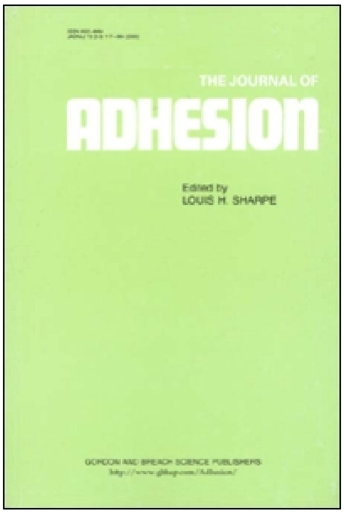

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Dynamic Mechanical Properties and Adhesive Strengths of Emulsion Polymer by Power Feed Technique, I.*

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Dynamic mechanical properties and adhesive strengths of power feed copolymer and random copolymer synthesized using styrene or methyl methacrylate and n-butyl acrylate were investigated. Although the two systems were synthesized from the same raw materials, power feed copolymer had a very broad transition compared with random copolymer. This fact was explained by the fact that the system synthesized through power feed method was an alloy of copolymers which are a continuous series from monomer A rich copolymers to monomer B rich copolymers. The dynamic mechanical behavior of film cast from solution was almost the same as that of emulsion film, which indicated more extensive application of power feed copolymer. In the P(nBA/St) system, power feed copolymer maintained its adhesive strengths over a wide temperature range compared with random copolymer. The absolute value, however, was not so high. This was due to the low cohesive strengths of the films.

KEY WORDS Emulsion polymer; power feed polymerization; adhesive strengths; broad transition; dynamic mechanical properties.

INTRODUCTION

It is known that adhesive strengths are closely associated with the rheological properties of adhesive polymers.[1–13] That is to say, adhesive strengths have their maximum value at the characteristic point of individual polymer systems. The characteristic point is the glass transition temperature. So, if we apply polymers having Tgs in a wide range of temperatures as adhesives, the adhesive strengths would be expected to show high values in the corresponding wide temperature range.

Adhesive strengths are measured by debonding the bonded material and governed by the way of the destruction test. For example, the peel strengths have their maximum when the storage modulus (E′) of the adhesive polymer is around 1×10^8 dyne/cm^2.[4,12] The cross-lap tensile adhesive strengths and the tensile shear adhesive strengths have their maximum at E′ of 5×10^9–1×10^{10} and 1×10^{10}–2×10^{10}

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dyne/cm^2, respectively. These values of E′ are considered almost the same even if the structure of the polymer is different. In a word, when the peel strengths are high, the shear (or tensile) adhesive strengths are low, and vice versa. It is said to be impossible to make both high. But actually, bonded materials are subject to various stresses. It is a common case that they have to maintain the adhesive strengths under both peel and shear stress. In such a case, E′ of the adhesive polymer having above performance should lower gradually. The polymer described above is nothing else but the polymer having a glass transition over a wide temperature range.

The most famous and effective way of broadening transitions of polymers is the IPN technique, which is reported and reviewed elsewhere.[14–20] IPNs, however, are crosslinked polymer composite, so once they are synthesized, they are not dissolved in any solvent but swelled. Consequently, the application of IPNs as adhesives would be somewhat difficult, except in the case when they can be synthesized and cured between the adherends.

Bassett et al. succeeded in broadening transitions of polymers using emulsion polymerization named "Power Feed Technique," where the procedure is to change the monomer feed composition during the polymerization.[21] They reported the process for continuously changing the composition of the monomer mix fed into a reactor producing, thereby, copolymers whose instantaneous compositions vary as the polymerization proceeds. As power feed polymers are emulsion ones, it is considered very easy to apply as adhesives. Furthermore, power feed polymers have the advantage of having broad transitions over a wide range of temperatures even though they are linear polymers.

In this study, we demonstrate the dynamic mechanical properties and their adhesive strengths of power feed polymers which consist of styrene and some acrylate monomers.

