

Thermoplastic Elastomer by Radiation Grafting.

I. Evaluation of Processability of Natural Rubber Grafted Methyl Methacrylate

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SYNOPSIS

Processability of thermoplastic elastomer (TPE) prepared by radiation-induced grafting of methyl methacrylate (MMA) onto radiation vulcanized natural rubber latex (RVNRL) has been evaluated using a kneader and a hot roll mill at 150°C. It was found that mixing time and revolution rate (rpm) of the kneader have significantly affected the processability. The longer mixing time and the higher revolution rate result in better processability. In such processing conditions, however, the mechanical properties were found to be inferior because the molecular chain scissions occurred during the mixing. A considerable improvement of mechanical properties was obtained when the mixing was carried out without added process oils. Blends of the grafted vulcanized natural rubber latex (RVNRL-*g*-PMMA) and MMA grafted on unvulcanized natural rubber latex (NRL-*g*-PMMA) improved processability where the better processability could be achieved at a shorter mixing time and a lower revolution rate. In addition, a comparable value of mechanical properties was obtained.

INTRODUCTION

Thermoplastic elastomer (TPE) prepared by block copolymerization and blend polymer having a hard segment and a soft segment have been widely used in some industries. The TPE could be synthesized by graft copolymerization of monomer on rubber material.¹

In 1957, Bateman² and Merret³ reviewed graft copolymers of methyl methacrylate and natural rubber (NR-*g*-PMMA). It was then believed that the PMMA graft on NR constitutes a precursor event to the microphase separated of triblock copolymer TPE.⁴ So far, however, processability of grafted rubber TPE has not been sufficiently eval-

uated, even now that TPE is made by a radiation technique.

Previously, we have reported that graft copolymer prepared by radiation-induced grafting of methyl methacrylate (MMA) onto natural rubber (NR) latex possesses potential application as an adhesive material.⁵ In preliminary experiments, we have found that dried rubber obtained from the casting of radiation-grafted MMA on NR latex did not produce a TPE, because it cannot be processed in a roll mill and it is also very sticky.

Recently, we have developed radiation vulcanization of natural rubber latex by using an effective radiation sensitizer such as 2-ethylhexylacrylate and *n*-butylacrylate.^{6,7} Accordingly, the NR latex can be vulcanized at a very low radiation dose (about 15 kGy) and it demonstrates good mechanical properties.

In the present work, an attempt was made to prepare graft copolymer by grafting MMA onto radia-

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tion vulcanized natural rubber latex (RVNRL), and then the cast-dried rubber was evaluated as a TPE. This paper presents the results of an evaluation of the processability of radiation-grafted MMA onto RVNRL.

EXPERIMENTAL

Materials

High-ammonium-concentrated natural rubber latex (60% total solid content) of DUNLOP was purchased from Malaysia. The latex was diluted with 1% ammonium solution to 50% of total solid content and stabilized by adding 0.2 phr KOH before use. Methyl methacrylate (MMA) monomer and other analytical-grade chemicals were used directly as received.

Preparation of TPE by Radiation Grafting

Radiation vulcanized natural rubber latex (RVNRL) was first prepared by using 5 phr normal-butylacrylate (*n*-BA) as sensitizer. The radiation vulcanization of natural rubber latex was carried out according to our standard procedure, as in our previous report.⁷ Briefly, 5 phr of *n*-BA was added into stabilized natural rubber latex (NRL) and then it was irradiated by gamma rays from a Co-60 source at a total dose of 15 kGy. The irradiation was conducted at a constant dose rate of 10 kGy/h at room temperature. The dosimetry was performed by using an alanine dosimeter developed by Kojima et al.⁸

The radiation-induced grafting of MMA onto the RVNRL was then carried out as follows: First, the obtained RVNRL was diluted with 1% ammonium solution to 30% of total solid content (TSC). Different concentrations of MMA monomer (25, 50, and 100 phr) in the form of emulsion was mixed thoroughly with the RVNRL and kept standing for 24 h. It was then irradiated by gamma rays using a Co-60 source at room temperature and at a total dose of 5 kGy. The obtained graft copolymer latex of RVNRL-*g*-PMMA was cast in a plate glass and dried at room temperature. The obtained dried rubber film was immersed in 1% ammonium solution for 24 h to remove remaining protein in the rubber film and dried subsequently at room temperature and at 70°C for 1 h. The dried rubber film was then masticated 15 times with a two-roll mill (diameter 150 mm). The revolution rate of each roll mill was adjusted to 15 and 8 rpm for front and back sides,

respectively. The gap between the two roll mills was adjusted to zero, and the temperature was kept constant at room temperature by flowing tap water.

