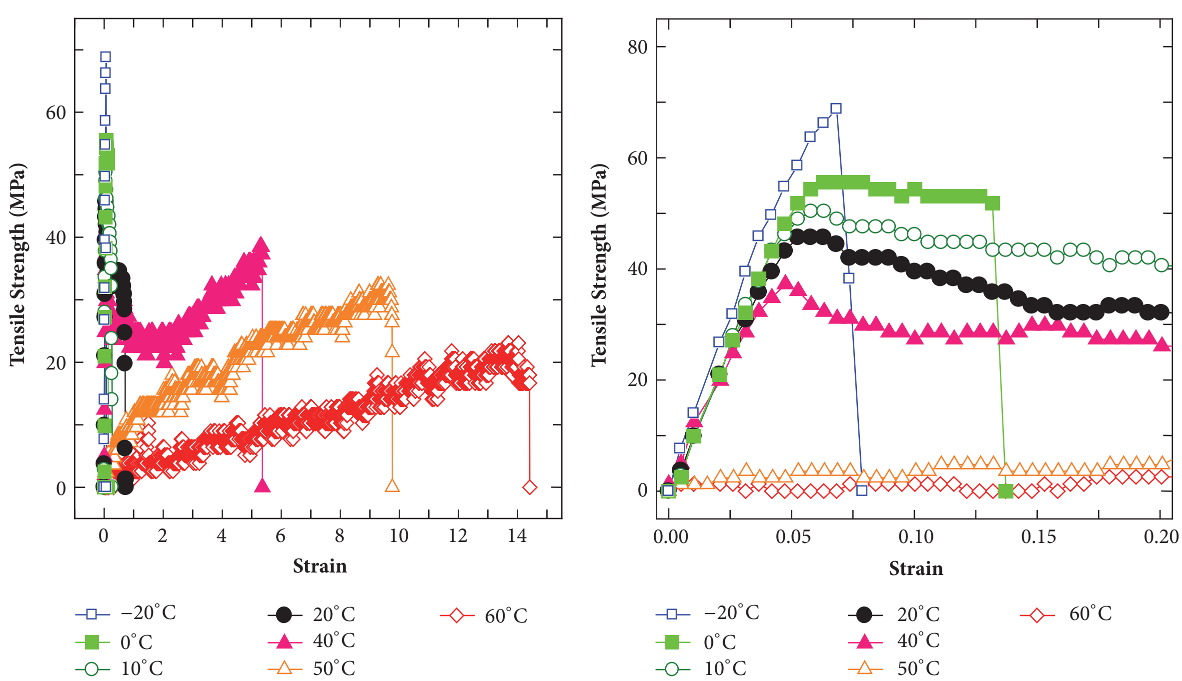
3.2. Mechanical Characteristics. Figures 4 and 5 show the stress-strain diagrams of PLA and PLA/PBAT. Figure 6 shows the tensile strengths at break obtained from these figures. While PLA had a tensile strength at break of about 90 MPa at −20°C, the tensile strength at break gradually decreased as temperature increased from −20°C to 40°C, and it sharply dropped between 40°C and 50°C. Meanwhile, PLA/PBAT had a tendency of showing a tensile strength at break about 20 MPa lower than that of PLA, and it gradually decreased



(a) Entire diagram

(b) Enlarged diagram

FIGURE 4: Enlarged stress-strain diagram of PLA.



(a) Entire diagram

(b) Enlarged diagram

FIGURE 5: Stress-strain diagram of PLA/PBAT.

as temperature increased from −20°C to 60°C. The tensile strengths at break for LDPE and PVC were between 10 and 20 MPa, lower than those of PLA and PBAT, and their tensile strengths at break did not change much with temperature.

Figure 7 shows breaking elongation obtained from Figures 4 and 5. While the breaking elongation of PLA exhibited little change from −20°C to 40°C, it sharply increased at temperatures over 40°C. The breaking elongation at 60°C was