EXPERIMENTAL

Power Feed Polymerization

Figure 1 shows a simple arrangement for gradually changing the comonomer composition of the feed stream entering the reactor. In this arrangement, the monomer A

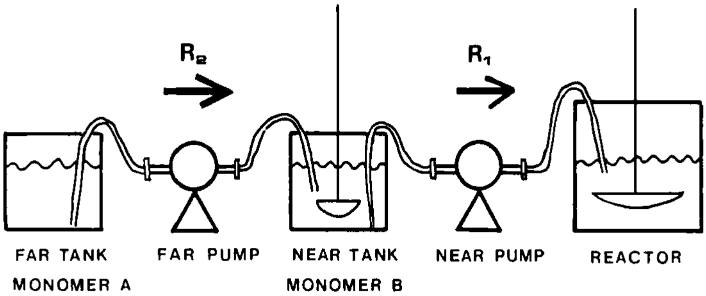

FIGURE 1 Monomer tank arrangement for continuously changing the monomer feed stream composition entering the reactor.

in the far tank is continuously added to the monomer B in the well-stirred near tank. The continuously changing comonomer mixture in the near tank is simultaneously fed into the reactor in the usual manner of monomer dropwise emulsion polymerization. If comonomer fed in the reactor is polymerized simultaneously, i.e. assuming there is no monomer left unreacted in the reactor, the composition of growing particle varies as the polymerization proceeds. Consequently, one emulsion particle is considered an alloy of composite polymers composed of all possible compositions of copolymers.

Synthesis of Polymers

Power feed copolymers were prepared by the conventional semi-batch technique in which the reactor initially contained only 550 mL of water and 1.5 g of Aerosol OT, an anionic surfactant. Monomers used were styrene (St) or methyl methacrylate (MMA) for the far tank and n-butyl acrylate (nBA) for the near tank. The initial monomer volume of each tank was 200 mL and the feed rate into the near tank R_2 and feed rate into the reactor R_1 could be changed variously. In the case of typical power feed copolymer, R_2 and R_1 were determined to be 1.0 and 2.0 mL/min, respectively. The initiator used was ammonium persulfate, 1 g of which was dissolved in 50 mL of water. Half of the solution was added just before the polymerization started, and the remaining half of the solution was divided into five portions and then added during the polymerization. The polymerization was carried out in the water bath of 85°C.

Further, random copolymer with comonomer previously mixed and seed copolymer by the two stage feed method was also synthesized in a similar manner as above. Random and seed copolymers can be said to be kinds of power feed copolymers, i.e. if $R_1 << R_2$, then the system should be a random copolymer, and if $R_1 >> R_2$, then the system should be a seed copolymer.

The polymers synthesized were cast onto a Teflon sheet and then dried for testing, which was named emulsion film. Solution type polymers were prepared by precipitating with methanol from acetone solution of emulsion film, then washing with water, drying in vacuo, and then reprecipitating. They were dissolved in a certain solvent and cast or molded into film, which we named solution film.

Mechanical Properties

All the film specimens were dried at 130°C for 8 h in vacuo. Dynamic mechanical data were measured with Rheovibron DDV-II (Toyo Baldwin Co.), at a frequency of 110 Hz and heating rate of 1°C/min over a temperature range between − 160 and 120°C. The tensile properties of films were determined by Tensilon tensile testing machine (Toyo Baldwin Co.) at 20°C and 65% RH, and the cross head speed was 10 mm/min.

Adhesive Strengths

Two types of testing method were applied for these polymers. One was the cross-lap tensile testing method as reported by Marra,[22-24] and the other was the tensile shear testing method. Adherends used were Birch (*Betula maximowicziana* Regel; Japanese Kaba). The sizes of specimens and bonding areas were as follows: 80 mm (length) × 25 mm (width) × 5 mm (thickness), 3.75 cm^2 for shear test; 65 × 25 × 25, 6.25 cm^2 for cross-lap test. The hot-melt method was employed as the adhesion procedure, as follows: cutting solution films of the same size of bonding areas; inserting the film between the adherends; bonding at the pressure of 10 kg/cm^2 after keeping them for an hour in a constant temperature chamber of 160°C.

The adhesive strengths were measured with a Tensilon tensile testing machine (Toyo Baldwin Co.) equipped with a temperature control chamber over the temperature range from −120°C to 120°C, and the cross head speed was 10 mm/min. Temperature control was performed by a combination of liquid nitrogen cooling and an electric heater. Five specimens were tested at each temperature.

