폴리우레탄 陽 아이오노머의 기본 구조 물성

이　종　철·김　병　규

부산대학교 고분자공학과

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Basic Structure Property Behavior of Polyurethane Cationomer

J. C. Lee and B. K. Kim

Dept. of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

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요 약 : Polytetramethylene adipate glycol(PTAd), isophoron diisocyanate(IPDI) 그리고 N-methyl diethanolamine(MDEA)을 사용하여 prepolymer mixing process로 polyurethane cationomer를 합성하였다. 자기유화로부터 얻어진 emulsion과 emulsion cast film의 기본 구조-물성 상관 관계를 PTAd 분자량, MDEA 함량, 중화도 및 쇄연장제의 관능기수에 따라 검토하였다. 입자크기는 PTAd 분자량과 중화도가 증가함에 따라 감소하였는데, 이를 각각 사슬의 유연성 증가와 친수성 증가로 설명하였다. Emulsion의 점도는 입자크기 의존성과는 반대의 경향을 보였다. Hard segment-rich상의 유리적이 온도(T_g)에 상응하는 주 전이온도는 MDEA 함량, 중화도 그리고 쇄연장제 관능기수가 증가함에 따라 단조증가하였으나, 분자량이 증가함에 따라 각각 상혼합의 증가(hard 함량의 감소)와 상분리의 증가(soft segment의 결정화)로 감소($\overline{M}_n = 1000$) 후 증가하였다($\overline{M}_n = 1500$, 2000). MDEA 함량, 중화도 및 쇄연장제 관능기수가 증가함에 따라 인장강도는 증가하였으며, 파단신율은 감소하였다.

Abstract : Polyurethane(PU) cationomers were synthesized from polytetramethylene adipate glycol (PTAd), isophoron diisocyanate(IPDI), and N-methyl diethanolamine(MDEA) by a prepolymer mixing process. Basic structure-property relationships of emulsion and emulsion cast film were studied with regard to the molecular weight($\overline{M}_n$) of PTAd, MDEA content, degree of neutralization, and functionality of the chain extender. Particle size of dispersion decreased asymptotically with increasing $\overline{M}_n$ of PTAd and the degree of neutralization, but by a completely different mechanism, i.e., the former from increased chain flexibility viscosity showed generally the opposite tendency with particle size dependence. The major transition temperature, corresponding to the glass transition(T_g) of hard segment-rich phase monotonically increased with MDEA content, degree of neutralization, and with increasing functionality of chain extender. However, with increasing $\overline{M}_n$ of PTAd, T_g first decreased ($\overline{M}_n = 1000$) and then increased($\overline{M}_n = 1500$, 2000), due respectively to the increased phase mixing (decreased hard content) and phase separation(soft segment crystallization). Tensile strength increased and elongation at break decreased with MDEA content, degree of neutralization and functionality of chain extender.

INTRODUCTION

Polyurethane(PU) ionomers are of considerable scientific and environmental value due to their unique structure-property behavior and the fact that they can be utilized in the form of aqueous dispersion for coating and adhesives.[1~5] PU ionomer contains pendant acid or tertiary nitrogen groups which are neutralized or quaternized to form salts. The ionic groups are hydrophilic in nature and source of Coulombic force of PU. Three types of PU ionomers can be prepared as cationomer, anionomer, and zwitterionomers according to the ionic charges on the polymer main chains.

The hydrophilicity of ionic groups enables the PU to be dispersible of self-emulsifiable without using any external emulsifier.[1,2] The dispersed domain size is dependent to a large extent on the concentration of ionic group.[4] A balance between a product producing a stable dispersion and one in which the derived films are not susceptible to re-emulsification has to be achieved.[6] In segmented PU, most ionic centers belong to the hard segments which are composed of urethane linkages and isocyanate fragments. Therefore ionic groups contribute to the hard segment content leading to increased modulus and strength of PU, aside from interchain interactions due to Coulombic forces.[7~10]

This paper considers structure-property behavior of PU cationomer synthesized from polytetramethylene adipate glycol(PTAd), isophoron diisocyanate(IPDI), and N-methyl diethanolamine (DMEA) as a potential ionic center. Effect of the molecular weight($\overline{M}_n$) of PTAd, content of MDEA and the degree of neutralization of MDEA, and the functionality of extender on the particle size, viscosity of dispersion, dynamic mechanical, and tensile properties of the emulsion cast films were studied.