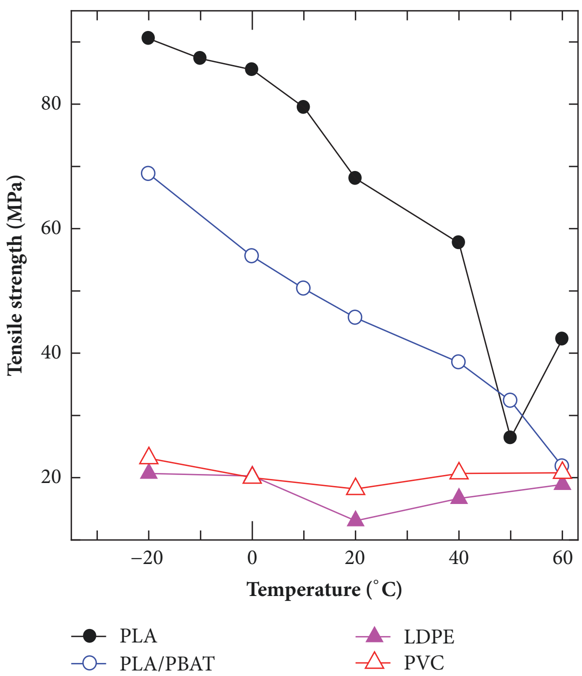


FIGURE 6: Tensile strengths at break of PLA and PLA/PBAT.

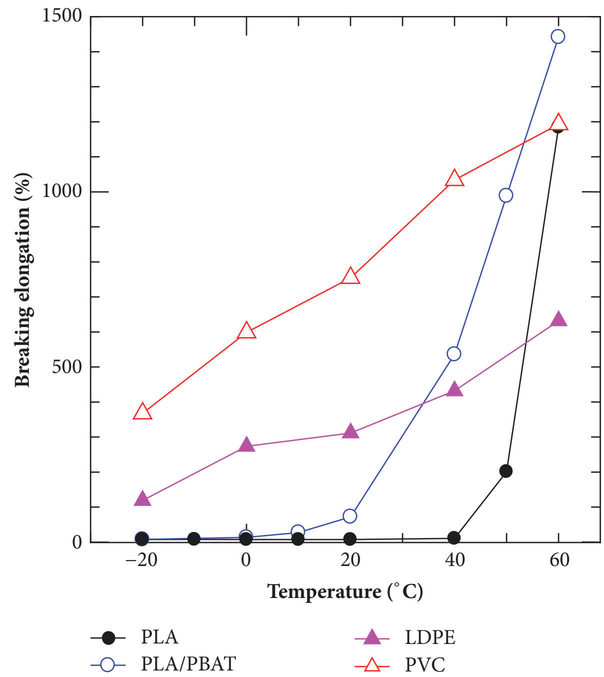


FIGURE 7: Breaking elongation of PLA and PLA/PBAT.

about 1200%, which was equivalent to that of LDPE. The breaking elongation for PLA/PBAT started to rise sharply at around 20°C, which was lower than the temperature at which the breaking elongation of PLA quickly rose. In addition, its breaking elongation at 60°C was about 1500%, higher than that of LDPE. The breaking elongation of LDPE and PVC gradually increased as the measurement temperature increased from −20°C to 60°C.

Figure 8 shows Young's modulus data obtained from Figures 4 and 5. For PLA, Young's modulus was about 10 GPa between −20°C and 40°C, showing little change over the measured temperature range. However, it quickly decreased above 40°C. Meanwhile, for PLA/PBAT, the temperature dependency of Young's modulus is similar to that of PLA, but its Young's modulus quickly decreased above 40°C and at a lower temperature than that of PLA. The Young's modulus values for LDPE and PVC gradually decreased as the temperature rose from −20°C to 60°C.

Figures 4–8 show that the addition of PBAT to PLA softens PLA, and at temperatures greater than 40°C, further softening occurs as the specimen temperature approaches T_g.

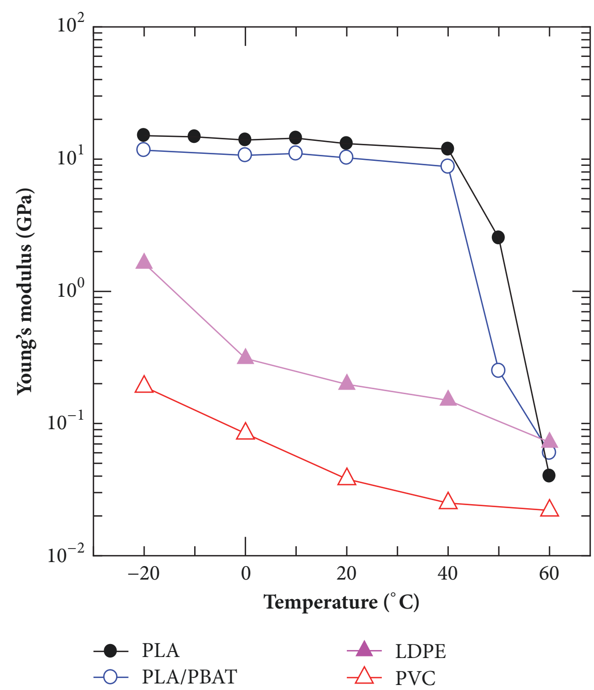


FIGURE 8: Young's modulus of PLA and PLA/PBAT.