RESULTS AND DISCUSSION

Dynamic Mechanical Spectroscopy

Figure 2 shows temperature dependencies of storage and loss moduli of emulsion films of the power feed and random copolymers for P(nBA/MMA) system. A sharp

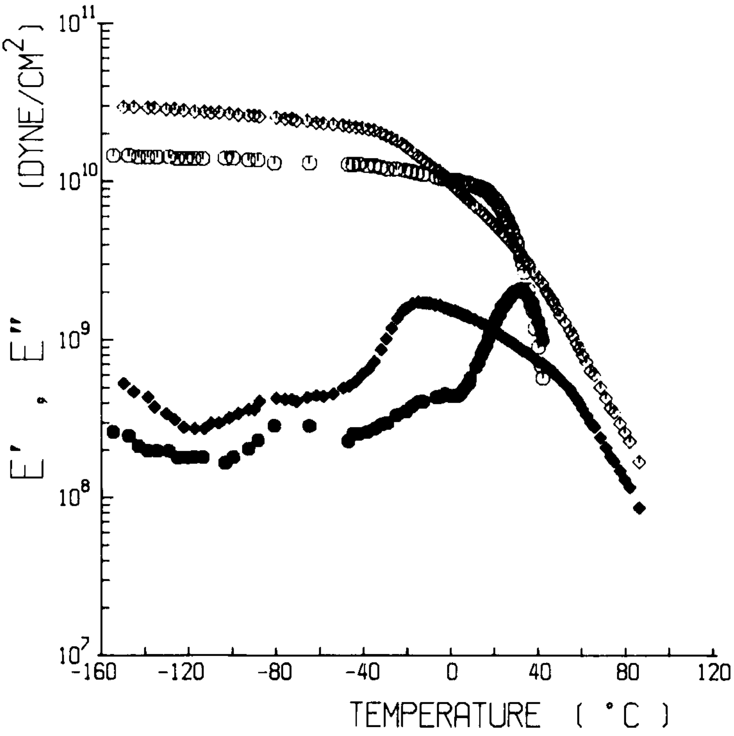

FIGURE 2 Dynamic mechanical data of power feed copolymer (◇ ◆) and random copolymer (○ ●) for P(MMA/nBA) system.

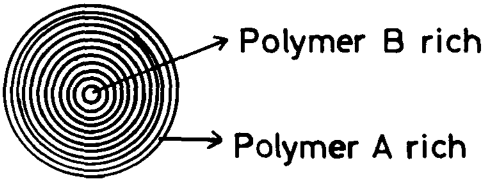

FIGURE 3 Schematic illustration for emulsion particle of power feed copolymer.

transition of E''_{max} for random copolymer was observed around 35°C, which was between the glass transition temperatures of homo-PMMA and homo-PnBA. On the other hand, power feed copolymers had a very broad E''_{max} transition over the temperature range of -40 and 40°C. This phenomenon can be explained as follows: emulsion polymerization proceeds as a growing particle, and monomer fed into the reactor polymerizes simultaneously; as the composition of comonomer fed into the reactor changes in every moment, a particle would grow like an onion, in which every skin consists of a different composition of copolymers. Schematically illustrated emulsion particle by power feed method is shown in Figure 3. In the beginning of polymerization, the inner side of the particle is rich in Polymer A, and the outer side of the particle rich in Polymer B at the end of the polymerization. Consequently, power feed copolymer is an alloy of copolymer whose variable composition is a combination of monomer A and monomer B.

As described above, power feed copolymer has a very broad glass transition because each particle consists of various combinations of copolymer. On the other hand, it is of interest how the solution film behaves in the dynamic mechanical properties. It is well known that emulsion polymer cannot form good films below the Minimum Film-Forming Temperature (MFT), which is generally a bit higher than the polymer's Tg. Consequently, the emulsion polymer having much higher Tg than room temperature is not applicable as adhesives or coatings. Figure 4 shows dynamic mechanical data of solution film of power feed copolymer for P(nBA/MMA) system. There was no large difference between the emulsion film and the solution one except that the glass transition in Figure 4 shifted a little to the higher temperature side than those in Figure 2, which can be explained by the fact that the emulsion film, compared with the solution one, might be plasticized by the residual monomer, surfactant, or initiator. However, power feed copolymer maintained its broad transition even if it was converted into solution film. This fact suggests the possibility of more extensive application of power feed copolymer.

Figure 5 shows the storage and loss moduli of typical copolymers with changing R_2 and constant R_1 of 2.0 mL/min for P(nBA/St). Here, power feed copolymer showed a broad transition, while random copolymer had a sharp E" peak and seed copolymer had two transition which were derived from Tgs of PnBA and PSt.

