

Conductivity of Crosslinked Poly(Epichlorohydrin-*co*-(Ethylene Oxide)-*co*-(Allyl Glycidyl Ether)) Compositions under Ambient Circumstances for Its Application to an Electrophotographic System

Y. Matoba,¹ S. Shoji,¹ Y. Ikeda²

¹Daiso Co., Limited, 9 Otakasu, Amagasaki, Hyogo 660-0842, Japan

²Kyoto Institute of Technology, Faculty of Engineering and Design, Matsugasaki, Sakyo, Kyoto 606-8585, Japan

Received 21 September 2004; accepted 10 January 2005

DOI 10.1002/app.22129

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Terpolymers were synthesized by copolymerization of epichlorohydrin with ethylene oxide (EO) and allyl glycidyl ether. The terpolymers were crosslinked by sulfur curing. Conductivity of the crosslinked terpolymer compositions was investigated for application to an electrophotographic system. The composition containing 71 mol % EO units in the terpolymer gave high and stable conductivity over a wide range from low temperature and low humidity to high temperature and high humidity conditions. The conductivity of crosslinked terpolymer composition satisfied Ohm's law against the applied voltage from 10 to 1000

V, which is necessary for the electrophotographic system. The conductivity increased by the addition of a small amount of electrolyte. The staining ascribable to the migration of electrolyte was not observed, when 3 parts per hundred rubber by weight of octadecyltrimethylammonium perchlorate was doped to the crosslinked terpolymer composition whose EO content in the terpolymer was 71 mol %. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 825–830, 2005

Key words: polyethers; amorphous; crosslinking; conductivity; electrophotographic system

INTRODUCTION

Copolymers of epichlorohydrin (EH) and ethylene oxide (EO), P(EH-EO)s, have been studied as a rubbery matrix for polymer solid electrolytes, the applications of which have been electronic or ionic devices, especially chemical batteries such as rechargeable lithium polymer batteries.^{1–11} Copolymerization of EO with EH resulted in the formation of an amorphous polyether matrix, although poly(ethylene oxide) (P(EO)) is a crystalline polymer. Comb-shaped poly(oxyethylene)s were also prepared by a copolymerization technique,^{12,13} and they afforded an excellent amorphous matrix for lithium ionic conduction.^{14–22} From the industrial synthetic viewpoints, however, the preparation of comb-shaped poly(oxyethylene)s is not so convenient as that of P(EH-EO)s. Since poly(epichlorohydrin) (P(EH)), P(EH-EO), and poly(epichlorohydrin-*co*-(ethylene oxide)-*co*-(allyl glycidyl ether)) (P(EH-EO-AGE)) have been industrially manufactured for years, these polymers may be preferable to comb-shaped poly(oxyethylene)s for practical applications.

Devices such as a solid-state chemical battery work under dry circumstances; therefore, investigation into the ionic conductivity of materials has been conducted

under anhydrous conditions. Semiconductive rubber materials such as charging rollers, developing rollers, and toner transfer rollers, on the other hand, have been applied to the electrophotographic system under ambient circumstances. In this case, the conductivity of the materials is affected both by the surrounding temperature and by the humidity. One of the authors (S. Shoji) reported the conductivity under ambient circumstances for crosslinked compositions made of P(EH-EO) or (P(EH-EO-AGE)).²³ However, the conductivity of the compositions was not fully sufficient, because these commercially available copolymers were not designed for semiconductive rubber materials, but for automotive heat- and fuel-resistant rubber materials. The EO content of the polymers, for instance, was limited up to 56 mol % for the applications of automobiles.

Electric conductivity of the semiconductive rubber rollers used in the electrophotographic system such as a laser beam printer and a plain paper copier must be precisely controlled in the region from 10^{-9} to 10^{-7} S/cm under ambient circumstances, not depending on the temperature and humidity.²⁴ Furthermore, the range of conductivity becomes wide up to 10^{-6} S/cm to cope with the demands for decreasing the load of the electric power source, increasing the rate, and color printing. The conductivity is also required to be stable against the applied voltage up to ~ 1000 V. If the conductivity satisfies Ohm's law, the applied voltage

Correspondence to: Y. Ikeda (yuko@kit.jp).