3.3. Dielectric Properties. Figure 9 shows the temperature dependencies of the relative permittivity (ε_r') and the relative loss permittivity (ε_r'') for PLA and PLA/PBAT. The PLA sample had ε_r' of about 3.0 from −25°C to 60°C; it gradually increased around 60°C and peaked at about 90°C. The fact that a peak ε_r' appeared at a temperature higher than T_g suggests that dipoles with the motions of main chain segments thermally activated by micro-Brownian motions tend to orient easily over around 60°C. This potentially increases ε_r' as the temperature rises, and as it passes the peak, the orientation of dipoles is disrupted by thermal agitation, decreasing ε_r' with a further increase in temperature [6]. ε_r' of PLA levelled off at about 3.5 at a temperature of about 100°C or higher. Meanwhile, ε_r' of PLA/PBAT was about 3.0 between about −25°C and 50°C. This is equivalent to that of PLA, and its peak appeared at about 80°C, which was about 10°C lower than that of PLA. As Figure 3 shows, the addition of PBAT

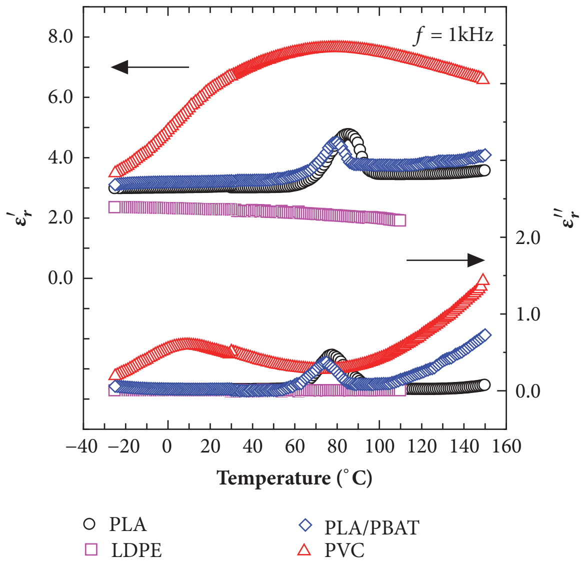


FIGURE 9: Values of ε_r' and ε_r'' of PLA and PLA/PBAT.

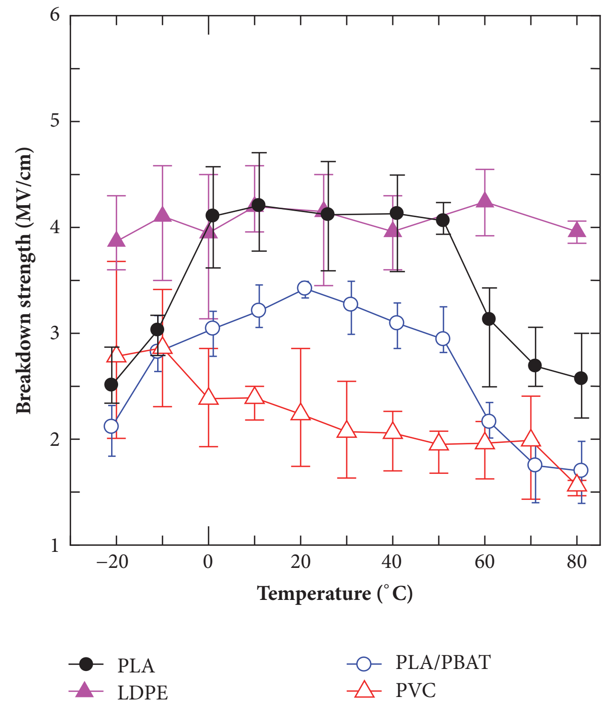


FIGURE 10: Dielectric breakdown strength of PLA and PLA/PBAT.

