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Effects of Epoxidation Content of ENR on Morphology and Mechanical Properties of Natural Rubber Blended PVC

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Summary: This research work has concerned a study on toughness of PVC/natural rubber (NR) blends compatibilized with epoxidized natural rubber (ENR). The aim of this work was to investigate the effect of degree of epoxidation on morphology and mechanical properties of the blends. Epoxidized natural rubber with a variety of epoxidation contents were prepared by reacting the NR latex with formic acid and hydrogen peroxide at various chemical contents. Chemical structure and epoxidation content of epoxidized natural rubber were evaluated by FTIR and ^{1}H-NMR techniques. After that, three grades of ENR with epoxidation contents of 15, 25 and 42 % (by mole) were further used for blending with PVC and NR in an internal mixer at 60 rpm and at 170 °C. From tensile and impact tests, it was found that tensile elongation and impact strength of the materials remarkably increased with degree of epoxidation. On the other hand, tensile strength and modulus of the materials rarely changed with the epoxidation content. An increase in toughness of the blends with epoxidation content was related to a better molecular interaction between PVC and ENR as suggested by torque-time curves of the materials.

Keywords: blends; compatibilization; poly(vinyl chloride) (PVC); rubber

Introduction

It has been known that poly(vinyl chloride) (PVC) is a notch sensitive plastic, having a low impact resistance. Various toughening agents have been compounded with PVC powders prior to a fabrication in order to improve toughness of the material. These toughening agents include methyl acrylate-butadiene-styrene (MBS), acrylonitrile-butadiene-styrene (ABS), and acrylate-methacrylate copolymer.[1] These toughening agents are phase separated from the PVC in a submicron level, capable of inducing crazing and shear yielding in the PVC matrix during a deformation process.[2]

Our interest in toughening of the PVC has concentrated on the use of natural rubber (NR) as an impact modifier. Because the NR is inexpensive and can be available in large quantities in south-east asia, it would be interesting and desirable if utilization and consumption of the NR could be extended. As mentioned earlier, in order to serve as a toughening agent, the rubber

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should be phase separated with PVC. This criterion could be achieved in our case owing to different polarity between PVC and the NR. However, compatibility between the two polymeric phases has yet to be improved. This is because of, again, the difference in polarity between the two polymers. In this regard, some kind of a compatibilizer should be used.

In this work, an epoxidized natural rubber (ENR) is considered to be a potential compatibilizer for this blending system. On one hand, chemical structure of the ENR is partially similar to that of a polyisoprene and/or the NR. On the other hand, epoxide groups in the ENR molecules could induce a high polarity nature of the rubber and thus promoting miscibility with PVC. In fact, extensive works on PVC-ENR blends [3-9] demonstrated that the two polymers are miscible, showing a hydrogen bonding peak in a FTIR spectrum as well as a single glass transition temperature in a DMTA thermogram. In relation to our work, it could be possible that the ENR would act as a compatibilizer, enhancing compatibility and adhesion between PVC and NR.

Unfortunately, little work concerning compatibilizing efficacy of ENR in PVC-NR system has been reported. Our previous study [10] demonstrated that the use of ENR could improve mechanical properties of PVC-NR blend. It was also found that the optimum blending composition with respect to toughness of the PVC/NR/ENR system is 80/10/10 weight ratio. However, an optimum degree of epoxidation of the ENR for this blend is still unknown and has to be clarified. Therefore, the aim of this work is to investigate the effects of epoxidation content of ENR on morphology and properties of the PVC/NR blends. Three types of ENR containing different epoxidation content were prepared and investigated.

Experimental

PVC resin (B0303 CLA, K-value = 58) was obtained from the Thai Plastic and Chemical Co. Ltd. Natural rubber (STR 5L) was supplied from the Thai Rubber Latex and Cooperation. Co., Ltd. High ammonia natural rubber latex (60 % d.r.c.) was supplied from the Rubber Research Institute of Thailand. Teric (16A16) used as a stabilizer for the latex was obtained from the East Asiatic (Thailand) Co., Ltd. Formic acid (98% w/w from BDH Ltd.) and hydrogen peroxide (from Merck Co., Ltd.) were analytical grade and were used as received.