EXPERIMENTAL

Materials. PTAd was dried and degased at 80℃, 1~2 mmHg until no bubble was observed. MDEA was purified by fractional distillation in vacuum and stored under nitrogen. Dimethyl formamide (DMF), ethylene diamine(EDA), diethylene triamine(DETA) and triethylene tetramine(TETA) were dried over 3Å molecular sieve before use.

Prepolymer Synthesis. Detailed procedures for prepolymer synthesis are available elsewhere.[1,5~7] A 500 ml 4-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, condenser with drying tube, and a pippet outlet was charged with PTAd, and the reactant was heated to 60℃ in a constant temperature water bath. Then IPDI dissolved in substantial amount of DMF was added, and the reaction proceeded for 3 h at 80℃. The change of NCO value during the reaction was determined using a standard dibutylamine back titration. Upon obtaining the theoretical NCO value which is calculated from [NCO]/[OH] index of feed, the reaction mixture was cooled to 35℃ and neutralized by acetic acid for 3 h.

Emulsification and Chain Extension. Dispersion of PU cationomer in water was obtained by adding water to the prepolymer solution at 60℃. Rate of water addition to the mixture was carefully controlled to obtain a stable inversion, using a tubing pump. The phenomenon of phase inversion, viscosity and conductivity change during the emulsification process are well documented in Dieterich[1] and our earlier papers.[7~9] Upon completing the phase inversion, TETA dissolved in water was fed to the emulsion for a period of 40 min, and chain extension was carried out for the next 2 h. The resulting product was stable over six months at room temperature, urea-urethane dispersion with a solid content about 20%.

Charaterizations. Particle size and its distribution were measured using an Autosizer(Malvern IIC). The viscosity of emulsion was measured by a Brookfield viscometer at 20℃. Contact angle at room temperature was measured by dropping a drop of water on the film(Erma G-1 type). Dynamic mechanical properties were measured using a Rheovibron(Toyo Baldwin DDV-II) at 11 Hz, with a sample size of 0.03×0.2×3 cm. Tensile properties of the emulsion cast films were measured on

a tensile tester(Tinius Olsen 1000) at a crosshead speed of 50 mm/min, and an average of at least five measurements was taken to report. Films for the above tests were prepared by casting the emulsion on a teflon plate, followed by drying at 80°C for 5 h. The resulting films were then heated overnight in an oven at 60°C under 2~3 mmHg. Microtensile test specimen were prepared according to ASTM D-1822 using a punch.

RESULTS AND DISCUSSION

Effect of Soft Segment Length. In this series of experiments, PTAds of different molecular weight ($\overline{M}_n$=600, 1000, 1500, and 2000) were used to prepare PU ionomers at a fixed content of MDEA (15.0 wt% based on total solid) which was 100% neutralized to eliminate the effect of ionic group content. The average molecular weight of NCO-terminated prepolymer was fixed at 5000.

As the $\overline{M}_n$ of PTAd increases from 600 to 2000, the block length of soft segment increases and the content of hard segment decreases from 68 to 61%. Fig. 1 shows the average particle size and emulsion viscosity as a function of $\overline{M}_n$ of PTAd. It is seen that the particle size decreases asymptotically and emulsion viscosity increases asymptotically with increasing $\overline{M}_n$ of PTAd. In PU dispersion, average particle size is, more or less, control-

led by the emulsification conditions such as agitation speed and temperature, but it is mainly governed by the hydrophilicity of the PU.[1,2] Generally, higher hydrophilicity leads to smaller particle size.[6] The hydrophilicity of PU, however, decreases with the soft segment length in PU cationomer when the soft segment is PTAd. The decreased particle size should be due to the increased chain flexibility of PU by the increase of soft segment content.[11,12] During the experiment, it was observed that emulsification was much easier with higher $\overline{M}_n$ of PTAd. In fact serious rod climbing was observed with low $\overline{M}_n$ of PTAd, at the early stage of emulsification. With the increase of chain flexibility of PU, prepolymer solution viscosity decreases. This leads to a finer breakup of dispersed phase during inversion, and easier formation of micelle structure in water.[10] These effects contribute to the decrease of particle size.