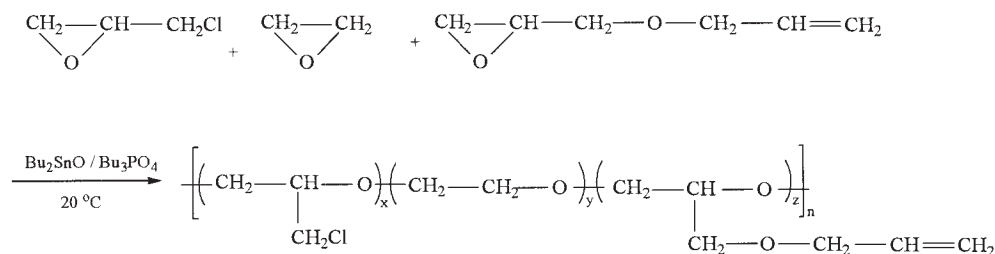


Figure 1 Synthesis of terpolymers.

must be changed to feed an adequate amount of electric charge to the photoconductor. Additionally, the charging roller and developing roller must not stain the surface of the photoconductor, which directly contacts the rollers, to avoid faults coming out on the print. Therefore, excess incorporation of additives such as electrolytes is undesirable, because of the possibility of bleeding out from the rubber rollers. The highly efficient electrophotographic device needs a rubber material that realizes all of these requirements. Thus, the purpose of this study is to clarify the conductive behavior of crosslinked P(EH-EO-AGE) compositions having high amounts of EO units under ambient circumstances and to determine the optimized terpolymer composition for application to semiconductive rubber materials.

EXPERIMENTAL

Materials

P(EH-EO-AGE)s were synthesized by coordination anionic polymerization of EH with EO and AGE in hexane using a catalyst of condensation product of dibutyltin oxide and tributylphosphate at 20 °C as shown in Figure 1.^{12,13} By changing the monomer ratio, four kinds of products, i.e., terpolymer -53, -62, -71, and -81, were obtained, whose EO contents were 53, 62, 71, and 81 mol %, respectively. Ho-

mopolymer, P(EO), was also prepared using the same technique. P(EH) was synthesized by coordination anionic polymerization in hexane using a catalyst of condensation product of alkoxy aluminum, silicon tetrachloride, and tributylphosphate under refluxed conditions.²⁵

Characterization of polymers

The composition of the polyethers was determined by ¹H-NMR measurement on a JEOL-JNM-GSX-270. Deuterated benzene was used as a solvent. The weight-average molecular weight (M_w), the number-average molecular weight (M_n), and the index of polydispersity (M_w/M_n) were measured by size exclusion chromatography (SEC) on a Shimadzu C-R4A/LC6AD/RID-6A and are summarized in Table I. The SEC measurement was carried out using *N,N*-dimethylformamide with 0.1 mM LiBr at 60 °C. Since the M_w , M_n , and M_w/M_n were calculated based on the calibration of columns using polystyrene standards, these values were relative ones, defined as linear polystyrene equivalents. Differential scanning calorimetry (DSC) was performed on a Seiko Instruments SSC 5200 Disk Station for determining the glass transition temperature (T_g) and on a PerkinElmer DSC-7 under nitrogen atmosphere for measuring the melting point (T_m) and heat of fusion (ΔH_m).