The epoxidation was carried out in a 100 ml glass vessel at a temperature of 50 °C, using *in-situ* performic acid generated from formic acid and hydrogen peroxide.[11] Firstly, the 60 % dry rubber content (d.r.c.) latex was diluted to 30 % d.r.c., using distilled water. After that, 3 phr of Teric 16A16 was added to the diluted latex and then the mixture was stirred vigorously for 24 hrs in order to remove ammonia. Subsequently, a required amount of formic acid was added and the mixture was stirred for 10 min. Finally, a required amount of hydrogen peroxide was slowly added and the reaction was allowed to proceed for further 24 hrs. In this work, the ENR with a variety of epoxidation contents, specifically, 25, 35, and 50 % mol, were expected. This would be achieved by varying the amount of formic acid and hydrogen peroxide. After performing the reaction for a given time, the reacted products were separated from the reaction mixture by coagulating in methanol and then washed with distilled water before drying in a vacuum oven at 40 °C for 48 hrs.

Chemical structure of an epoxidized natural rubber (ENR) was confirmed by using Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) techniques. Sample preparation for the FTIR experiment was conducted by casting a thin film of the material onto a ZnSe window cell. The experiment carried out by using a Bio-Rad (FTS 175) spectrophotometer. NMR experiment was carried out by using a Bruker (ADVANCE 300) spectrometer and the sample was prepared by dissolving about 15 mg of the ENR in 1 ml of $CDCl_3$. In order to determine an epoxidation content of an ENR, two characteristic ^{1}H-NMR peaks were considered in relation with the following equation;

$$\text{Epoxidation content (\% by mole)} = [A / (A + B)] \times 100 \qquad (1)$$

where

A = Integrated area under the ^{1}H-NMR peak at about 2.70 ppm, representing the oxirane proton

B = Integrated area under the ^{1}H-NMR peak at about 5.14 ppm, representing an olefinic proton

PVC/NR/ENR blends with a weight composition of 80/10/10 were prepared by using an internal mixer (Haake Polylab Rheomex CTW 100, equipped with roller blade rotors). Blending process was carried out at a mixing temperature of 170 °C and at a rotor rotating speed of 60 rpm. In a typical blending process, PVC resin was firstly added to the mixer for 4 min in order to soften and melt the resin and then NR and ENR were concurrently added into the mixing chamber and the blending process was allowed to be continued for further 10 min. It is worth mentioning that no sign of a degradation of the PVC (such as a de-hydrochlorination) has been observed during the blending process. After blending, the material obtained from an internal mixer was crushed into small pieces by using a grinding machine. The grinded blend was then pass through a hot two roll mill operated at 190 °C and then fabricated in a compression mould. The molding process was carried out by using a LabTech

Engineering machine (L10-S-20) at 195 °C and at a clamping force of 17 ton. Mechanical properties of various blends were determined by tensile test and impact test. In a typical tensile test, dumbbell shaped specimens were prepared by stamping a sheet of polymer blend in accordance with an ASTM D638 (Type I). The test was carried out by using a Shimadzu AGS-500D at a crosshead speed of 50 mm/min, at a temperature of 25 °C. Specimens for the impact test were prepared in accordance with ASTM D256 to generate notched rectangular bars (63 mm ×12 mm × 3 mm) with 2.5 mm notch depth, 0.25 mm notch radius and at 45° notch angle. The impact test was carried out by using a Yasuda machine connected with a 4 J pendulum size.