Radiation-induced grafting of MMA onto unvulcanized natural rubber latex was also prepared by using the same above-mentioned procedure except the natural rubber latex was not vulcanized. The obtained grafted MMA on NR latex (NRL-*g*-PMMA) was blended to RVNRL-*g*-PMMA at certain compositions of (1 : 3), (1 : 5), and (1 : 7). The blended latex was treated by the same above-mentioned procedure and evaluated for its processability as a TPE.

Determination of Degree of Grafting

A certain amount of RVNRL (30% TSC) was mixed with different concentrations of MMA monomer (25, 50, and 100 phrs). The mixed latex was irradiated by using gamma rays from a Co-60 source at room temperature and at a total dose of 5 kGy. The irradiated latex was cast in a plate glass, dried at room temperature, immersed in dilute ammonia solution (1%), dried again subsequently at room temperature and at 70°C, and, finally, dried under vacuum at room temperature and weighed. The dried rubber was cut into samples, weighed, and extracted in acetone for 48 h to remove homopolymer in the grafted sample. It was dried under vacuum at room temperature and weighed.

The degree of grafting was determined by the percentage increase of rubber weight using the following formula:

$$G (\%) = (W_g - W_i) \times 100 / W_i$$

where *G* is grafting percentage, *W_g* represents the weight of the rubber sample after extraction, and *W_i* represents the weight of the rubber content in the test sample, which can be calculated from initial rubber content in NR latex.

Evaluation of Process Ability

Forty grams of masticated rubber was mixed with 0.4 g (0.1 phr) butylated hydroxy toluene (BHT) and 0.2 g (0.05 phr) stearic acid in a kneader (Labo Plastomill, Toyoseiki-sho, Ltd.) at different mixing times and revolution rates (rpm). Oil (2 g) was also added if necessary. The mixing temperature was kept constant at 80°C. After mixing, it was pressed with roll-mill (diameter 15 cm) at 150°C to obtain a sheet with a thickness of 0.7 mm.

The processing ability was then evaluated visually by observing the smoothness and flatness of the sheet surface. A smooth and flat surface indicates better processing ability.

Mechanical Properties

Tensile strength and elongation at the break of the film sheet were measured by a Toyoseiki tension meter (Strograph-R1) according to the Japanese industrial standard (JIS-K6301) method. Before being measured, the sheet was pressed using a spacer of 0.5 mm under 100 kg/cm² pressure at 150°C, in order to obtain the film sheet. All those properties were automatically calculated by a general tensile test of the NEC-9801 VM computer program. The dimensions of all tensile strength test specimens were measured by an automatic micrometer (KS Automation Co. Ltd.). Shore-A hardness of the film sheet was measured by a plastic hardness tester (Asker DD2).

Swelling Ratio

A weighed sample of the film sheet was immersed in toluene and kept for 24 h at room temperature. The surface of the swelled sample was then immediately blotted with filter paper and weighed. The swelling ratio was calculated based on the initial weight of the sample using the following equation:

$$\text{Swelling ratio (\%)} = (W_s - W_i) \times 100 / W_i$$

where W_s and W_i represent the weights of swelled and initial samples, respectively.

