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Effects of emulsification on properties of quaternary ammonium ion-based polyurethane anionomer

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Summary

Quaternary ammonium ion-based Polyether polyurethane anionomer solution and emulsion are studied. In the un-ionized film, the soft segment crystallites are not present. Ionization creates soft segment crystallites and produces increased phase separation between the soft and hard domains, which leads to an increase in both tensile strength and elongation at break. Emulsification of the PU ionomer solution can lead to slightly increased phase mixing. During the emulsification, conductivity and viscosity variations show that water is first adsorbed on the surface of the hard-segment microionic lattices and then enters successively into the more disordered and less disordered hard domains. The morphology of the un-ionized film shows that the hard domains are dispersed in the soft domains and that the size of hard domain increases greatly after the ionization. After dispersion, the hard segments originally distributed in the dispersed phase can be inverted to become a hard domain network.

Introduction

Polyurethane (PU) ionomers can be prepared by incorporation of a chain extender containing an amino group with NCO-terminated PU prepolymer and subsequent modification with an ionizable component (1-4). There are three types of PU ionomers: zwitterionomer, anionomer and cationomer. Anionomer can also be formed by using either a diol or diamine chain extender that contains a pendant acid group, which is subsequently neutralized with different cations or bases (5).

By addition of water to an organic solution of the ionomer followed by removal of the organic solvent, a so-called PU emulsion can be obtained. The PU emulsion can be cast into a film to provide the same usage as PU solution but without pollution. However, studies on the mechanism of the emulsification process and of the morphology and physical properties of emulsion-cast films are limited. Lorenz et al. (6,7) reported tensile strength of emulsion-cast films without comparison with that of solution-cast films. One of us and Chan (3,4) studied three series of PU cationomers. It was found that in the un-ionized and ionized systems, the hard segments exhibit disordered and ordered arrangements respectively. After ionization, disruption of the order and enhancement of cohesion through the Coulombic interaction in the hard domains occur simultaneously. The dispersion process can be divided into three stages involving a separation of hard segment aggregates due to adsorption of water on their surface, water entering into disordered and then ordered hard domains, and

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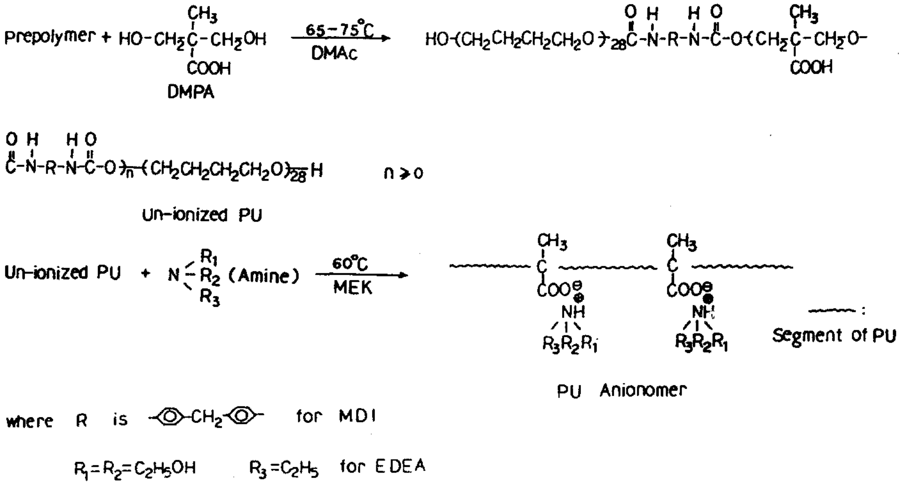
*To whom offprint requests should be sent finally a rearrangement of agglomerates to form microspheres. In this work, films cast from solution and emulsion of polyether PU anionomer with quaternary ammonium ions as counterion were prepared and characterized using various experimental techniques in order to elucidate effects of the ionization and emulsification on physical properties. In addition, the phase inversion mechanism during emulsification is studied based on the conductivity and viscosity measurements.

