CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 MECHANICAL PROPERTIES OF RUBBER-MODIFIED EPOXY RESIN

4.1.1 Compression Test

The compression test was used to calculate the modulus of elasticity, the maximum stress and the fracture strain of the epoxy and the rubber-modified ones. In this experimental work, the results of the compression test are achieved as the load-deformation curve as shown in Figure 4.1.

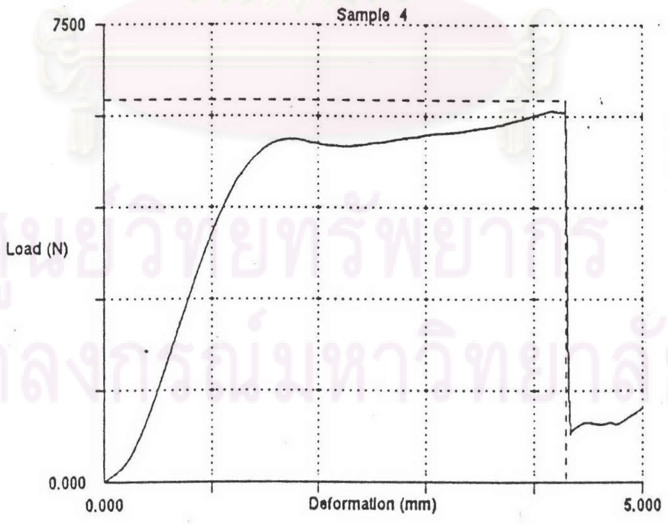

Figure 4.1: The load-deformation curve of 2.5% CTBN with 30% AN-filled epoxy system from the compression test.

This compression behaviour of pure epoxy was compare with those of the epoxy filled with various amount of rubber under compressed condition. Pure epoxy was found to be more brittle than the rubber-filled epoxy. This was clearly shown by the easy initiation and propagation of crack when pure epoxy was compressed. When various amount of rubber was filled in the epoxy resin, the rubber-modified epoxy samples tend to show buckling behaviour beyond the compressive yield point. The buckling is believed to have occured due to the shear yielding in the rubber-modified samples. For untreated NBR and treated NBR-filled epoxy systems, adverse effect was observed, i.e. crack took place easily when too much rubber particle was applied. The level found in the present study is beyond 25% by volume of rubber. However, for the epoxy modified with CTBN rubber at 15 and 30 % acrylonitrile content, crack was not observed. Instead, the specimens tend to deform and buckle more easily under compression.

The effect of the various types of rubber and the rubber content on the compressive modulus of the rubber-filled epoxy systems is shown in the plot of Figure 4.2.