Emulsion viscosity is of great importance in practical application, and is influenced by the average particle size, particle size distribution, interparticle interactions and swellability of the particles.[14] If the particle size decrease is mainly due to the increased hydrophilicity, the sum of effective particle volume increases due to the increased swell of water, and the viscosity increases linearly, or often more pronounced than linearity. The increase of viscosity with the $\overline{M}_n$ of PTAd is asymptotic as shown in Fig. 1, which implys that the decrease of particle size is not driven by the hydrophilicity of the PU ionomer. Hydrophilicity is decreased with the $\overline{M}_n$ of PTAd, which is evidenced from contact angle measurement discussed below.

Fig. 2 shows contact angle of the film with water, where a nearly linear increase of contact angle with $\overline{M}_n$ of PTAd is obtained. This indicates that the hydrophilicity of PU cationomer is decreased with increasing $\overline{M}_n$ of PTAd, and indirectly confirms that the decrease of particle size is due to the increased flexibility of PU with increasing soft segment content.

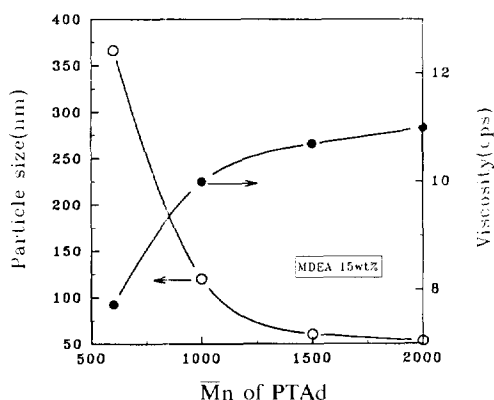Dynamic mechanical properties of the emulsion cast films with different $\overline{M}_n$ of PTAd are shown in

Fig. 1. Particle size and emulsion viscosity(20°C) vs. $\overline{M}_n$ of PTAd.
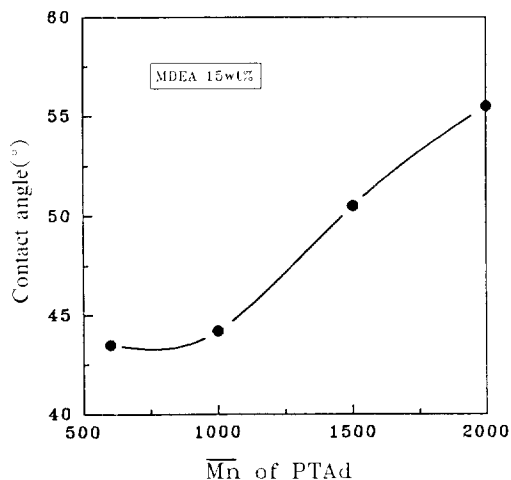
Fig. 2. Contact angle of the emulsion cast films with water vs. $\overline{M}_n$ of PTAd(20℃).

Fig. 3. Relatively higher value of storage modulus (E′)(Fig. 3a) above room temperature is probably related to the crystalline part of the soft segment. The beginning of rubbery plateau, which is not well defined in any of the samples due probably to the relatively high degree of soft-hard phase mixing of ester polyols, corresponds to the melting of soft segments.[15]

Tan δ peak(Fig. 3b) show two relaxations, one at about −30℃ and the other at about 40℃. The lower temperature relaxation should correspond to the glass transition of soft segment which is very small compared to the high temperature relaxation perhaps due to the small soft segment content and relatively high degree of phase mixing. For the higher temperature relaxation, the peak temperature decreases as the $\overline{M}_n$ of PTAd increases from 600 to 1000, and increases with further increase of $\overline{M}_n$, and shows a maximum at 2000. The decrease should be due to the decreased hard fraction of PU, and the increase should be related to the crystalline part of the soft segment. This view can be supported by the significant decrease of peak area as $\overline{M}_n$ of PTAd increases because the loss peak represents the interactions in amorphous domains.