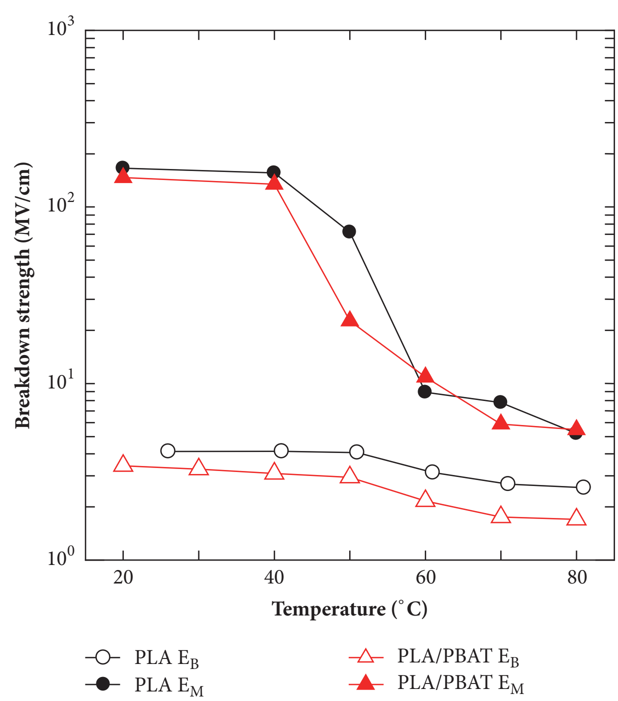
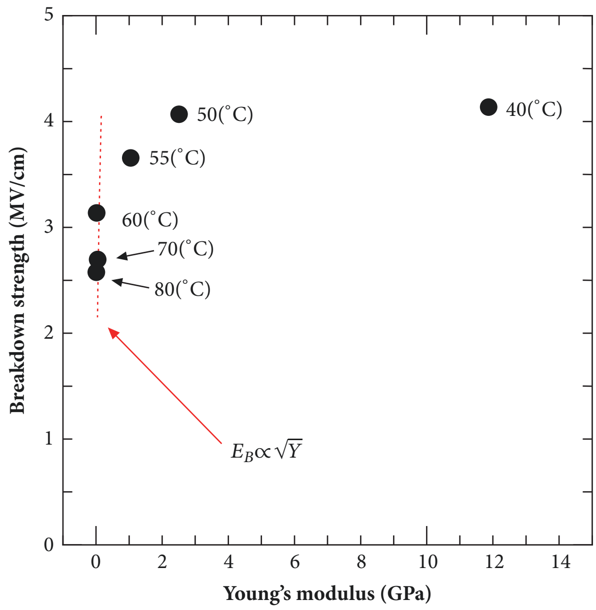


FIGURE 11: Comparison between measured values of dielectric breakdown strength E_B and theoretical values of electromechanical breakdown E_M in PLA and PLA/PBAT.

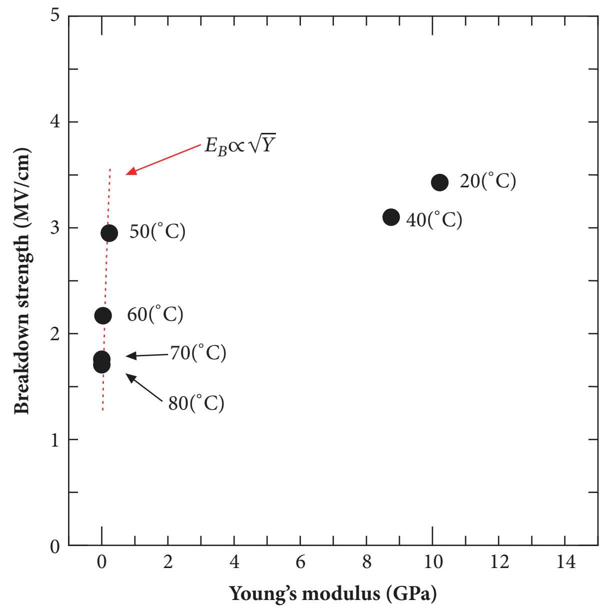
to PLA decreased T_g by about 10°C, and the added PBAT is thought to help widen the molecular chains of PLA to ease their molecular motions at relatively low temperatures, which made the orientation of dipoles easier, and consequently the temperature at the ε_r' peak of PLA/PBAT decreased to a point about 10°C lower than that of PLA. The ε_r' values of PLA and PLA/PBAT were higher than that of LDPE and lower than that of PVC at all temperatures.

ε_r'' of PLA started to increase gradually at about 60°C and it demonstrated absorption at about 80°C. As this absorption appears at a temperature range above T_g, this is probably the α absorption [6]. Meanwhile, ε_r'' of PLA/PBAT demonstrated absorption at about 75°C and, as in the case of ε_r', the addition of PBAT lowered the temperature of the peak ε_r''. For PLA/PBAT, its ε_r'' started to rise as the temperature approached 100°C. Although the applied voltage is a low electric field of 1 Vrms, it is as high as 50°C or more than T_g of PLA/PBAT near this temperature. This is probably because the addition of PBAT helped generate ionic space charge polarization. While the ε_r' values of PLA and PLA/PBAT changed little at all temperatures and that of LDPE changed little in the measured temperature range, that of PVC tended to be higher than that of PLA.