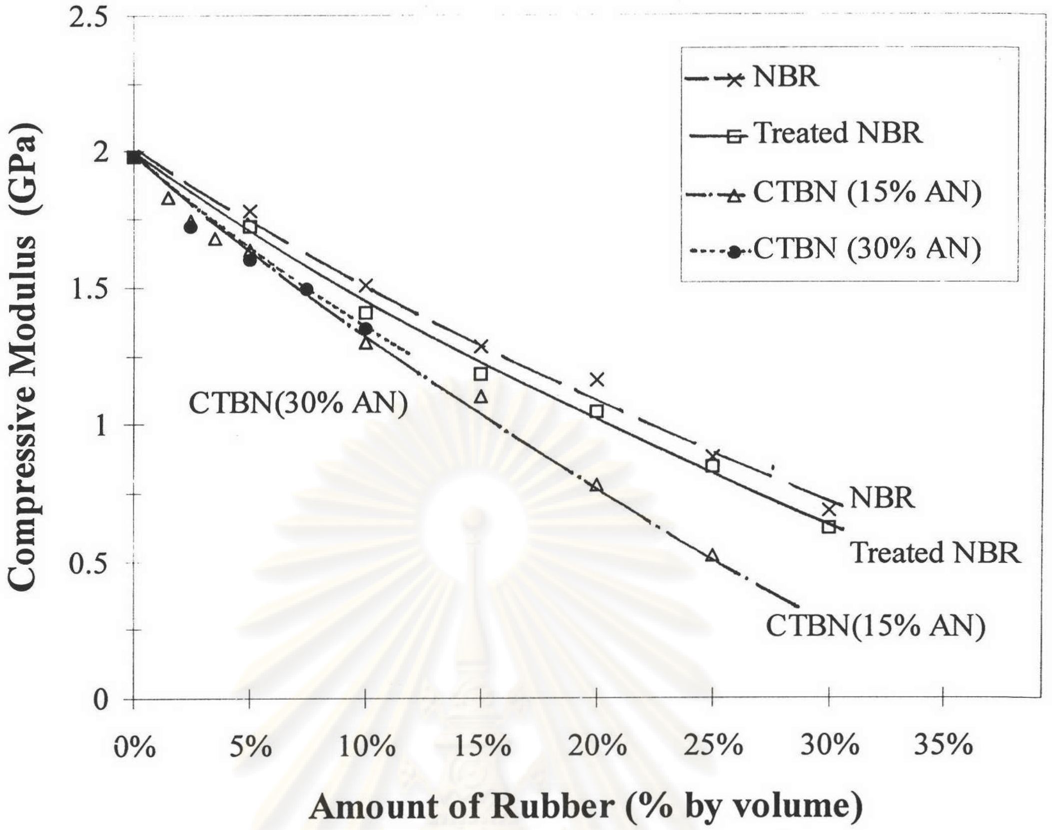

Figure 4.2: The compressive modulus for pure epoxy and the various types of rubber-filled epoxy systems.

For various types of rubber-filled epoxy systems in Figure 4.2, it is apparent that the compressive modulus for all types of rubber-filled epoxy decreases with the rubber content. This is induced by the softness of the rubber phase filled in the epoxy resin. The rubber can absorb the applied load and distribute it among the rubber phase. As a result, more deformation and lower compressive modulus than that of the pure epoxy was observed.

The effect of the titanate coupling agent is clearly depicted in Figure 4.2. The epoxy modified with titanate treated-NBR possesses lower compressive modulus than that of the pure epoxy with untreated NBR. The titanate coupling agent improves the surface of the NBR rubber by enhancing a better bonding with the epoxy resin. However, the compressive modulus of the treated NBR is not much lower than that of the untreated NBR. For comparison, pure epoxy resin has a compressive modulus of 2 GPa while those with 20 and 30 % by volume of untreated NBR-filled can have their modulus reduced by 41 and 65 % respectively. The reduction is more pronounced with titanate treated NBR where a reduction of 47 and 69 % of the compressive modulus was observed. Hence, it is evident that titanate coupling agent is an effective chemical for decreasing the compressive modulus of the NBR-filled epoxy.

For epoxy filled with CTBN with the acrylonitrile content (AN) of 15% and 30%, the compressive moduli are decreased and lie close to each other. This is shown in Figure 4.2. For example, for pure epoxy with 5 and 10 vol% of rubber, the compressive modulus of the CTBN with 15% AN can reduce the compressive modulus by 17 and 34 %. For the CTBN with 30% AN, the compressive modulus is reduced by 19 and 32 % respectively.

The sequence of the ability of rubber to decrease the compressive modulus of epoxy is NBR < treated NBR < CTBN (30% AN) < CTBN (15% AN) respectively. But it is not yet clear which type of CTBN rubber would yield easily at a lower compressive modulus.

The effect of the various types of rubber and the rubber content on the yield stress of the rubber-filled epoxy systems is shown in Figure 4.3.