Experimental

PU prepolymer was prepared at 65-75°C under nitrogen in a stirred-glass reaction kettle with a reflux condenser. The 4,4'-diphenylmethane diisocyanate (MDI) (4 moles) was charged into the kettle first and heated up to 65-75°C. Then poly(tetramethylene oxide) (PTMO) (1 mole) in N,N-dimethylacetamide (DMAc) was added slowly such that one of the two hydroxyl groups in each polyol molecule could react with one molecule of MDI to yield prepolymers. The reaction was allowed to proceed until the theoretibcal isocyanate content was reached as determined by the di-n-butylamine method (8).

The prepolymer was then diluted to 30 wt% with DMAc to lower the rate of heat generation and to avoid a substantial increase in viscosity during the subsequent chain extension reaction. Dimethylolpropionic acid (DMPA) (3 moles) in DMAc was added slowly to the diluted prepolymer solution at 65-75°C. The reaction was continued until the NCO groups were reacted, as confirmed by the disappearance of the IR absorption at 2270 cm^{-1}. The reaction mixture was then precipitated from water to give the crude product. The crude product was dried in vacuum oven to give the un-ionized PU. The carboxylic acid content of the un-ionized PU was determined by acid-base titration with KOH solution. Result of titration showed that approximately 88% by mole of the carboxylic acid group originally added was remained in the un-ionized PU. A given quantity of the un-ionized PU was dissolved in methyl ethyl ketone (MEK) and then an appropriate amount of N-ethyl diethanol amine (EDEA) was added to the PU solution. The ionization process was carried out at 60°C for 1 hour. The degree of ionization was dependent on the amount of ionization agent added. The above reaction procedure can be summarized as the following scheme:



Emulsification was carried out by adding de-ionized water slowly with constant agitation at constant temperature (20°C) to a solution of polyether PU anionomer, 10% by weight, in MEK. During the addition, a conductivity probe and a spindle were used to monitor conductivity and viscosity. When the conductivity of the solution reached a constant level, the phase inversion was considered to be complete and addition of water was stopped. The emulsion was then subject to dynamic vacuum pumping for removing the organic solvent, MEK.

Films for physical testing were prepared by pouring the solution or the emulsion into a Teflon mold. After standing at room temperature for 4 days to allow evaporation of the solvent, the film was vacuum-dried at 60°C for 48 hours in order to remove residual solvent completely.

Samples were designated so that, for example, ME-1.0-20°C means 1.0 mole ratio of EDEA to the carboxylic acid of the un-ionized PU and the dispersion temperature is 20°C, the initial letters "M" and "E" refer to MDI and EDEA respectively. The un-ionized PU was designated as M-0.0.

Conductivity was measured using a conductivity meter from Crison Instrument Co. and viscosity using a Brookfield Synchro-Lectric viscometer with spindles LVT no. 1-4.

Tensile properties were measured at room temperature using a Shimadzu Universal Testing Machine, Model 502, with a cross-head speed of 20 mm/min. The dumbell type specimen was 25 mm wide at the two ends, 0.1 mm to 0.4 mm thick, and 10 mm wide at the neck (JIS K6301 method).

Differential scanning calorimetric (DSC) thermograms over the temperature range -30°C to 180°C were recorded using a Du Pont 910 apparatus with a heating rate of 20°C/min, under nitrogen purging.

Infrared spectra (IR) were recorded using an IR spectrophotometer, Model 983 from Perkin-Elmer Co., at a resolution of 3 cm^{-1}.

Dynamic mechanical properties over a temperatures range of -150°C to 140°C were measured using a Rheometric Dynamic Spectrometer Model RDS-II from Rheometrics Inc.

A JEOL 200CX scanning transmission electron microscope (STEM) from Japan Electronic Optics Laboratory operating at 120 KV and 20000X magnification was used to examine the morphology of the samples. Microtomed specimens were directly mounted on the 400-mesh copper grids without a supporting film and then stained with OsO_4 by a well developed technique (9) applicable to polyurethane (10).