3.4. Dielectric Breakdown Properties. Figure 10 shows the graph of dielectric breakdown strength (E_B) against temperature for PLA and PLA/PBAT. For PLA, E_B was about 4 MV/cm over a temperature range of 0°C to 50°C, which is equivalent to that of LDPE. At temperatures over 50°C, E_B sharply decreased as the temperature increased and reached about 2.5 MV/cm at 80°C. Below 0°C, E_B sharply dropped to about 2.5 MV/cm at −20°C, which was equivalent to that of PVC. Meanwhile, for PLA/PBAT, E_B was about 1 MV/cm lower than that of PLA from 0°C to 50°C and was equivalent to that of PLA from −20°C to −10°C. Figures 4–8 shows that the addition of PBAT to PLA can soften PLA but reduces E_B, as shown in Figure 11. However, E_B of PLA/PBAT tended to be higher than that of PVC from −10°C to 60°C.



(a) PLA



(b) PLA/PBAT

Figure 12: Relation between E_B and Young's modulus of PLA and PBAT.

Electromechanical breakdown is one of the potential mechanisms that can explain the decrease in E_B with an increase in temperature for temperatures above T_g. Maxwell stress occurs, and it is expected that electromechanical breakdown will take place easily here. According to the electromechanical breakdown theory [10, 11], the relationship between the dielectric strength and Young's modulus is

$$E_M = \sqrt{\frac{Y}{\varepsilon_0 \varepsilon_r}} \exp\left(-\frac{1}{2}\right), \quad (1)$$

where E_M is the electromechanical breakdown strength, $\varepsilon_0 \varepsilon_r$ is the dielectric permittivity, and Y is Young's modulus. The relationship between temperature and E_M calculated using the relative permittivity (ε_r) by Figure 9 and Young's modulus of PLA and PLA/PBAT (Figure 8) is shown in Figure 11 for the results of this experiment. The measured value of the dielectric breakdown strength (E_B) shown in Figure 10 is also shown in the figure. As can be seen from this figure, the calculated value (E_M) was higher than the measured value (E_B). This tendency is also reported for other polymer films [12, 13]. Inuishi and Ieda [14] consider that the above tendencies are shown in local mechanical weak points. That is, where $E_M \propto E_B$ even if $E_M > E_B$, it is likely that electromechanical breakdown may have occurred. Since E_M and E_B are in proportional relation, replacing E_M in (1) with E_B and E_B and the square root of Young's modulus are proportional. Here, if (1) is simplified, the relationship between E_B and Young's modulus can be given as follows:

$$E_B \propto \sqrt{Y}. \quad (2)$$

The relationships between E_B and Young's modulus for PLA and PLA/PBAT are shown in Figure 12. The dotted line in the figure shows the curve of (2). For PLA, this figure shows that the relationship in (2) is found in the temperature domain from 60 to 80°C. This shows that local mechanical weak points occur here. It is thought that a high temperature domain of 60°C and above causes electromechanical breakdown as well as thermal breakdown. In this figure, the relationship of formula (2) is visualized for PLA from 60°C to 80°C. In other words, this indicates that mechanical fragility increases locally in this temperature domain and that temperatures above 60°C could cause electromechanical and thermal breakdown. Meanwhile, for PLA/PBAT, the relationship of formula (2) appears at a temperature of 50°C or higher, which is lower than that of PLA by 10°C. Figures 4–8 show that although the addition of PBAT to PLA can soften PLA, doing so lowers the melting point by 10°C and could potentially cause electromechanical breakdown.

In addition, I would like to conduct electric treeing test in order to investigate dielectric insulation deterioration of PLA/PBAT in detail. Also, since T_g of PLA/PBAT is as low as about 50°C, I would like to make improvements such as providing heat resistance to PLA/PBAT in order to apply it to electrical wire sheathing.

4. Summary

This paper reports on the study that assumed the application of polylactic acid (PLA), a hard bioplastic, to electrical wire sheathing. 20 wt% of aliphatic-aromatic polyester (PBAT), a soft resin, was added to PLA and the softened PLA was then investigated for its mechanical and electrical properties.

As a result of adding PBAT to PLA, T_g shifted to about 10°C lower than PLA. In addition, adding PBAT to PLA made the PLA softer and even more so at temperatures above 40°C.

Furthermore, adding PBAT to PLA decreased the electric breakdown strength (E_B) of the PLA by about 1 MV/cm over the temperature range of 0°C to 50°C, and E_B was slightly higher than that of PVC over the temperature range of −10 to 60°C.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The author declares that there are no conflicts of interest.

Acknowledgments

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