TABLE I
Properties of Polymers

Sample code	P(EH)	Terpolymer-53	Terpolymer-62	Terpolymer-71	Terpolymer-81	P(EO)
Composition (mol%)						
EH	100	43	33	25	16	0
EO	0	53	62	71	81	100
AGE	0	4	5	4	3	0
M_w (g/mol)	2.0×10^6	1.5×10^6	1.4×10^6	1.4×10^6	1.9×10^6	1.8×10^6
M_n (g/mol)	4.9×10^5	3.1×10^5	3.7×10^5	3.4×10^5	4.5×10^5	5.6×10^5
M_w/M_n	4.1	4.6	3.8	4.2	4.2	3.3
T_g (°C)	-26	-50	-54	-56	-59	-61
T_m (°C)	98	41	42	34	34	62
ΔH_m (J/g)	4.0	4.0	0.7	0.6	7.7	187
ΔV^a (%)	1.5	7.6	49	96	200	Dissolved
σ^b (S/cm)	4.8×10^{-12}	1.1×10^{-9}	4.5×10^{-9}	1.7×10^{-8}	1.3×10^{-8}	9.1×10^{-11}

^a Measured by swelling in water at 70 °C for 70 h.

^b Measured at 23 °C and 50% RH.

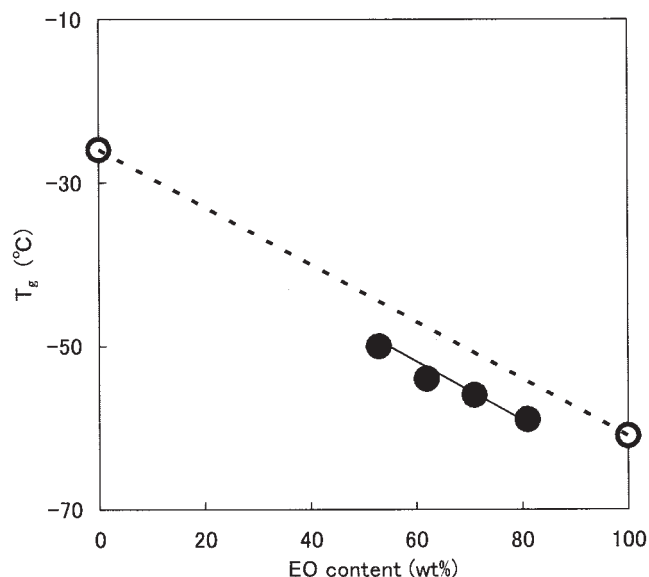


Figure 2 Effect of EO content on T_g of polyethers. The dotted line was drawn using the Gordon-Taylor equation.

Preparation of films

The films of P(EH-EO-AGE)s, P(EO), and P(EH) were prepared by compression-molding at 130 °C for 4 min, followed by water cooling of the mold. The films were 150 × 150 mm × 2 mm in size. The crosslinked terpolymer compositions were prepared by curing using compression molding at 170 °C for 15 min after mixing polymers and ingredients on a two-roll mill of 7 in. diameter. The ingredients were commercially available and used as received. The recipe for preparation of the compounds for curing was as follows: one part per hundred polymer by weight (phr) of stearic acid, 5 phr of ZnO, 1 phr of sulfur, 1 phr of dibenzothiazyl disulfide, 0.5 phr of tetramethylthuram monosulfide, 1 phr of sorbitan monostearate, and 1 phr of 2-mercaptobenzimidazole. One, two, or three phr of octadecyltrimethylammonium perchlorate or 30 phr of carbon black (N-550) was also added for the preparation of electrolyte-doped samples and a reference sample, respectively. The size of the films was 150 × 150 × 2 mm.

Measurements of conductivity and properties

Conductivity (σ) was measured according to a JIS K 6911 procedure on a Hiresta IP instrument (Mitsubishi Petrochemical Co.) at applied voltage of 10 V and on a Digital Ultra High Resistance Tester R8340A (Advantest Corp.) at applied voltages from 10 to 1000 V. Tensile measurement was carried out according to JIS K 6251. Density and volume change by swelling in water (ΔV) of the films were measured by JIS K 6350 and JIS K 6258, respectively.