Results and discussion

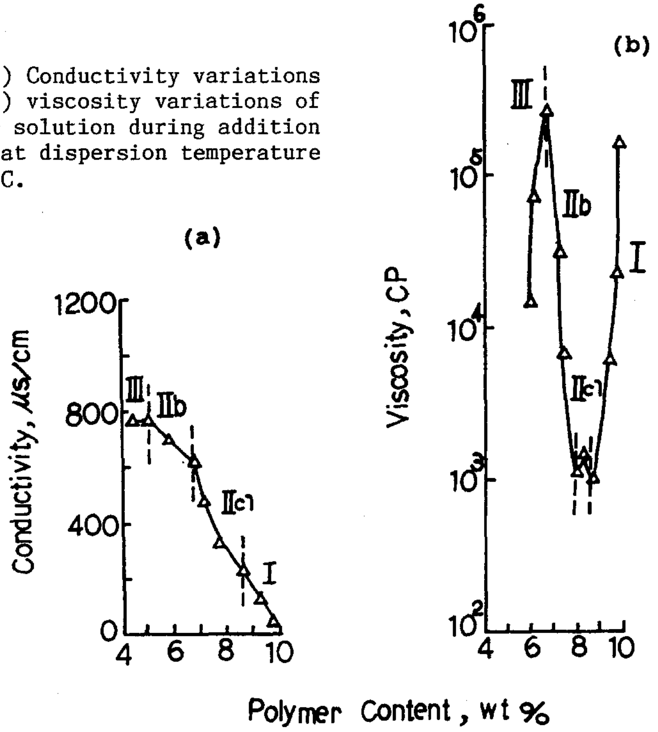
1.Conductivity and viscosity measurements

The conductivity and viscosity variations of the solution of ME-1.0 during addition of water at the dispersion temperature, 20°C, are shown in Figure 1. The inversion process can be clearly divided into three regions, as marked on the figure. In stage I, as water is added slowly to the ionomer solution, it is adsorbed by the carboxylate anions situated on the surface of the hard segment microionic lattices, causing a separation of neighboring chains and aggregates. Each microionic lattice, which is considered to form in the organic medium, is an aggregation of unsolvated salt segments stabilized by Coulombic forces (1). The conductivity curve is slightly concave upward and the viscosity of the solution decreases rapidly to a lower limit. The increase in conductivity and decrease in viscosity indicate that the ionic groups on the surface of the hard-segment microionic lattices are almost completely dissociated.

At the beginning of stage II (stage IIa), as more water is added, it starts to enter into the interior of the more disordered hard-segment microionic lattices. The hydrophobic segments (soft segments) lose their solvation sheath, and subsequently aggregate to form aligned hydrophobic aggregates, which eventually become dispersed phases. The solution becomes turbid and the turbidity increases with further addition of water. During this stage, as water is added, conductivity increases slightly concave upward and slower than in stage I. This result indicates that water enters less easily into the more disordered hard-segment microionic lattice. The viscosity increases slightly owing to the increased number of hydrophobic aggregates and passes through a small maximum. The presence of this maximum indicates dissociation of the more disordered hard domains, accompanied by increased association of hydrophobic segments. Further addition of water causes a decrease in viscosity which also supports the idea that some of the more disordered hard-segment microionic lattices are dissociated.

In stage IIb, continuing addition of water causes the viscosity to increase sharply to another maximum, indicating dissociation of the hard-segment less disordered microionic lattices accompanying an increased association of the hydrophobic segments. The conductivity curve is linear with smaller slopes than that in stage IIa, indicating that the entrance of water into the less disordered hard-segment microionic lattices is more difficult than into the more disordered hard domains in stage IIa. In stage III, the viscosity drops sharply and the conductivity remains almost constant. At this stage the phase inversion is complete.

Fig. 1. The (a) Conductivity variations and (b) viscosity variations of ME-1.0 solution during addition water at dispersion temperature of 20°C.