Ultimate Tensile Strengths of Solution Films

As described above, the solution film has the advantage of practical application compared with the emulsion one. The phase structure, however, is expected to be

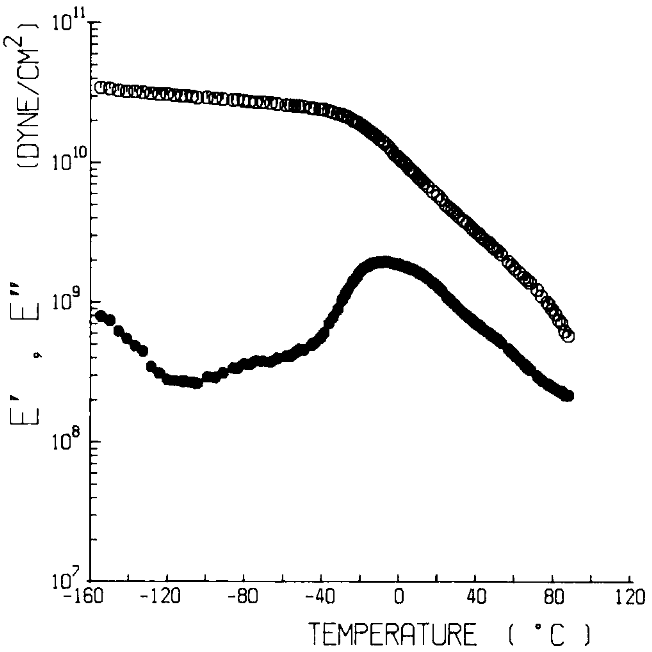

FIGURE 4 Dynamic mechanical data for power feed copolymer cast from dioxane solution for P(MMA/nBA) system.

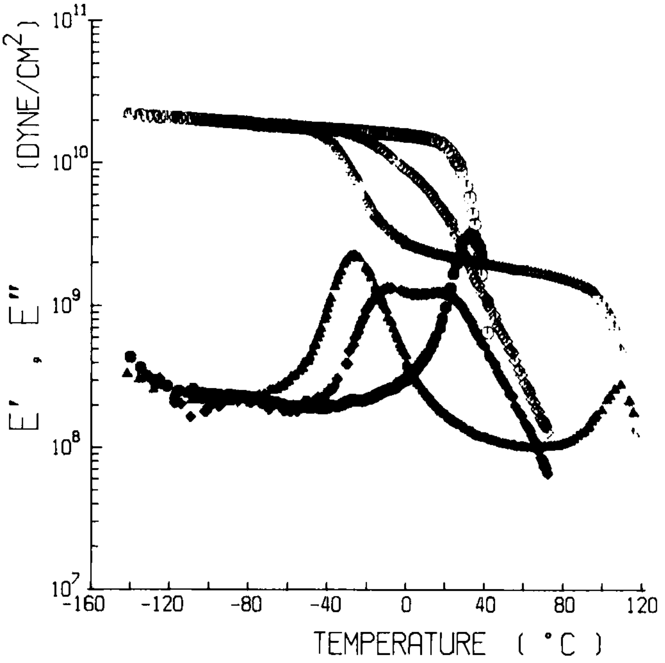

FIGURE 5 Dynamic mechanical data of power feed copolymer (◇ ◆), random copolymer (○ ●) and seed copolymer (△ ▲) for P(St/nBA) system.

TABLE I
Tensile strengths of films cast from various solvents for P(MMA/nBA) system

Polymer	Tensile strengths (kg/cm^2)
PFC[a] Cast from ethylacetate	58.3
PFC[a] Cast from acetone	74.8
PFC[a] Cast from dioxane	100.0
RC[b] Cast from ethylacetate	1112.5

[a]Power feed copolymer
[b]Random copolymer

TABLE II
Tensile strengths of films cast from dioxane for P(St/nBA) system

Polymer	Tensile strengths (kg/cm^2)
Power feed copolymer	119.4
Random copolymer	616.9

different depending on the solvent from which the film is cast.[25-27] Because the strengths of films are considered to be closely dependent on the phase structure of the system, in the case of application, the control of phase structure is essential.