RESULTS AND DISCUSSION

Properties of polymers

Table I shows the polymer composition, M_w , M_n , M_w/M_n , T_g , T_m , ΔH_m , ΔV , and σ of the polyethers. The highly active catalysts^{12,13,25} gave high-molecular-weight polymers with wide polydispersities ($M_w/M_n = 3.3\text{--}4.6$). With the increase of EO content in the terpolymer, T_g decreased monotonously as shown in Figure 2. The T_g values of the terpolymers were fitted on a parallel line with the dotted one calculated by the Gordon-Taylor equation,²⁶ as shown in eq. 1:

$$T_g(C) = \varphi T_g(A) + (1 - \varphi) T_g(B) \quad (1)$$

where $T_g(C)$, $T_g(A)$, and $T_g(B)$ are the glass transition temperatures of the components C, A, and B, and they correspond to the T_g of P(EH-EO), P(EO), and P(EH) in this study, respectively. φ is the volume ratio of EO component in the copolymers. Figure 2 suggests that the obtained terpolymers were random copolymers. The difference between the measured and the calculated T_g is ascribable to the presence of the AGE component in the terpolymers, which was introduced as reactive sites for sulfur curing.

As shown in Figure 3, the ΔV increased with the increase of EO content, which is a reasonable trend when we consider the hygroscopic nature of oxyethylene unit. However, the conductivity at 23 °C and 50% relative humidity (RH) shows the maximum for terpolymer-71, whose EO content was 71 mol %. Generally, the conductivity increases with the decreases of T_g and crystallinity and with the increase of hygroscopicity. Therefore, the factors to give the maximum conductivity should be taken into account for terpolymer-71. Since it is well known that oxyethylene segments are easily crystallized and followed by a de-

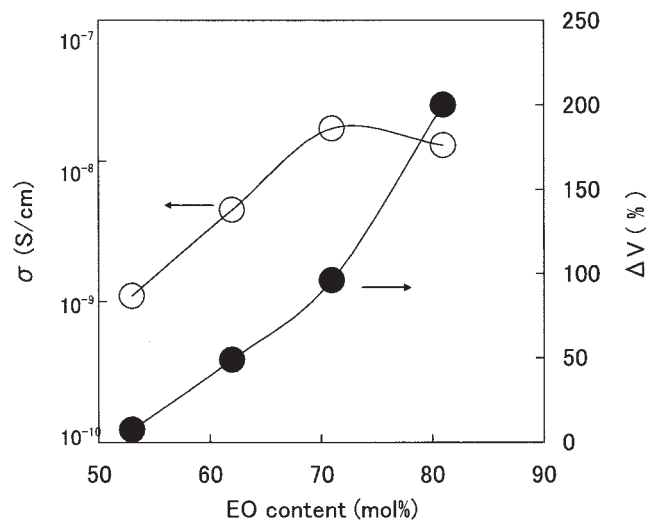


Figure 3 Effect of EO content on conductivity at 23 °C and 50% RH and ΔV at 70 °C for 70 h of terpolymers.

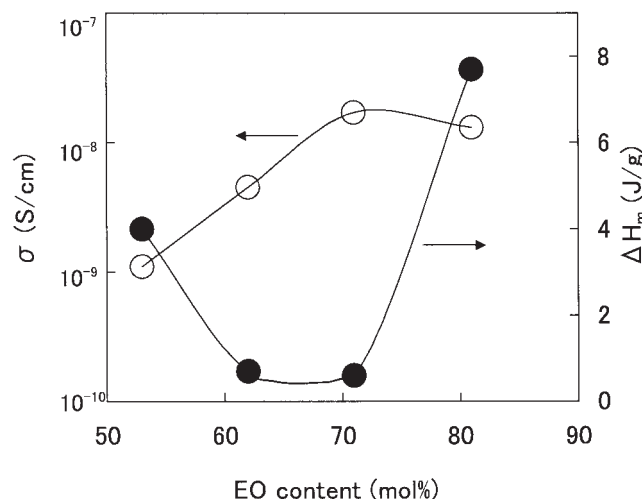


Figure 4 Effect of EO content on conductivity at 23 °C and 50% RH and ΔH_m of terpolymers.

cease in conductivity, the melting behaviors of terpolymers were investigated by DSC to evaluate the degree of crystallinity of oxyethylene segments. As shown in Figure 4, terpolymer-71 whose EO content was 71 mol %, gave the minimum ΔH_m , whereas terpolymer-81 possessed the largest ΔH_m . These results imply that the high crystallinity of terpolymer-81 brought about the lowering of its conductivity. The simultaneous effects of low T_g , low crystallinity, and high hydrophilicity of terpolymer-71 resulted in the maximum conductivity.