Morphology of various blends was examined by using a scanning electron microscope (JEOL-JSM-5800) equipped with a backscattering electron detector. Specimen for the SEM experiment was prepared by cryo-microtoming the material under liquid nitrogen atmosphere. After that, the specimen was stained with OsO_4 vapor for 12 h before coating with gold using a sputtering unit. The SEM experiment was conducted by using an accelerating voltage of 15 kV.

Results and Discussion

Figure 1 shows an FTIR spectrum of the NR latex. Some characteristic absorption peaks, corresponding to functional groups in the natural rubber molecules can be noted, including the peaks at 1664 cm^{-1} (>C=CH-, stretching) and 836 cm^{-1} (=CH-, bending). This spectrum is significantly different from that of the product obtained from an epoxidation (Figure 2). From the Figure 2, it can be seen that new absorption peaks at about 874 cm^{-1} and 1250 cm^{-1} emerged. These are attributed to the presence of an epoxide ring or an oxirane ring in the ENR molecule. In addition, Figure 2 also shows a broad peak at about 3200-3500 cm^{-1}. This peak could only be observed when the epoxidation was carried out by using high amount of formic acid and hydrogen peroxide. This peak might be related to the presence of a hydroxyl group, which was obtained from a ring opening of the epoxy groups.

Results from ^{1}H-NMR spectrum of the product (Figure 3) further confirm the presence of epoxide ring in the product molecule. Peaks at about 2.7 ppm and 1.3 ppm could be observed and these represent the proton attached to the epoxide ring and the proton from a methyl group attached to the epoxide ring, respectively. Additionally, peaks at 3.4 and 3.9 ppm can also be observed and those could be attributed to some functional groups such as hydroxyl and hydrofuran, which were generated from a ring opening of the epoxy groups. [12-14] However, for the reaction carried out by using a relatively low formic acid and hydrogen peroxide content, those peaks were not detected.

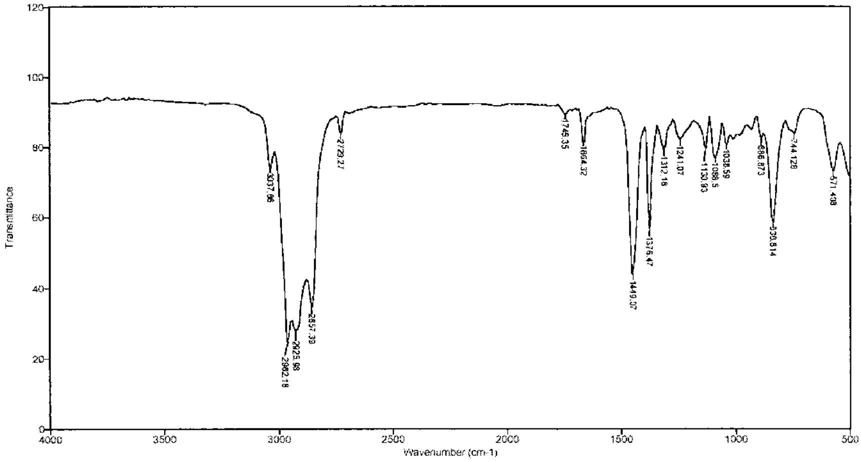

Fig. 1. FTIR spectrum of natural rubber.