Power feed copolymer can be said to be an alloy of copolymers of which composition is slightly different from one to another. Consequently, copolymers of which composition differ greatly from one another would result in phase separation. On the other hand, copolymers of which composition is similar would be compatible, one with another. In order to make films have high performance, it is indispensable to find an appropriate solvent which dissolve all copolymer uniformly. If a solvent which dissolves copolymer rich in polymer A more than copolymer rich in polymer B is used, the strengths of the film would be lower because of the occurrence of macrophase separation. On the other hand, using a solvent which dissolves all kinds of composition of copolymers well, the system would show microphase separation, and the film is expected to show higher strengths. Tables I and II show the tensile strengths of the films for P(nBA/MMA) and P(nBA/St) systems, respectively. Although the film cast from dioxane showed a higher value than that of other solvents, the value itself of power feed copolymer was not high absolutely. This is due to the phase separation of the system, which is also known by the fact that the solution film of power feed copolymer is less clear than that of random copolymer.

Adhesive Strengths

Figures 6 and 7 show the temperature dependencies of adhesive cross-lap tensile strengths of power feed copolymer and random copolymer for P(nBA/MMA) system, respectively. The temperatures of maximum adhesive strengths were 0°C and 30°C for power feed copolymer and random copolymer, respectively. The

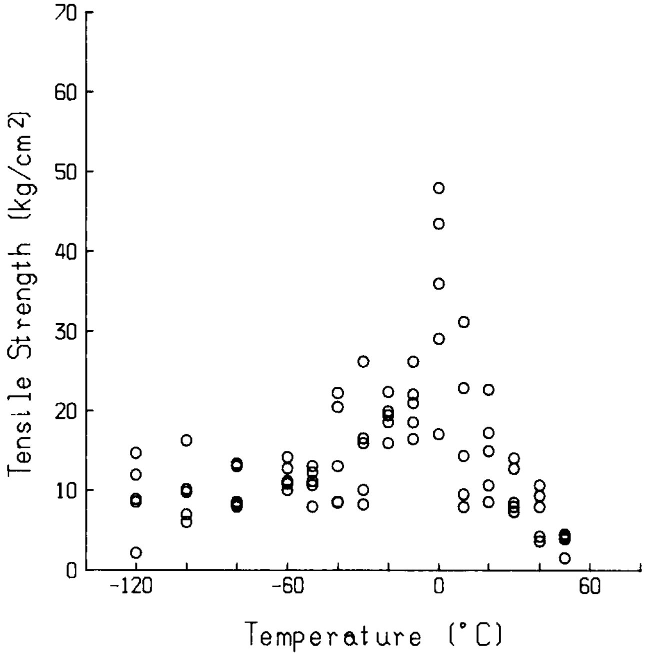

FIGURE 6 Temperature dependencies of adhesive cross-lap tensile strengths of power feed copolymer for P(MMA/nBA) system.

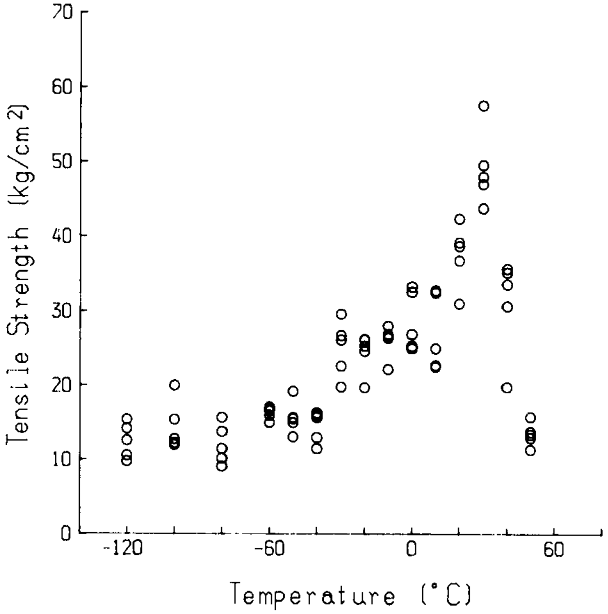

FIGURE 7 Temperature dependencies of adhesive cross-lap tensile strengths of random copolymer for P(MMA/nBA) system.

temperatures above correspond to the T(E$''_{max}$) of each copolymer. Figures 8 and 9 show the temperature dependencies of adhesive tensile shear strengths of power feed copolymer and random copolymer for P(nBA/MMA) system, respectively. The temperatures of maximum adhesive strengths were −30°C and 10°C for power feed copolymer and random copolymer, respectively. The facts above suggest that the mechanical properties, especially the relaxation behavior, govern the adhesive performance. Further, the fact that the temperature of maximum adhesive strengths for the shear test is lower than that for the cross-lap test, correspond to our past data.[3-12]