Properties of crosslinked terpolymer compositions

The properties of crosslinked terpolymer compositions are summarized in Table II. "Sample" and "number" in the codes mean "a crosslinked terpolymer composition" and "EO content," respectively. For example, "Sample 53" shows a crosslinked terpolymer composition prepared from Terpolymer-53, whose EO

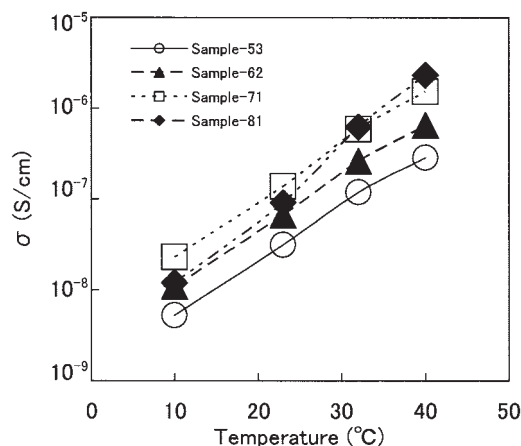


Figure 5 Conductivity under ambient temperature and humidity of crosslinked terpolymer compositions.

content was 53 mol %. The tensile properties of all samples were good enough for the application to semiconductive rubber rollers in the electrophotographic system.²⁴ Especially, the hardness of Samples 62 and 71 was preferable for the application, which is ascribable to their low crystallinity. The roller must be soft enough not to damage the surface of the photoconductor, which directly contacts the roller during its rotation. The ΔV values of the cured terpolymers in water were smaller than those of uncured terpolymers, and showed a steep increase after exceeding 71 mol % EO content.

Figure 5 shows the conductivity of the samples from the low temperature and low humidity condition to the high temperature and high humidity condition. Sample 71 showed the highest conductivity at the low temperature and low humidity condition, and Sample 81 showed a steep increase in conductivity at the high temperature and high humidity condition compared with the others. To investigate the effect of environmental temperature and humidity on the ionic conductivity, the parameter (D) is de-

TABLE II
Properties of Crosslinked Terpolymer Compositions

Sample code	Sample 53	Sample 62	Sample 71	Sample 81
Tensile properties				
Modulus at 100% elongation (MPa)	1.2	0.9	0.9	0.9
Tensile strength at break (MPa)	3.0	2.9	3.4	3.1
Elongation at break (%)	335	385	465	515
Hardness ^a	46	41	43	46
ΔV^b (%)	11	16	36	156
Conductivity				
σ (S/cm) at 10°C and 15% RH	5.3×10^{-9}	1.1×10^{-8}	2.3×10^{-8}	1.2×10^{-8}
σ (S/cm) at 23°C and 50% RH	3.1×10^{-8}	6.7×10^{-8}	1.4×10^{-7}	9.1×10^{-8}
σ (S/cm) at 32°C and 80% RH	1.2×10^{-7}	2.6×10^{-7}	5.9×10^{-7}	6.3×10^{-7}
σ (S/cm) at 40°C and 90% RH	2.9×10^{-7}	6.5×10^{-7}	1.5×10^{-6}	2.3×10^{-6}

^a By JIS A.

^b Measured by swelling in water at 70°C for 70 h.