RESULTS AND DISCUSSION

Grafting of MMA onto RVNRL

Figure 1 shows the relationship between degree of grafting and irradiation dose obtained from different initial concentrations of MMA monomer. As can be seen, the degree of the grafting curves increases as the irradiation dose increases and then levels off at a certain dose. At a same irradiation dose, the higher initial concentration of MMA results in a higher degree of grafting. Figure 1 also shows conversion curves obtained from the different initial monomer concentrations. The conversion curves represent the percentage increase of the rubber sample before the homopolymer is removed by the extraction. There-

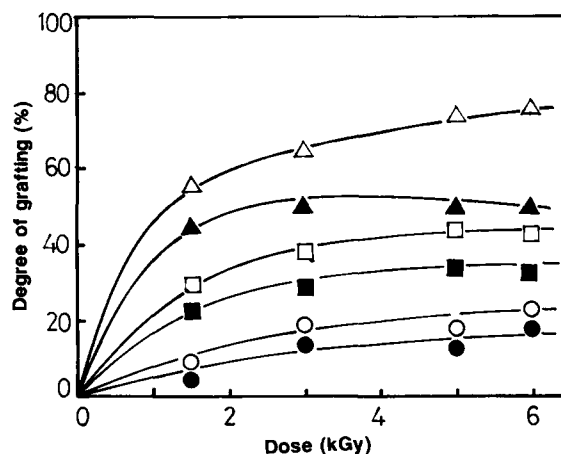


Figure 1 The relationship between degree of grafting and irradiation dose obtained from different initial concentrations of MMA monomer. Initial MMA concentration: (○) 25 phr; (□) 50 phr; (△) 100 phr. Filled symbols represent degree of grafting after removing homopolymer.

fore, homopolymer contained in the sample to be evaluated as a TPE can be estimated from the differences of the two curves. For instance, the samples that were irradiated at 5 kGy and were of the initial MMA concentration of 100, 50, and 25 phr had homopolymer content of about 23, 10, and 4%, respectively. This demonstrates that higher initial monomer concentration results in higher homopolymer content in the grafted sample. In case of initial monomer concentration of 50 phr, the grafted sample may contain 32% grafted PMMA and 10% homopolymer PMMA.

Effect of Mixing Time on Processability

The effect of mixing time on processability of RVNRL-*g*-PMMA is shown in Figure 2. It can be seen that the surface of the sheet obtained from a mixing condition of 20 rpm for 20 min was neither flat nor smooth. In addition, the edge of the sheet was found to be split and rough. However, it became smooth and flat when a longer mixing time was employed. For example, at a mixing time of 40 min, the split edge disappeared, and at a mixing time of 60 min, the surface of the sheet was very smooth and flat. This means that at a constant revolution rate (rpm) the longer mixing time results in better processability. Accordingly, processability of RVNRL-*g*-PMMA can be evaluated from the observation of the sheet after it is pressed by the hot roll mill.

Figure 3 shows a boundary curve area of processability as a function of revolution rate and mix-

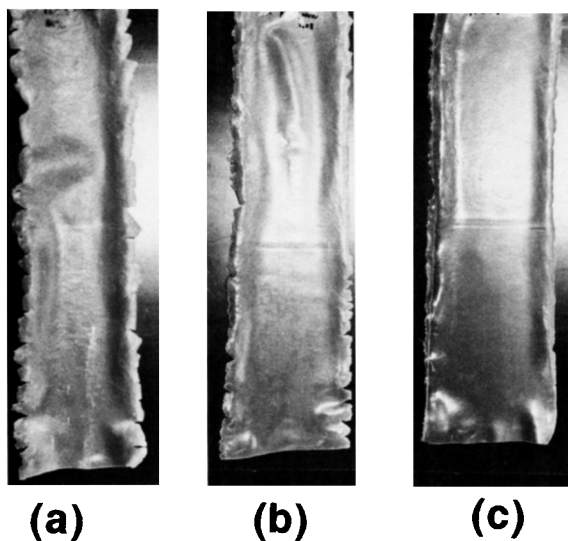


Figure 2 Photographs of rubber sheet obtained after masticated rubber was subjected into a kneader and hot roll mill. Effect of mixing time on the processability. Mixing time: (a) 20 min; (b) 40 min; (c) 60 min.

ing time. A good processability is represented by the area at the upper side of the boundary curve area. On the other hand, the below side of the boundary curve area represents poor processability. In the