Fig. 4 shows the tensile properties of the emulsion cast films, where strength decreases and elo-
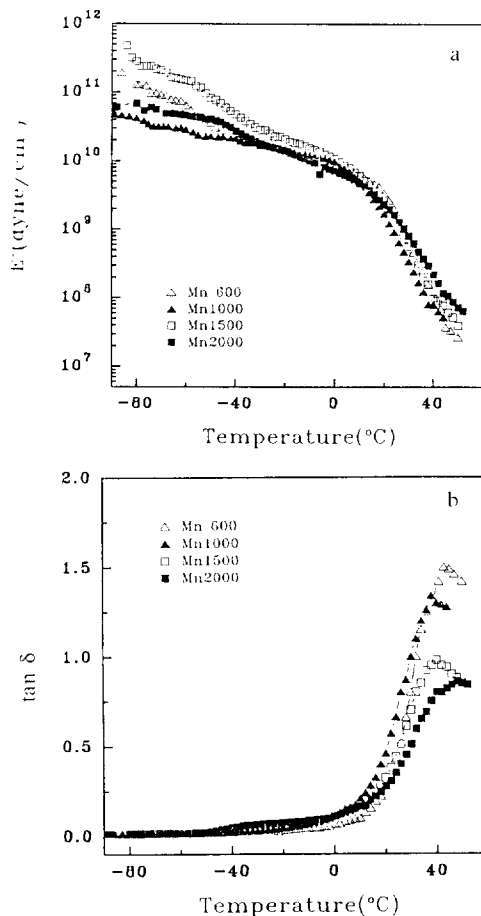

Fig. 3. Dynamic mechanical properties of the emulsion cast films prepared from different $\overline{M}_n$ of PTAd : a) storage modulus(E′), and b) tan δ.

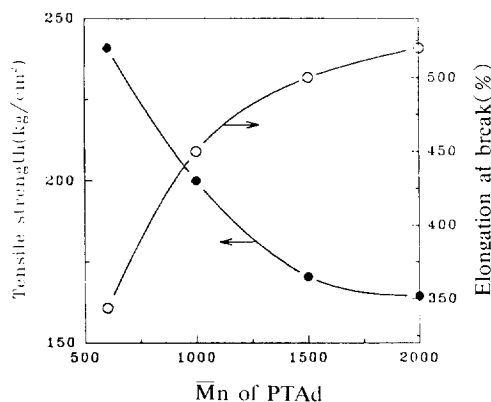**Fig. 4.** Tensile properties of the emulsion cast films vs. $\overline{M}_n$ of PTAd(20℃).

ngation at break increases with increasing $\overline{M}_n$ of PTAd. Basic structure-property relationship in PU indicates that hard segment of the PU affects strength and it is controlled by the total NCO content. With the increase of soft segment length, less amount of urethane linkage are formed to result in decreased strength. The asymptotic decrease in strength and increases in ultimate elongation may assure the partial crystallzation of soft segment.

Effect of MDEA Content. This experiments were formulated with PTAd 1000, and MDEA content varied 9.0~15.0%, which were completely neutralized.

Fig. 5 shows the variation of particle size and emulsion viscosity with MDEA content, where an asymptotic decrease of particle size and an accelerative increase of emulsion viscosity, an opposite behavior to the increasing $\overline{M}_n$ of PTAd discussed above, are obtained. In self-emulsification of ionomer, particle size typically decreases with increasing hydrophilicity which is to a large extent governed by the ionic content of PU.[1~3] Since in this system MDEA was 100% neutralized, hydrophilicity increases with the MDEA content. In ionomer dispersion, particles are stabilized by the electrical double layer formation, which is increased with increasing ionic groups. In addition to the electrical double layer, effective particle diameter is also increased by water swell.[13,14] Therefore, the effects of increasing MDEA content are to reduce the pa-
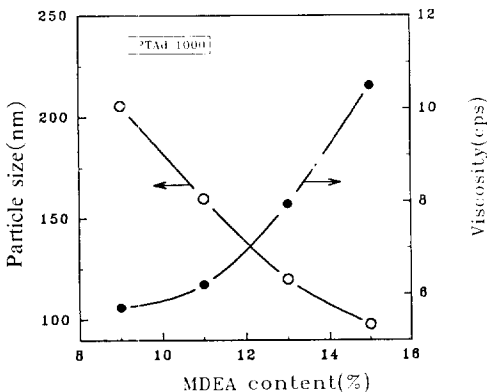
rticle size due to the increased hydrophilicity, and to increase the particle size due to the thickened electrical double layer and increased water swell. The swellability should be more pronounced with increasing hydrophilicity, and the overall effect would be an asymptotic decrease of particle size, i.e., rapid at low and slow at high MDEA content. On the other hand, emulsion viscosity increases with the increase of effective volume of the dispersed particle, and a linear or more rapid increase at high MDEA content can be obtained.