2.Infrared spectroscopy (IR)

IR spectra of the films cast from solution and emulsion are shown in Figure 2. For the un-ionized PU (M-0.0), the C=O bands from urethane group (NHCO) and carboxylic acid group (COOH) overlap and have a peak at 1729

cm^{-1} (corresponding to un-bounded C=O). In the region of the NH band (3000-3500 cm^{-1}), a peak at 3286 cm^{-1} is present due to the hydrogen-bonded NH group; but the peak at 3460 cm^{-1} due to free NH is not present, indicating that the NH groups appear to be completely hydrogen-bonded. For the un-ionized PU, the C-O-C band from polyether soft segment has a peak at 1109.5 cm^{-1}. Upon ionization, this peak shift to 1113.5 cm^{-1}. For the ionized film, the absorption range of COO^- overlaps with that of aromatic C=C bond and has a peak at 1600 cm^{-1}. Its relative intensity increases significantly after the ionization, indicating that after the ionization the carboxylate ion (COO^-) actually exists in the film. Since the un-ionized PU has a COOH group on each hard segment, the COOH group can form hydrogen bond with both another COOH group from neighboring hard segments and C-O-C group of the soft segments. Upon ionization, the COOH group was converted to COO^- group and the number of hydrogen bonds between soft/hard segment diminish, hence, the C-O-C band shifts from 1109.5 cm^{-1} to 1113.5 cm^{-1}.

For the ionization film, the C=O band is split into two peaks; that centered at 1713 cm^{-1} is due to bonded C=O, and that at 1721 cm^{-1} to free C=O. This is due to that each EDEA counterion has two OH groups and the OH group can form hydrogen bond with both another OH group and C=O group of the hard segment, so the bonded C=O appears after ionization.

For the emulsion-cast film, the absorption frequency of the C-O-C group is the same as that of the solution-cast film. But the absorbance of the bonded C=O of the emulsion-cast film is more intense than that of the solution-cast film. These results indicate that some of the OH groups previously bonded with another OH groups now switch to form hydrogen bonds with C=O groups. Thus, disruption of the packing arrangement in the hard domains occurs during the dispersion process.

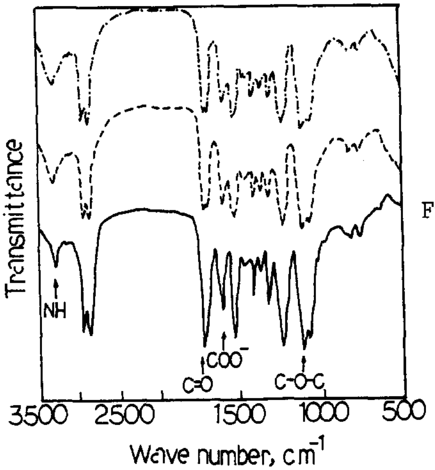


Fig. 2. IR spectra of the films
(——) M-0.0,
(- - -) ME-1.0,
(-·-) ME-1.0-20°C.

3.Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements of films cast from solution and emulsion are shown in Figure 3. Three peaks are observed in the tanδ curves. The β peak is taken as the glass transition temperature of the soft domains (T_{gs}). The presence of the γ peak (below the β peak) between -131°C to -148°C can be attributed to a relaxation process involving local motion of the methylene sequences of the polyether segments (11). The α peak is taken as the glass transition temperature of the disordered hard segments

(T_{gh}).

For the present system, after ionization to the content of 1.0, the T_{gs} drop by 63°C and the T_{gh} decrease by 3°C. These would indicate that the degree of phase separation increases after the ionization. The slight decrease of T_{gh} might indicate an increased extent of disorder due to disruption by ionization. For ME-1.0-20°C, T_{gs} and T_{gh} of the emulsion-cast film both are 5°C higher than those of the corresponding solution-cast film ME-1.0, indicating that the dispersion leads to an increased phase mixing and increased order of the hard domains.

4.Differential scanning calorimetry (DSC)

DSC curves for all the films are shown in Figure 4. For all films except the un-ionized PU, an endothermic peak was found below room temperature. The temperature of this peak corresponds to the melting peak of the flexible soft domains (12). While the hard domain has no detectable order, different from those of the conventional PU (composed of PTMO/MDI/1,4-butanediol (13)) and PU cationomer of PTMO/MDI/MDEA/glycolic acid studied by Chen and Chan (3,4) for which the short range order-disorder transition temperatures of hard domains are 70°C and 82-90°C.