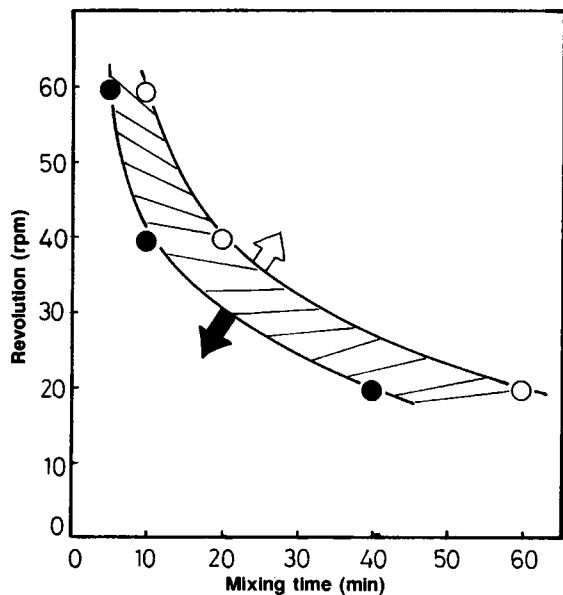


Figure 3 Processability boundary curve of RVNRL-*g*-PMMA. In the boundary area, the processability is recognized as fair; at the upperside and underside of the boundary area, there is good and poor processability, respectively.

boundary curve area itself, a fair processability is achieved. According to Figure 3, it can be said that a good processability can be achieved at a very short mixing time, such as 10 min, when a very high revolution rate, such as 60 rpm, is employed. Another way to get good processability is to apply a lower revolution rate, such as 20 rpm, and a longer mixing time, such as 60 min. It is clear that the processability is strongly influenced by revolution rate and mixing time.

Mechanical Properties

The effect of revolution rate on tensile strength of RVNRL-*g*-PMMA sheets is shown in Figure 4. At any revolution rate, the tensile strength was found to decrease as the mixing time increased. At a constant mixing time, however, the tensile strength of RVNRL-*g*-PMMA sheets was found to be higher at a lower revolution rate rather than at a higher revolution rate. Figure 4 clearly shows that a higher tensile strength is achieved only when a lower revolution rate, such as 20 rpm, is used. In this case, the shorter mixing time results in higher tensile strength. For example, the highest tensile strength is given by 20 min mixing time at a revolution rate of 20 rpm. As Figure 3 shows, however, the processability was poor when a shorter mixing time, such as 20 min, and lower revolution rate, such as 20 rpm, were used. Therefore, it will be an important task to improve processability when using a lower

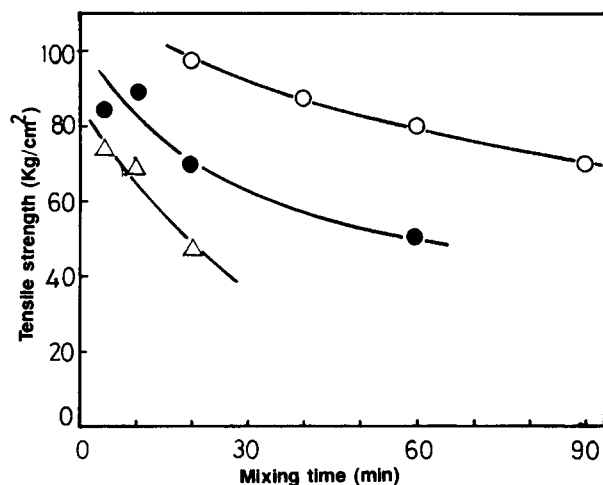


Figure 4 Effect of kneader's blade revolution rate on the tensile strength of RVNRL-*g*-PMMA: (○) 20 rpm; (●) 40 rpm; (△) 60 rpm. Initial MMA concentration: 50 phr; process oil: 10 phr; mixing temperature: 80°C.

blade revolution rate and a shorter mixing time to achieve a higher tensile strength of the RVNRL-*g*-PMMA sheet.