Fig. 6 shows that the contact angle of the film with water decreases with increasing MDEA content of the film. Since the ionic group is hydrophilic in nature, the increase of MDEA content gives the film more hydrophilicity, leading to a decreased contact angle with water.

The E' and tan δ as a function of temperature is shown in Fig. 7, where the major transition moves toward the higher temperature. Since the PTAd 1000 does not crystallize at normal conditions and ester polyol forms strong hydrogen bondings with NH of urethane group,[16] relatively high degree of phase mixing is expected. Therefore, the increase of peak temperature with increasing MDEA content is mainly due to the increased hard content. However, sign of increased phase separa-
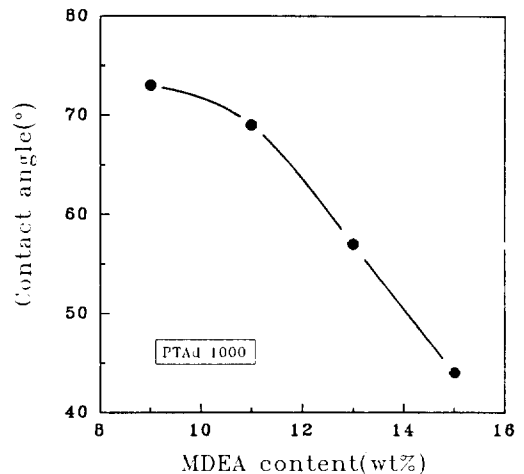

Fig. 5. Particle size and emulsion viscosity(20℃) vs. MDEA content.

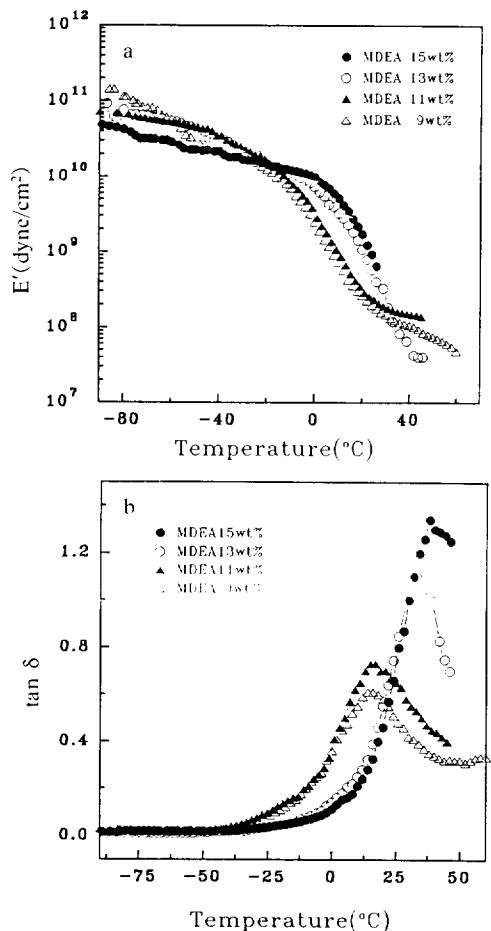**Fig. 6.** Contact angle of the emulsion cast films with water vs. MEDA content(20℃).

Fig. 7. Dynamic mechanical properties of the films prepared from different MDEA content : a) storage modulus, and b) tan δ.
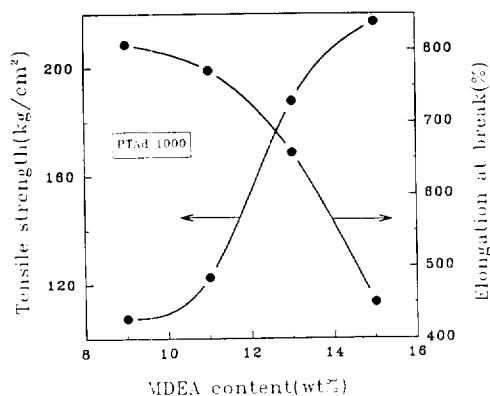
tion with increasing MDEA content is also seen from a shift of the onset of a sudden drop in E' and maximun in tan δ toward the higher temperature.[15] Soft segment relaxation is not observed due to its small content and high degree of phase mixing.