It, however, cannot be said that the power feed copolymer maintains its adhesive strengths over a wide range of temperatures compared with random copolymers. The result above is due to the low cohesive strengths of solution films. The tensile strengths of solution films for power feed copolymer are one tenth of those for random copolymer. As mentioned above, power feed copolymer is basically considered to be a multicomponent phase separation system, and the morphology of the system is dependent on the solvent from which the film is cast. Although dioxane is a good solvent compared to acetone or ethyl acetate, there might be a need to find a better solvent.

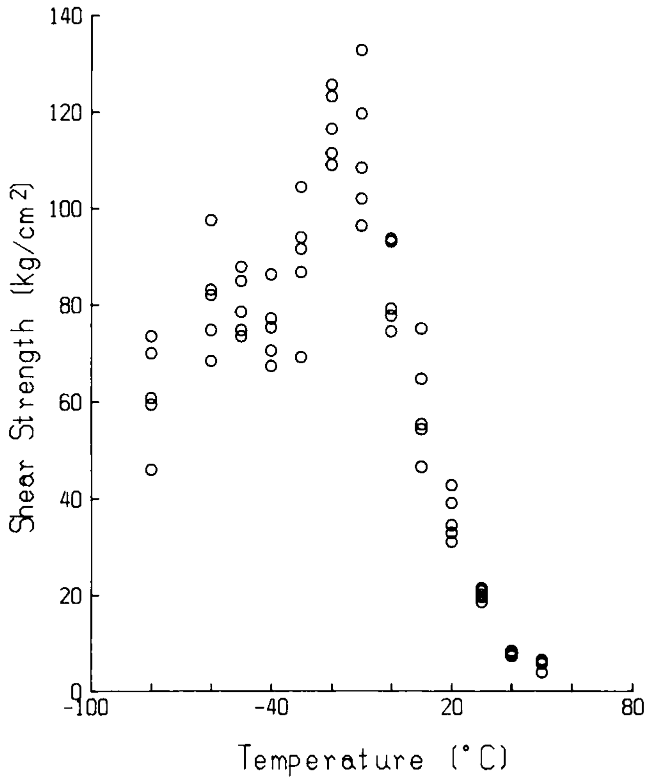

FIGURE 8 Temperature dependencies of adhesive tensile shear strengths of power feed copolymer for P(MMA/nBA) system.