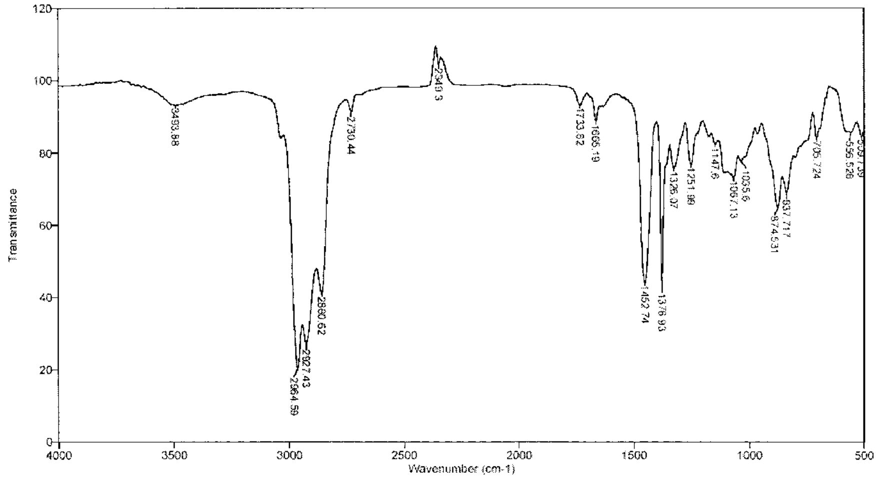

Fig. 2. FTIR spectrum of epoxidized natural rubber.

Table 1 shows different reaction parameters used and degree of epoxidation of an ENR determined by ^{1}H-NMR. Three types of ENR were successfully prepared i.e. ENR with epoxidation contents of 15, 25 and 42 %mol, that was controlled by varying the amount of formic acid and hydrogen peroxide, at a fixed temperature, time and the molar ratio of hydrogen peroxide to formic acid. It can be clearly seen that increasing the amount of formic acid and hydrogen peroxide resulted in increasing the degree of epoxidation. The results are in accordance with the work of Tanessriyanon et al.[15]

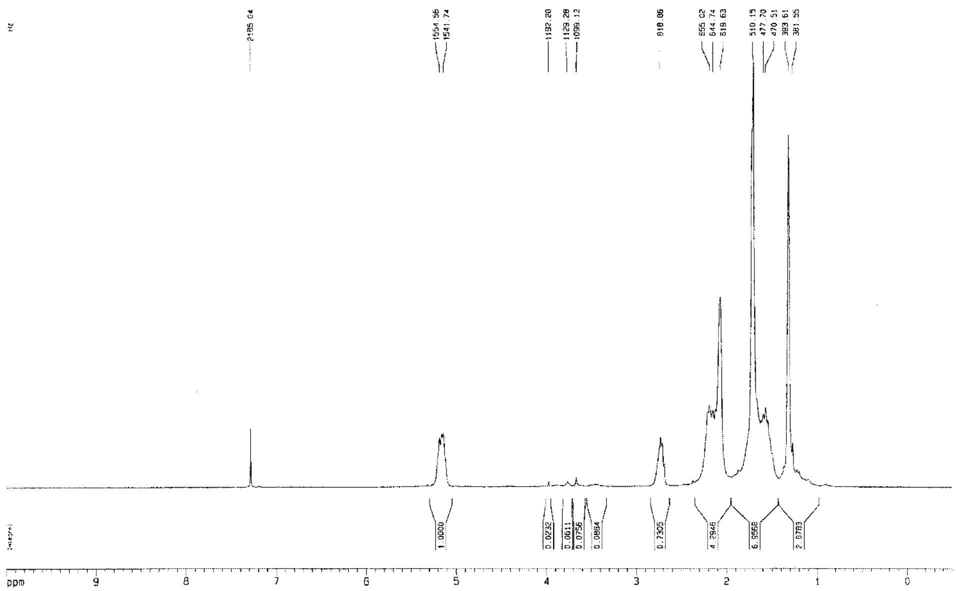

Fig. 3. ^{1}H-NMR spectrum of epoxidized natural rubber.

Table 1. Epoxidation content of various ENR as a function of reaction parameters.