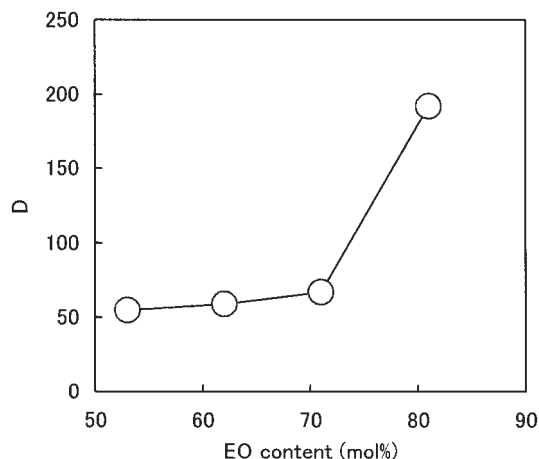


Figure 6 Effect of EO content on the D value of crosslinked terpolymer compositions.

defined as eq. (2), and it is plotted against the EO content as shown in Figure 6.

$$D = \frac{\text{Conductivity at } 40^\circ\text{C and } 90\% \text{ RH/}}{\text{Conductivity at } 10^\circ\text{C and } 15\% \text{ RH}} \quad (2)$$

The conductivity increased with the increase of EO content and with the decreases of T_g and crystallinity in the region of 53–71 mol % EO contents under the low temperature and low humidity condition. After exceeding 71 mol % EO content, the conductivity decreased with the increase of crystallinity. Under high temperature and high humidity conditions, on the other hand, the most hygroscopic sample (Sample 81) showed a steep increase in conductivity. These results brought about the following considerations, i.e., the mechanisms (A) and (B) on the conductivity of the crosslinked terpolymers under ambient circumstances.

Mechanism A. Under the low temperature and low humidity condition, water in the polymer seems to be complexed with oxyethylene segment in the terpolymers. The conductivity is considered mainly governed by the movement or migration of the dissociated water coupling with the movement of the oxyethylene segment in the amorphous region. Therefore, the conductivity increases with the increases of free volume and ion concentration and with the expansion of the amorphous region.²⁷

Mechanism B. Under high temperature and high humidity condition, the dissociated water, i.e., proton and hydronium ion, seem to be transferred through the continuous water phase based on Grotthuss-type conduction.²⁸ In the most hygroscopic polymer composition, mechanism B plays a dominant role.

Effect of doping of electrolyte on conductivity and staining

To increase the ionic conductivity of the crosslinked terpolymer compositions, the addition of electrolyte

was conducted. Octadecyltrimethylammonium perchlorate was used as an electrolyte in terms of its hydrophobic nature and solubility in the terpolymer. Since a lot of electrolyte may bleed out and stain the surface of photoconductor leading to faults on the image, the amount of electrolyte was restricted to 3 phr in this study. The addition of octadecyltrimethylammonium perchlorate resulted in the increase of conductivity ascribable to the migration of the ions. Figure 7 shows the effect of the amount of electrolyte on the conductivity of the crosslinked terpolymer compositions. There were no significant differences on the conductivity by the amount of electrolyte for both Sample 53 and Sample 81 series. The doping of 3 phr electrolyte to Sample 53 stained the polycarbonate plate of the surface of photoconductor after the layered material composed of electrolyte-doped Sample 53 was left to stand and plate at 40 °C for 3 days. The electrolyte-doped Sample 71, however, did not stain the plate at all. The results imply that the bleeding of the electrolyte was suppressed by increasing the EO content in the terpolymers.

Effect of applied voltage on conductivity

For practical applications of the crosslinked terpolymer compositions to the electrophotographic system, the dependence of conductivity on the applied voltage was investigated from 10 V up to 1000 V. The conductivity of the carbon black-dispersed semiconductive rubber materials was changed by the applied voltage. This has been one of the crucial problems of carbon black-loaded materials for the application to semiconductive rollers. Thus, the effect of applied voltage on the conductivity of crosslinked terpolymer compositions was investigated in this study by comparison with that of carbon black-filled composition. Figure 8