To confirm the reason why the low tensile strength is given by a high revolution rate, the swelling behavior the RVNRL-*g*-PMMA sheet processed at different revolution rates and mixing times was measured. The correlation between swelling ratio and mixing time used for the RVNRL-*g*-PMMA sheet is depicted in Figure 5. It can be seen that the swelling ratio increases as the mixing time increases for all revolution rates. The swelling ratio of the RVNRL-*g*-PMMA sheet processed at a higher revolution rates, such as 40 rpm, was found to be higher than that processed at a lower blade revolution rate, such as 20 rpm, at all mixing times. Since the swelling ratio indicates inversely of the degree of cross-linking, it can be said, then, that the RVNRL-*g*-PMMA sheet processed at a higher revolution rate possesses a lower degree of cross-linking. On the other hand, the RVNRL-*g*-PMMA sheet produced at a lower revolution rate has a higher degree of cross-linking. This demonstrates that the higher revolution rate may cause molecular chain scission and, thereafter, that the degree of cross-linking decreases. Consequently, it could be said that the tensile strength of the RVNRL-*g*-PMMA sheet was also reduced as the degree of cross-linking decreased.

The effect of revolution rate on the hardness of the RVNRL-*g*-PMMA sheet was also studied. The results are depicted in Figure 6. As can be seen in this figure, the revolution rate of 20 rpm gives the highest value of hardness. Since a lower revolution rate gives a higher degree of cross-linking, then it can be said that the degree of cross-linking plays an important role in producing the higher hardness

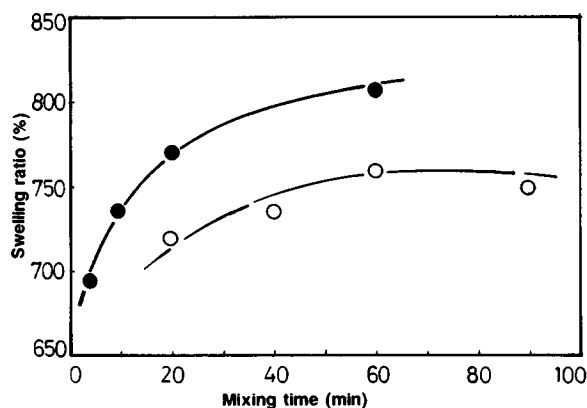


Figure 5 Effect of revolution rate of kneader on swelling ratio of RVNRL-*g*-PMMA: (○) 20 rpm; (●) 40 rpm.

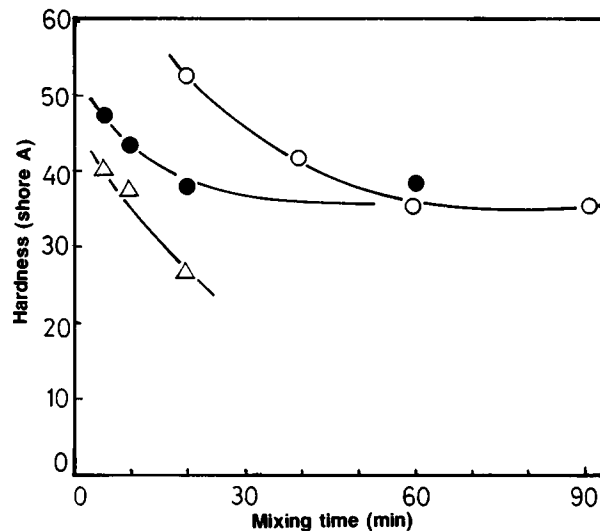


Figure 6 Effect of revolution rate on hardness of RVNRL-*g*-PMMA: (○) 20 rpm; (●) 40 rpm; (△) 60 rpm. MMA content: 50 phr; process oil: 10 phr; mixing temp: 80°C.

value. In other words, a higher degree of cross-linking will result in a higher value of hardness.