Reaction No.	Formic acid Content (ml)	Hydrogen peroxide content (ml)	Epoxidation content (%)
1	12.6	111.1	15
2	17.6	155.6	25
3	20.9	221.9	42

Figure 4 shows overlaid torque-time profiles of various blends obtained from an internal mixer. The first peak at about 4 min. could be ascribed to a fusion peak of PVC resin whereas the latter peak could be attributed to a loading peak of both rubbers. After this peak, torque value gradually decreased with time and finally reaching equilibrium. It is interesting noting that an equilibrium torque of these materials changed with epoxidation content of the ENR in the blends. Generally speaking, the higher the epoxidation content, the higher the equilibrium torque value. In our opinion, this effect could be attributed to two main factors. Firstly, it might be possible that molecular interaction or miscibility between PVC and ENR increased, due to the fact that polarity of the ENR increased with the epoxidation content. In addition, it was also possible that viscosity of the ENR increased with the epoxidation content, leading to the higher mixing torque.

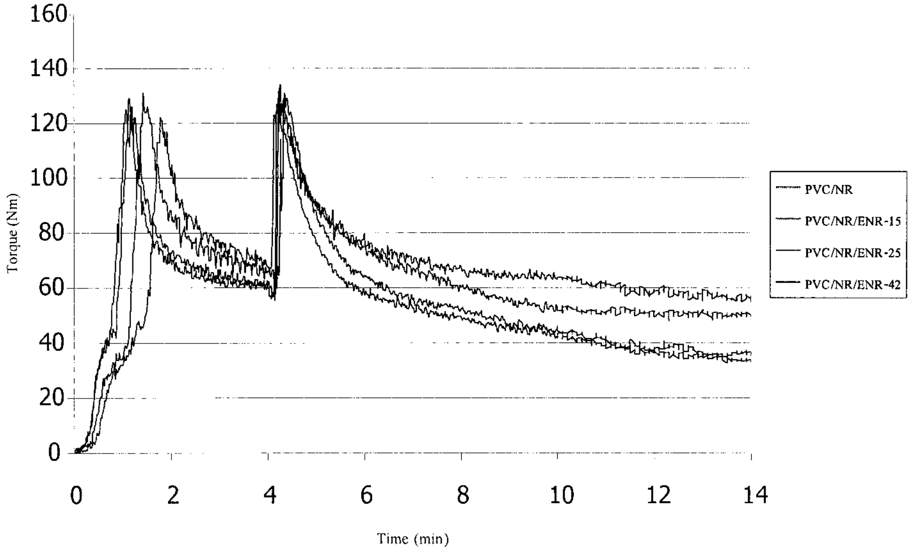

Fig. 4. Torque-time curves of various blends.

Figures 5-8 show SEM images of various blends. Dispersion of bright particles, representing the stained rubber phases, in PVC matrix (the darker background) could be observed. It is worth noting that some of the dispersed rubber phase has been etched, probably due to the cryo-microtoming process. Nevertheless, comparison between Figure 5 and 6 reveals that particle size of the NR phase significantly decreased after the ENR with 15 % epoxidation content was added. This result suggests that the ENR might acts as an emulsifier, reducing phase size of the NR phase. Furthermore, Figures 7-8 show that by blending with ENR containing higher degree of epoxidation (25 and 42 % mole), number of bright particles representing the rubber phases decreased. This result could be attributed to two main factors. Firstly, the higher the epoxidation content, the less the number of unsaturated bonds available for staining with OsO_4. In addition, it could be possible that the higher the degree of epoxidation, the greater the miscibility between ENR and PVC.

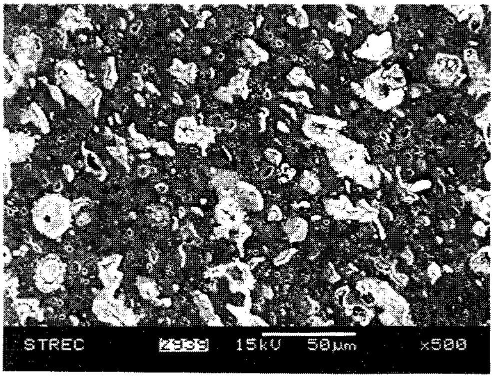

Fig. 5. SEM micrograph of PVC/NR blend.