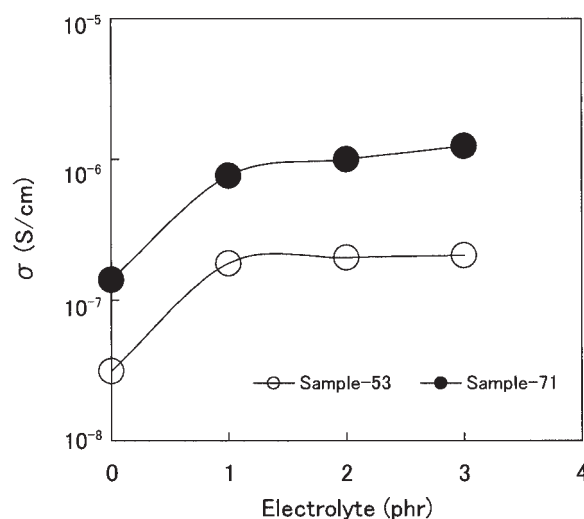


Figure 7 Effect of electrolyte on conductivity at 23 °C and 50% RH of Samples 53 and 71.

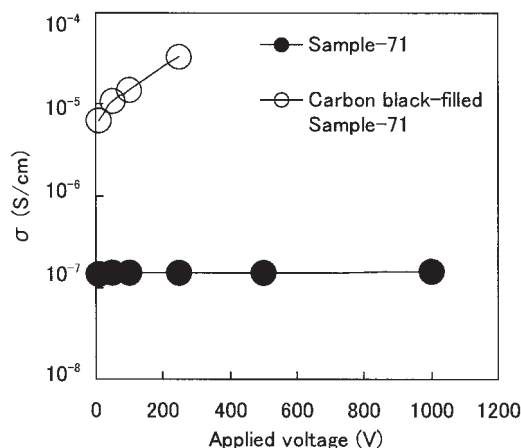


Figure 8 Effect of applied voltage on conductivity at 23 °C and 50% RH of Sample 71 and carbon black-filled Sample 71.

shows the results on Sample 71 and the carbon black-filled sample. The conductivity of the crosslinked terpolymer composition without carbon black was almost same in the range of 10–1000 V, whereas that of the carbon black-filled composition increased with the increase of applied voltage. The phenomenon observed on the carbon black-filled composition was already explained by Polley and Boonstra²⁹ or Beek³⁰ as ascribable to the intrinsic mechanism of conduction in carbon black composition. The stable conductivity of crosslinked terpolymer composition against the rise of applied voltage makes the electrophotographic system without any devices that can set the variable voltage. This point of crosslinked terpolymer composition is very advantageous for application to semi-conductive rubber rollers.

CONCLUSIONS

Crosslinked P(EH-EO-AGE) composition, of which the molar ratio was EH : EO : AGE = 25 : 71 : 4, showed high and stable conductivity under ambient circumstances, not depending on the applied voltages from 10 to 1000 V. The conductivity of crosslinked P(EH-EO-AGE) compositions depends on two factors, i.e., the amount of EO unit and the crystallinity of EO segments. The introduction of EO units into the polyether contributed to the increase in conductivity under ambient circumstance. However, the excess EO units brought about a decrease in conductivity under low temperature and low humidity conditions due to the increase of crystalline phase. The optimum EO content in the terpolymer was 71 mol %. The doping of 3 phr of octadecyltrimethylammonium perchlorate to the crosslinked terpolymers composition whose EO content in the terpolymer was 71 mol % increased conductivity without any staining. This material is expected to be useful for application to the semiconductive rubber rollers of an electrophotographic system.

The authors thank Prof. Dr. S. Kohjiya of Kyoto University for his valuable discussions. This research was partially supported by Grant-in-Aid for Scientific Research (C) (No. 1550185) from JSPS and Grant-in-Aid for Scientific Research on Priority Areas (B) (No. 740/11229202) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