Tensile strength increases and elongation at break decreases with MDEA content(Fig. 8). Since MDEA gives PU more hard segment content and increased ionic crosslinking density, Coulombic force and hydrogen bondings, increased strength and decreased ductility is expected.

Effect of Degree of Neutralization. This series of experiments were formulated with a PTAd 1000 at a fixed MDEA content(15 wt%). The only variable was the degree of neutralization(DN) of MDEA.

Fig. 9 shows that particle size decreases asymptotically and emulsion viscosity increases almost linearly with increasing DN. Since DN was the only variable in this experiments variation of particle size with increasing DN is due to the increased hydrophilicity of PU with the increase of ionic group content. At low hydrophilicity particle size decreases with increasing hydrophilicity, but at high hydrophilicity the decrese of particle size can be offset due to the higher swellability, and an equilibrium particle diameter would be obtained to give an asymptotic decrease of particle size at high DN. On the other hand, emulsion viscosity increa-
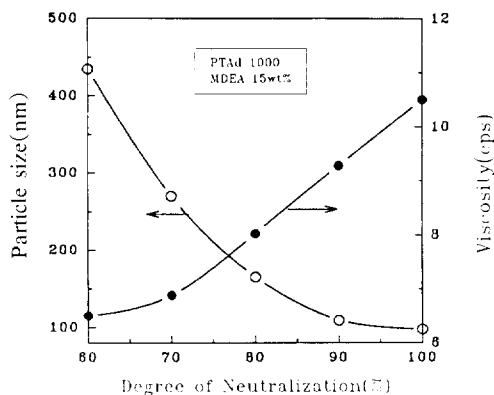

Fig. 8. Tensile properties of the emulsion cast films vs. MDEA content(20℃).

Fig. 9. Particle size and emulsion viscosity(20℃) vs. degree of neutralization.
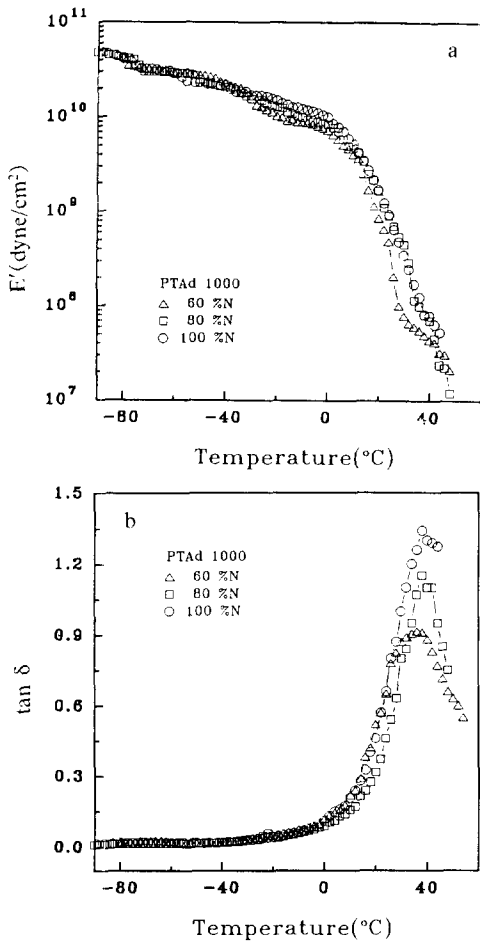
Fig. 10. Dynamic mechanical properties of the emulsion cast films prepared with different degree of neutralization : a) storage modulus, and b) tan δ.

ses in proportion to the effective particle volume, and its dependence on DN should be more or less direct, as our results indicate.

Storage modulus and tan δ peak(Fig. 10) increase with increasing DN. The increased DN resulted in an increase in the ionic crosslinking density, Coulombic force, and hydrogen bondings.[1,16,17] As a result, modulus, strength(Fig. 11), and glass transition temperature increase. Following earlier studies by others,[17] T_g of different types of ionomer depend on the ionic group content and that a linear relationship existed between T_g and the ion concentration. In our case, T_g increases mono-
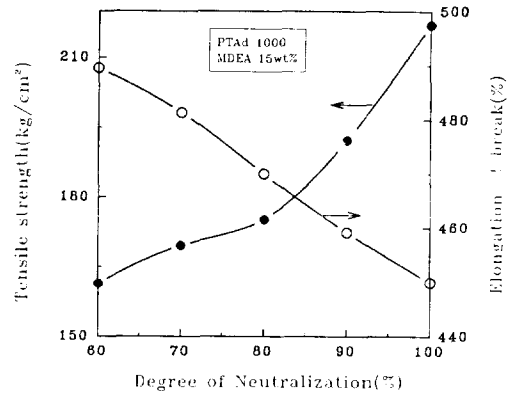