Oil is often used to improve the processability of TPE. The effect of oil on the tensile strength of the RVNRL-*g*-PMMA sheet was observed, and the results are shown in Figure 7. Both the tensile strength and hardness are shown in Figure 7 as a function of mixing time. It can be seen that the tensile strength of the RVNRL-*g*-PMMA sheet processed without oil is always higher than that processed with oil. Similarly, hardness of the RVNRL-*g*-PMMA sheet

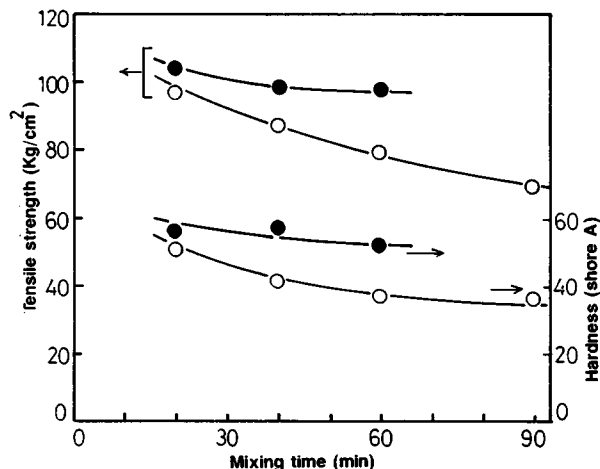


Figure 7 Effect of process oil on tensile strength and hardness of RVNRL-*g*-PMMA: (○) with oil; (●) without oil. MMA content: 50 phr; revolution rate: 20 rpm; mixing temp: 80°C.

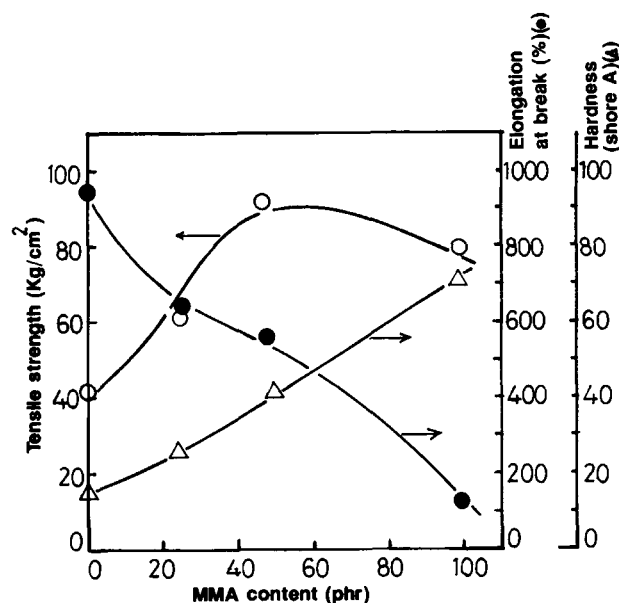


Figure 8 Effect of MMA content on tensile strength, elongation at break, and hardness of RVNRL-*g*-PMMA. Process oil: 10 phr; mixing temp: 80°C.

was also found to be higher when the processing was carried out without oil. The results show that oil is actually not necessary when high mechanical properties of TPE are desired.

Figure 8 shows the effect of MMA content on tensile strength, elongation at break, and hardness of the RVNRL-*g*-PMMA sheet. The tensile strength increases up to maximum and then decreases as the initial MMA concentration increases. An optimum concentration of MMA to give RVNRL-*g*-PMMA with the highest tensile strength was found to be around 50 phr.

On the other hand, elongation at break was found to be decreased when the concentration of MMA increased. The hardness of the RVNRL-*g*-PMMA sheet also increases as the MMA concentration increases. This suggests that the increased initial concentration of MMA may cause the increase of the hard segment given by PMMA grafted chain and PMMA homopolymer.

Improvement of Processability by Blending

As we mentioned above, a good processability could be achieved by using a lower revolution rate, but this takes a longer mixing time. Another alternative was that the RVNRL-*g*-PMMA sheet could be processed using a higher revolution rate, and in this case, only a shorter mixing time is needed. Both alternatives, however, give inferior mechan-

ical properties—particularly, much lower tensile strength was found in the latter process. Therefore, an attempt was made to obtain an optimum tensile strength of the RVNRL-*g*-PMMA sheet by using a shorter mixing time while keeping a good processability.