1. Florjanczyk, Z.; Krawiec, W.; Listos, T.; Wieczorek, W.; Przyłuski, J. *Synth Met* 1990, 35, 249.
2. Florjanczyk, Z.; Krawiec, W.; Wieczorek, W.; Przyłuski, J. *Angew Makromol Chem* 1991, 187, 19.
3. Wolfenson, A. E.; Torresi, A. E.; Bonagamba, T. J.; De Paoli, T. J.; Panepucci, H. *Solid State Ionics* 1996, 85, 219.
4. Zoppi, R. A.; Fonseca, C. M. N. P.; De Paoli, M. A.; Nuntes, S. P. *Acta Polym* 1997, 48, 193.
5. Wolfenson, A. E.; Torresi, R. M.; Bonagamba, T. J.; De Paoli, M.-A.; Panepucci, H. *J Phys Chem B* 1997, 101, 3469.
6. Goulart Silva, G.; Lemes, N. H. T.; Polo da Fonseca, C. N.; De Paoli, M.-A. *Solid State Ionics* 1997, 93, 105.
7. del Rio, C.; Acosta, J. L. *Polym Bull* 1997, 38, 63.
8. Kohjiya, S.; Horiuchi, T.; Yamashita, S. *Electrochim Acta* 1992, 37, 1721.
9. Kohjiya, S.; Horiuchi, T.; Miura, T.; Kitagawa, M.; Sakashita, T.; Matoba, Y.; Ikeda, Y. *Polym Int* 2000, 49, 197.
10. Matoba, Y.; Ikeda, Y.; Masui, H. *ISE-2003*, 2–4 April 2003, Kyoto, Japan.
11. Yamashita, S.; Kohjiya, S.; Matoba, S.; Kitagawa, M.; Uemiya, T. *Jpn. Pat.* 2, 757, 004 (1998).
12. Nakata, T.; Kawamata, K. *U.S. Pat.* 3, 773, 694 (1973).
13. Nakata, T. In *Coordination Polymerization*; Price, C. C.; Vandenberg, E. J., Eds.; Plenum: New York, 1983.
14. Ikeda, Y.; Masui, H.; Shoji, S.; Sakashita, T.; Matoba, Y.; Kohjiya S. *Polym Int* 1997, 43, 269.
15. Nishimoto, A.; Watanabe, M.; Ikeda, Y.; Kohjiya, S. *Electrochim Acta* 1998, 43, 1177.
16. Watanabe, M.; Endo, T.; Nishimoto, A.; Miura, K.; Yanagida, M. *J. Power Source* 1999, 81, 786.
17. Ikeda, Y.; Wada, Y.; Matoba, Y.; Murakami, S.; Kohjiya, S. *Electrochim Acta* 2000, 45, 1167.
18. Ikeda, Y.; Wada, Y.; Matoba, Y.; Murakami, S.; Kohjiya, S. *Rubber Chem Technol* 2000, 73, 720.
19. Matoba, Y.; Ikeda, Y.; Kohjiya, S. *Solid State Ionics* 2002, 147, 403.
20. Kohjiya, S.; Ikeda, Y.; Miura, K.; Shoji, S.; Matoba, Y.; Watanabe, M.; Sakashita, T. *U.S. Pat.* 5, 837, 157 (1998).
21. Miura, K.; Shoji, S.; Sakashita, T.; Matoba, Y. *U.S. Pat.* 6, 162, 563 (2000).
22. Miura, K.; Shoji, S.; Sakashita, T.; Matoba, Y. *U.S. Pat.* 6, 239, 204 (2001).
23. Tanaka, H.; Ohnuki, K.; Shoji, S. *Kautsch Gummi Kunst* 1998, 51, 9, 586.
24. Shimada, A. *J Polym Soc Rubber Ind Japan* 2003, 76, 141.
25. Unoura, K.; Oda, A.; Hayashi, Y.; Kimura, N.; Nakata, T.; Tokuda, S. *U.S. Pat.* 3, 880, 779 (1975).
26. Gordon, M.; Taylor, J. S. *J Appl Chem* 1952, 2, 493.
27. Williams, M. L.; Landel, R. F.; Ferry, J. D. *J Am Chem Soc* 1955, 77, 3701.
28. Conway, B. E.; O'M Bockris, J.; Linton, H. *J Chem Phys* 1956, 24, 834.
29. Polley, M. H.; Boonstra, B. B. S. T. *Rubber Chem Technol* 1957, 30, 110.
30. van Beek, L. K. H.; van Pul, B. I. C. F. *J Appl Polym Sci* 1962, 6, 24, 651.