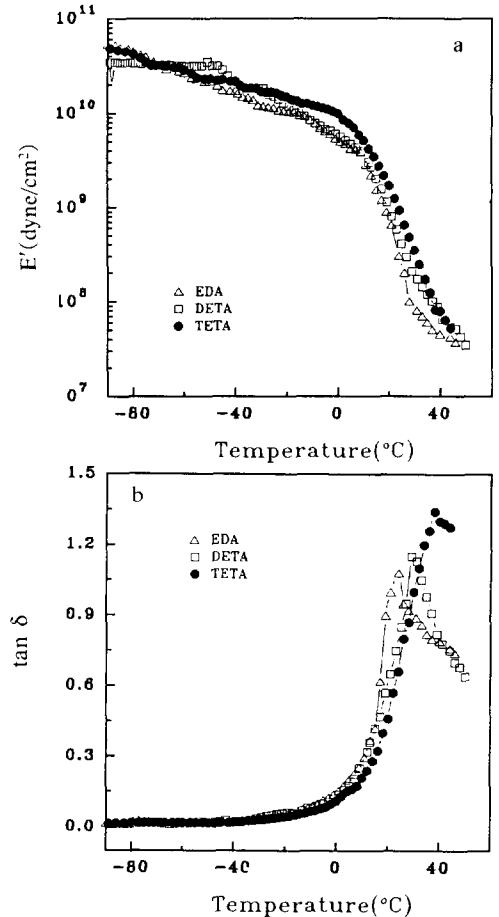**Fig. 11.** Tensile properties of the emulsion cast films vs. degree of neutralization.

Fig. 12. Dynamic mechanical properties of the emulsion cast films prepared with different chain extender : a) storage modulus, and b) tan δ.
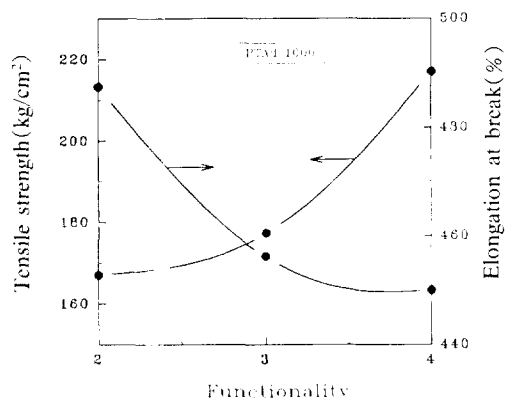
Fig. 13. Tensile properties of the emulsion cast films vs. extender functionality.

tonically with DN.

Effect of Extender Functionality. This experimes-nts were formulated with PTAd 1000 at a 15% MDEA content, which were completely neutrali-zed. The functionality of chain extender has been varied as 2(EDA), 3(DETA), and 4(TETA). Fig. 12 shows that E' increases and tan δ peak moves toward the higher temperature with increasing ex-tender functionality. This is simply due to the inc-rease of chemical crosslinking density. With EDA, only linear PU can be obtained, but with di- and trifunctional extenders, chemical crosslinks are in-troduced in PU and chain rigidity and thermal re-sistance increase. Tensile strength increases and elongation at break decreases with the increase of extender functionality(Fig. 13).

CONCLUSION

It was found that particle size of polyurethane (PU) emulsion can be varied over two order of magnitude depending on the soft segment length, soft/hard segment content, and degree of neutrali-zation(DN) of potential ionic center. Viscosity measurement showed some light on the mecha-nism of particle size reduction.

The glass transition temperature(T_g) of PU ca-tionomer was governed crystallizable soft segment

length, soft/hard segment content, the DN, and the crosslinking density of PU. Among these variables, effect of hard content was most pronounced.

Tensile properties increased and elongation at break decreased with hard content, DN and func-tionality of chain extender.

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