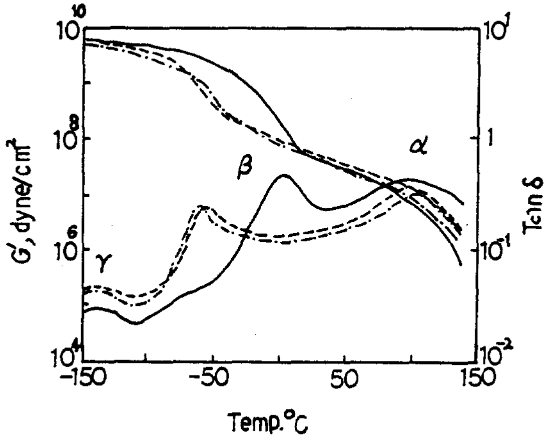


Fig. 3. Dynamic mechanical analysis (——) M-0.0, (---) ME-1.0, (-·-) ME-1.0-20°C.

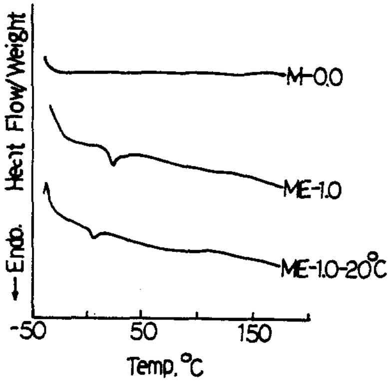
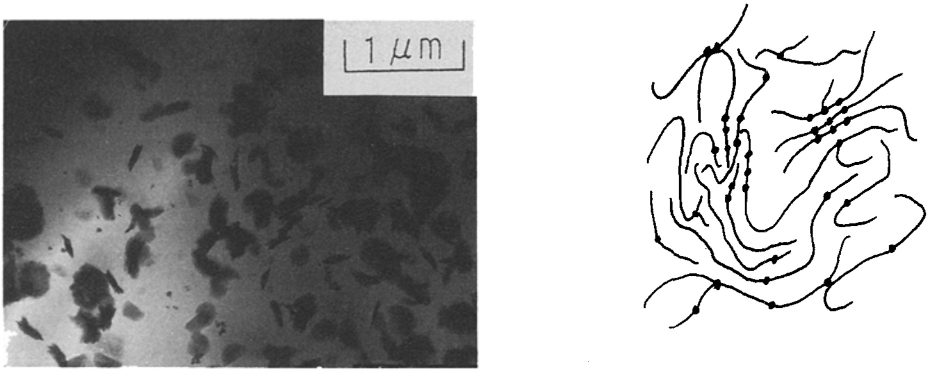


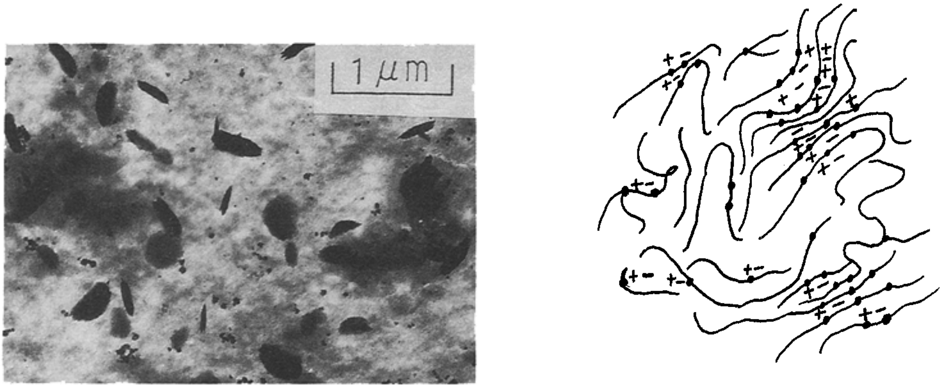
Fig. 4. DSC curves of the films.