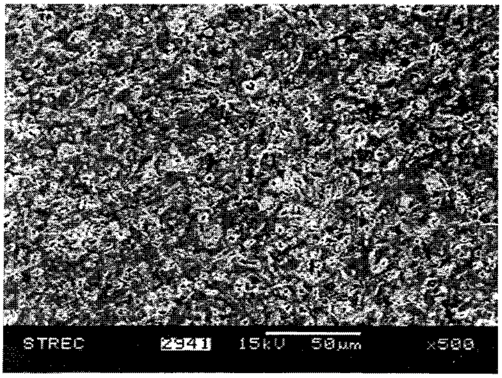

Fig. 6. SEM micrograph of PVC/NR/ENR-15 blend.

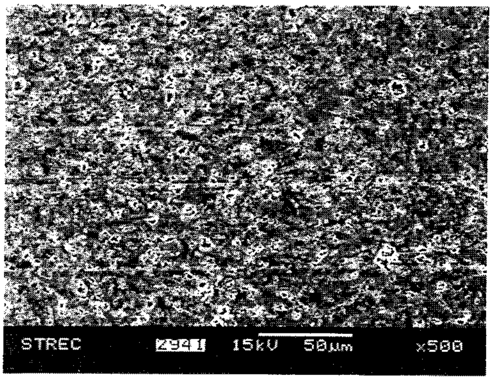

Fig. 7. SEM micrograph of PVC/NR/ENR-25 blend.

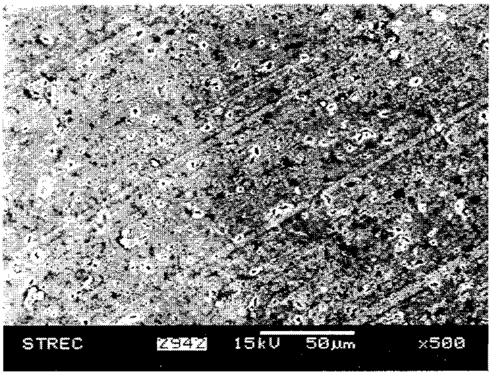

Fig. 8. SEM micrograph of PVC/NR/ENR-42 blend.

Changes in tensile properties of various blends as a function of epoxidation content could be seen from Figures 9-12. Ultimate tensile strength and modulus of these blends rarely changed with the epoxidation content. This might be related to the fact that weight composition between PVC and rubber phase is still 80/20 %, regardless of the epoxidation content. However, Figure 11 shows that tensile elongation of the blends significantly increased with epoxidation content. The above results imply that tensile toughness of the materials might be increased. In addition, result from the impact test (Figure 12) further confirms that impact strength of the blends increased with the epoxidation content. In theory,[15] impact resistance of a rubber toughened plastic could be related to morphology of the material. Particularly, particle size and ligament thickness are considered to be important factors, determining toughness of the material. For example, work by Liu *et al.* [16-17] on PVC/nitrile rubber blends shows that a critical ligament thickness of the blend corresponding to the transition from tough to brittle zones was 0.036 µm.

In relation to our work, however, addition of the ENR containing 15 % epoxidation content did not improve toughness of the blend even through the particle size has been remarkably decreased. In this regard, it seems that the effect of epoxidation content on impact properties of the PVC/NR blends might be attributed to some other factors, including miscibility between PVC and ENR phases. This statement has been supported by results from literature works [6] showed that by blending ENR with PVC, toughness of the materials could be improved even through the two phases are miscible. According to work by Ishiaku *et al* [6], FTIR spectrum of the PVC/ENR blend revealed an absorption peak representing a hydrogen bonding. In addition, some other relevance work [7] found a single T_g from a DMTA thermogram of the blends. In relation to toughness of the blends, it was believed that some of the ENR rubber phases were retained in a form of finely dispersed particles and cross-linked particles. In other words, the ENR rubber phases did not disappeared completely as is the case of a plasticizer. Therefore, the presence of these finely dispersed particles could contribute to an improved toughness of the blends. In relation to our work herein, it could be possible that an increase in miscibility between ENR and PVC lead to an increase in toughness of the blends.