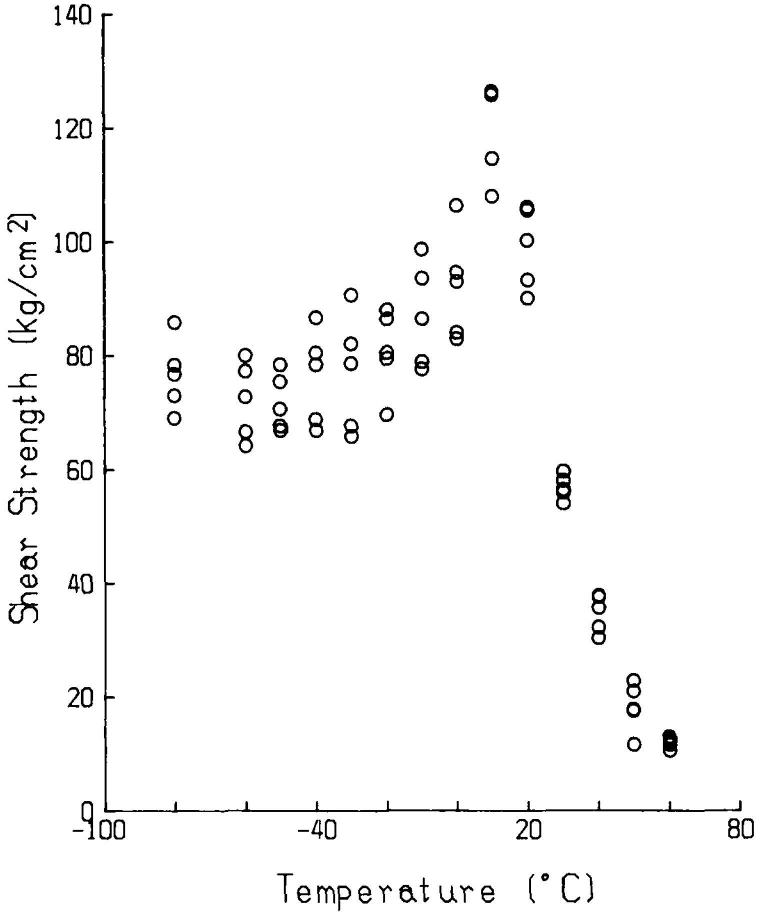

FIGURE 9 Temperature dependencies of adhesive tensile shear strengths of random copolymer for P(MMA/nBA) system.

Figure 10 shows the temperature dependencies of adhesive cross-lap tensile strengths of power feed copolymer and random copolymer for P(nBA/St) system. The adhesive strengths of power feed copolymer were almost the same value at temperatures between −50°C and 20°C, which means that power feed copolymer maintains its adhesive strength over a wide range of temperatures. On the other hand, the adhesive strengths of random copolymer showed a maximum around the Tg of 20°C, and they become lower rapidly above Tg and slowly below Tg.

In both systems above, the film strengths of power feed copolymer were one tenth to one fifth of those of random copolymer. The adhesive strengths of power feed copolymer cannot be said to be high over a wide temperature range in comparison with random copolymer due to the above fact. So if the morphology of the system can be controlled and the film strengths can be increased, the power feed copolymer would show high adhesive strengths over a wide temperature range.

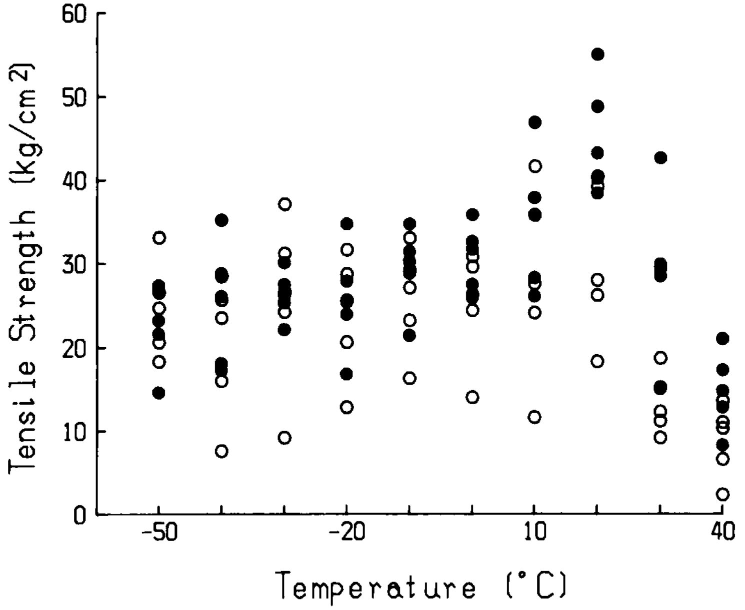

FIGURE 10 Temperature dependencies of adhesive cross-lap tensile strengths of power feed copolymer (○) and random copolymer (●) for P(St/nBA) system.

CONCLUSIONS

Power feed copolymer has a broad transition temperature compared with random copolymer, which is reasonable considering that the system is an alloy of copolymers of all possible compositions. There is less difference in the dynamic mechanical properties between the emulsion film and the solution one. This fact suggests that power feed copolymer has the possibility of more extensive application.

The tensile strengths of the solution film depend on the solvent from which the film is cast. Therefore, it is necessary to select an appropriate solvent which dissolves all copolymers compatibly for practical utilization.

It cannot be said that power feed copolymer maintains its adhesive strengths over a wide temperature range compared with random copolymer for P(nBA/MMA) system. This result is due to the smaller film strengths of power feed copolymer. Power feed copolymer keeps its adhesive strength to some extent, but the absolute value is not as high as that of random copolymer for P(nBA/St) system.

Power feed copolymer has the possibility of extensive application of not only adhesives but also coatings, noise damping materials, etc. The problem, however, is the low tensile strengths of the films. The introduction of grafting, using water soluble polymers as protective colloids instead of low molecular weight surfactant, would increase the film strengths because it is expected that the cohesion of each phase would increase.[28] We would like to argue this point in the next paper.

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