5.Morphological changes after ionization and dispersion

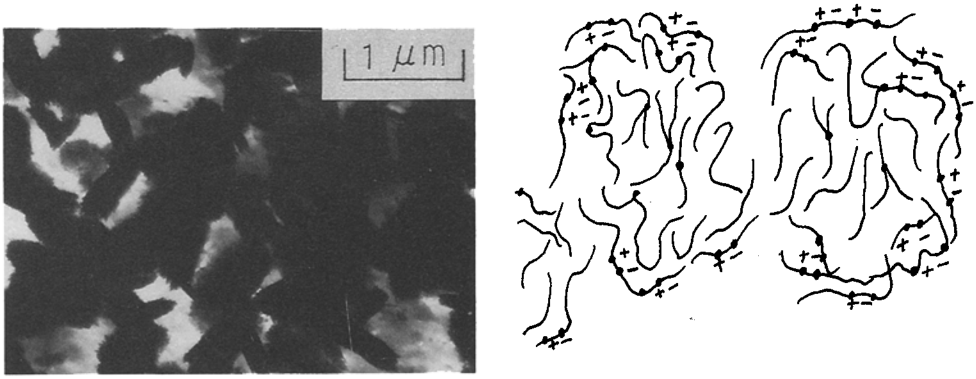
TEM-micrographs of the un-ionized film and ionized film cast from solution and emulsion as well as the schematic representation are shown in Figure 5. For model descriptions, the line segments with and without dots denote hard segments and soft segments respectively; carboxylate anion and counterion are represented by the symbols "-" and "+" respectively. The M-0.0 sample (Fig. 5(a)) shows a morphology with soft domains as the continuous phase and hard domains as the dispersed phase, the size of the hard domains is about 0.2 µm. Upon ionization, the hard domains aggregate to form agglomerate, the size of the hard domains increase to about 1 µm



(a) M-0.0



(b) ME-1.0



(c) ME-1.0-20°C

Fig. 5. TEM-micrograph and schematic representation of the films (a) M-0.0, (b) ME-1.0, (c) ME-1.0-20°C.

along with some smaller size of hard domains and still present as the dispersed phase (Fig. 5(b)). After the dispersion at 20°C, partial phase inversion occurs and most of the hard segments are exposed on the particle surfaces in the emulsion (Fig. 5(c)). During film formation, the particles coagulate to form a film with a morphology of interwoven soft and hard domains (Fig. 5(c)). Continuous and dispersed phase are no longer distinguishable.

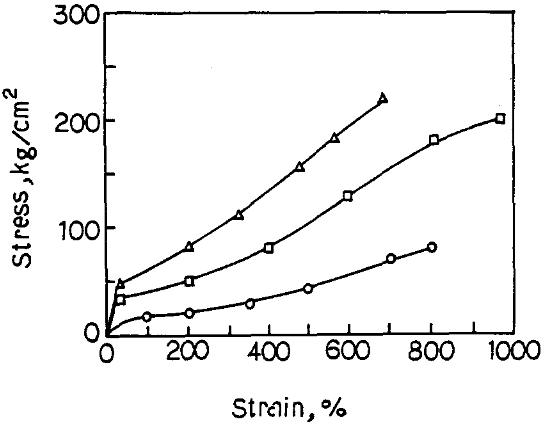


Fig. 6. Stress-strain curves of the films
(○) M-0.0,
(□) ME-1.0,
(△) ME-1.0-20°C.

6.Tensile properties

Tensile properties of all the films are shown in Figure 6. Upon ionization, both the tensile strength and elongation at break increases, owing to the significant increase in phase separation as confirmed by the DMA result. The emulsion-cast film have slightly higher tensile strength and lower elongation at break than the respective solution-cast film. This is due to partial phase inversion to give the interwoven hard/soft domain morphology. The size of hard domains increases resulting from increased order of the hard segments as confirmed by the result of DMA, leading to higher tensile strength.

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