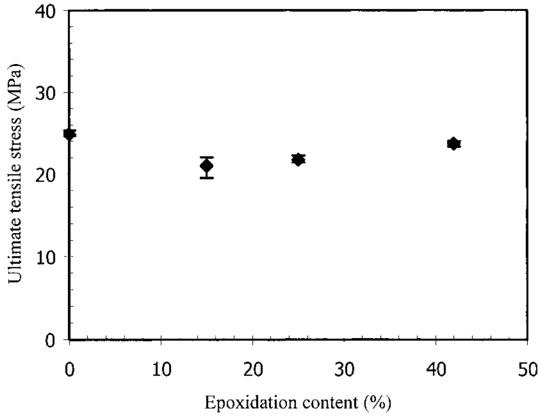

Fig. 9. Tensile strength of the PVC/NR/ENR blends as a function of epoxidation content.

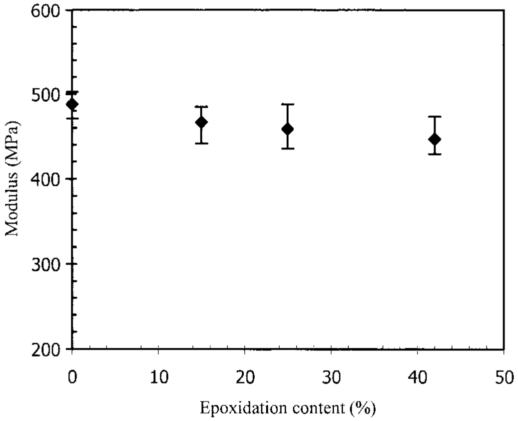

Fig. 10. Modulus of the PVC/NR/ENR blends as a function of epoxidation content.

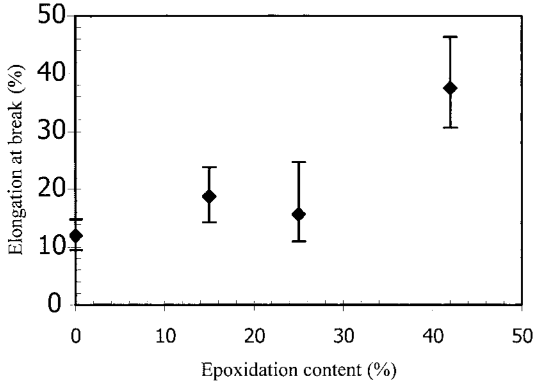

Fig. 11. Elongation of the PVC/NR/ENR blends as a function of epoxidation content.

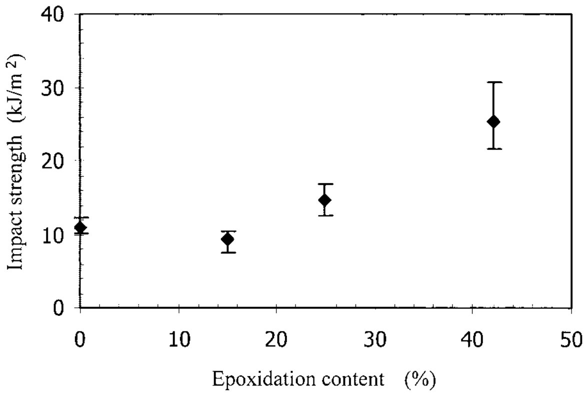

Fig. 12. Impact strength of the PVC/NR/ENR blends as a function of epoxidation content.

Conclusion

It has been shown that impact properties of PVC blended with natural rubber (NR) could be improved by adding an epoxidized natural rubber. It was also found that the greater the degree of epoxidation, the higher the toughness. The effect was related to an increase in mixing torque of these blends with the epoxidation content.

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