Figure 9 shows processability curves of TPE prepared by blending RVNRL-*g*-PMMA and NRL-*g*-PMMA. It can be seen that the mixing time shifts to the left or to the shorter time as the amount of NRL-*g*-PMMA added to RVNRL-*g*-PMMA increases. This means that the additional NRL-*g*-PMMA into the RVNRL-*g*-PMMA results in improved processability when a good processability can be achieved by using lower revolution rate and shorter mixing time. For example, formerly, a good processing ability was achieved only at a revolution rate of 20 rpm when 60 min of mixing time was employed. In the case of blending between RVNRL-*g*-PMMA and NRL-*g*-PMMA, a good processability can be achieved by using a lower revolution rate (20 rpm) and a shorter mixing time such as 30, 20, and 10 min, depending on the blending composition.

It was found that the more NRL-*g*-PMMA contained in the RVNRL-*g*-PMMA the shorter the mixing time needed to achieve a good processability. However, the shorter mixing time also will cause a

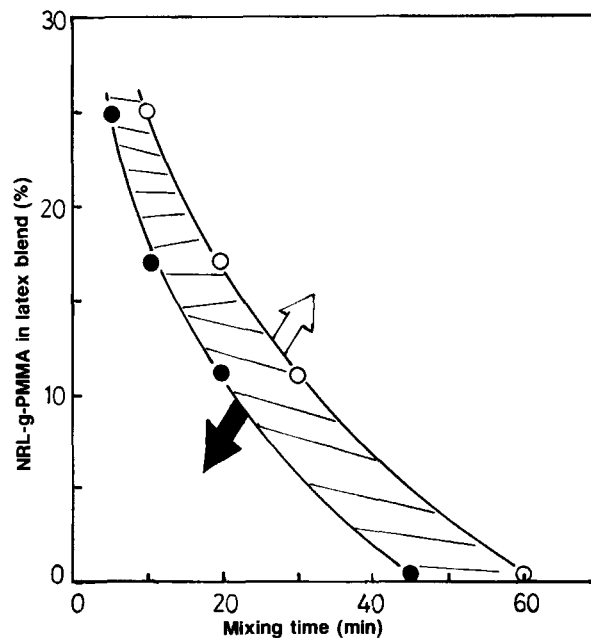


Figure 9 Processability curves of blends between RVNRL-*g*-PMMA and NRL-*g*-PMMA. In the boundary area, the processability is recognized as fair, whereas the upsides and undersides of the boundary area represent a good and poor processability, respectively.

reduction in tensile strength, as shown in Figure 10.

It can be seen from Figure 10 that the tensile strength curve of the blending composition of 3 weight parts of RVNRL-*g*-PMMA and 1 weight part of NRL-*g*-PMMA is the lowest one. On the contrary, the highest tensile strength is given by the RVNRL-*g*-PMMA sheet without blending. The tensile strength curve of blends of RVNRL-*g*-PMMA and NRL-*g*-PMMA with composition of 5 : 1 is fortunately close to the tensile strength of RVNRL-*g*-PMMA without blending. This demonstrates that the blending composition (5 : 1) is useful to reach a good processability within a relatively shorter mixing time. For example, the blending composition of 5 : 1 results in good processability at a revolution rate of 20 rpm within 20 min mixing time (see Fig. 10) while keeping a comparable value of the tensile strength (see Fig. 9).

In addition, the hardness of the blends of RVNRL-*g*-PMMA and NRL-*g*-PMMA was found to be almost the same as that of RVNRL-*g*-PMMA without blending, as can be seen in Figure 11. These results clearly show that the processability of RVNRL-*g*-PMMA could be improved significantly by blending with NRL-*g*-PMMA.

In general, thermoplastic elastomers are formed by block copolymerization or by the blending of hard

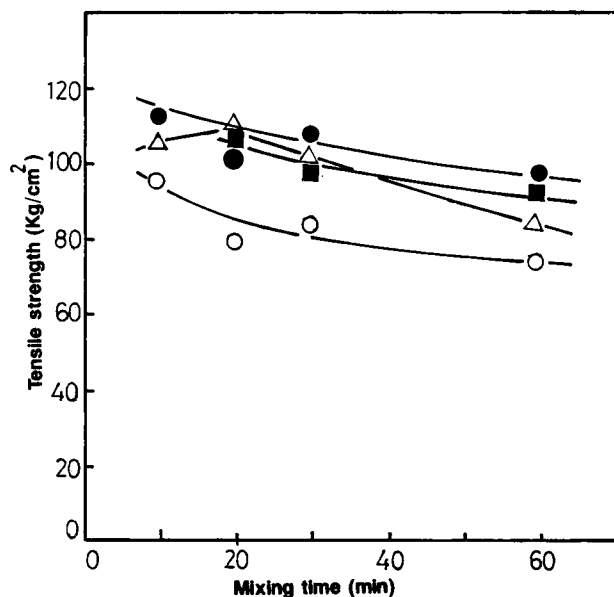


Figure 10 Tensile strength of blends between RVNRL-*g*-PMMA and NRL-*g*-PMMA as a function of mixing time. Blending composition between RVNRL-*g*-PMMA and NRL-*g*-PMMA: (○) 3 : 1; (□) 5 : 1; (△) 7 : 1; (●) without blend. Revolution rate: 20 rpm; mixing temp: 80°C.

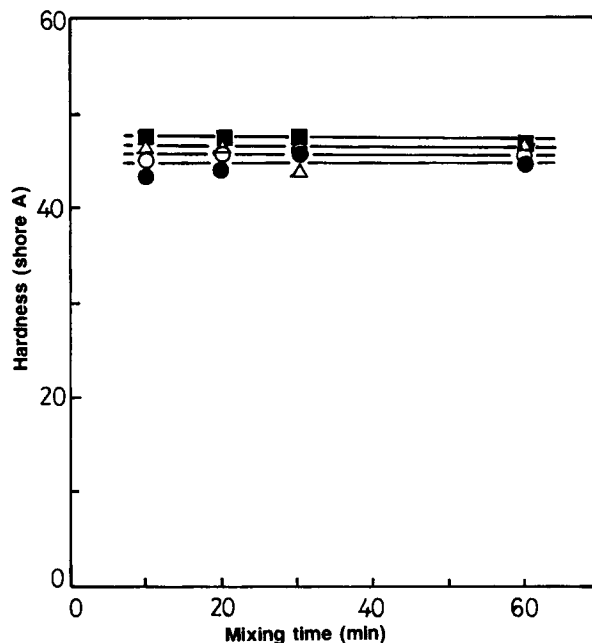


Figure 11 Hardness of blends between RVNRL-*g*-PMMA and NRL-*g*-PMMA as a function of mixing time. The mixing condition was the same as in Figure 10.

and soft segments of polymers. The hard domain structure is observed in TPE. In case of RVNRL-*g*-PMMA, the domain structure of PMMA is probably still smaller. Thus, vulcanization on latex before grafting is needed.

There are now some TPEs available in the market. For instance, TPE of olefin, styrene, polyester, polyamide, and polyurethane types.^{9,10} Accordingly, the physical properties of RVNRL-*g*-PMMA TPE prepared in this study are almost similar to that of olefin- and styrene-type TPE. The two types of TPEs have been used widely as materials for making car parts.

CONCLUSION

RVNRL-*g*-PMMA thermoplastic elastomer (TPE) has been prepared by radiation-induced grafting of methyl methacrylate (MMA) onto radiation vulcanized natural rubber latex (RVNRL). Processability of this TPE has been evaluated thoroughly by using a kneader and hot roll mill. The processability was found to be strongly affected by mixing time and revolution rate of the kneader.

It was also found that blending of RVNRL-*g*-PMMA and NRL-*g*-PMMA results in TPE with a good processability that can be achieved within a shorter mixing time such as 20 min and a lower rev-

olution rate such as 20 rpm while keeping considerable mechanical properties. The RVNRL-*g*-PMMA TPE has an almost similar tensile strength with commercially available olefin- and styrene-type thermoplastic elastomers.

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