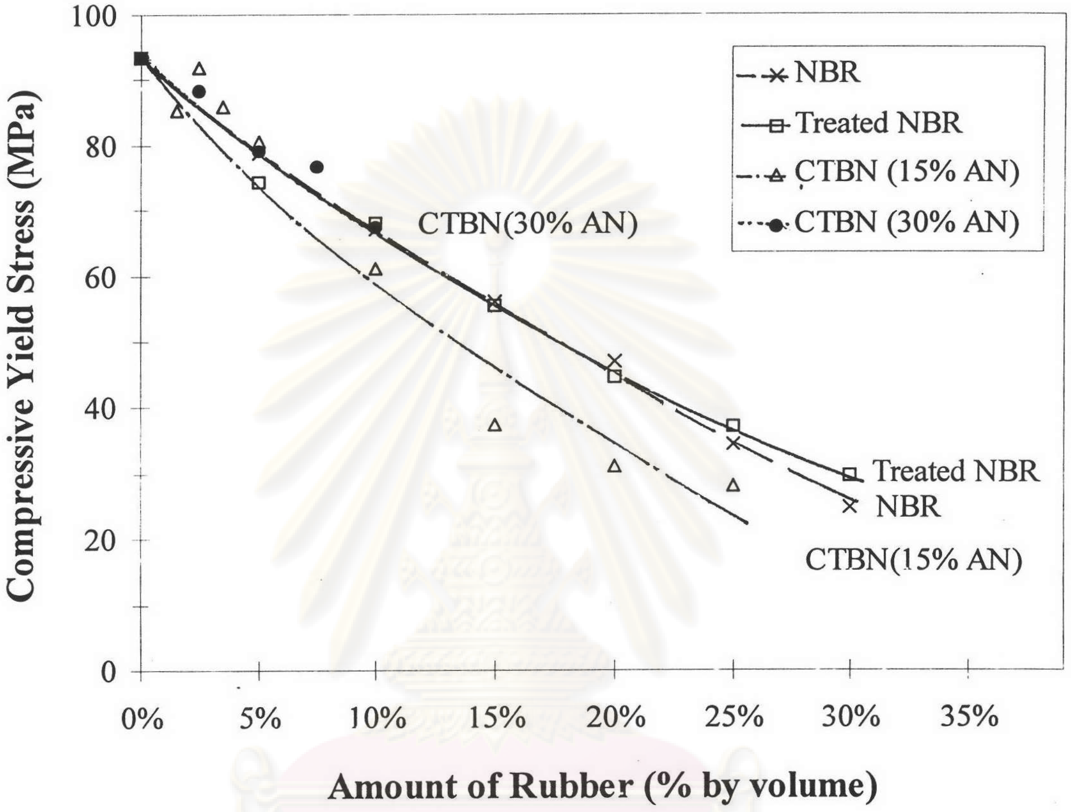

Figure 4.3: The compressive yield stress for various types of rubber-filled epoxy system.

For the various types of rubber filled epoxy systems as shown in Figure 4.3, it is apparent that the compressive yield stress for all types of rubber-filled epoxy is decreased when the rubber content is increased. This result goes in the same direction as those of the compressive modulus. The decrease in the compressive yield stress is because with the presence of rubber, it is now easier for strain softening to take place. When polymer is compressed, only the initial portion of the stress-strain plot follows the Hookean behavior in which the stress-strain curve is linear. After that, the stress still increases with an increase in the strain but the curve is no longer linear. The onset at which the stress tends to decrease when the strain is increased is called the *Yield point*. Beyond this point, epoxy tends to undergo strain softening. The lower the yield point, the easier will the permanant deformation occur. In this experimental work, the decrease in the compressive yield stress shows that the epoxy filled with rubber is softer than the pure epoxy.

A comparison of the epoxy with untreated and treated NBR in Figure 4.3 shows a close yield stress for both systems. The compressive yield strength of pure epoxy is 93.5 MPa. With 20 and 30 % untreated NBR, the compressive yield stress of the NBR-filled epoxy system was reduced by 50 and 73 % respectively. For the treated NBR, the compressive yield stress of the titanate treated NBR-filled epoxy system is reduced by 52 and 68 % respectively.

The system modified by CTBN with 15% acrylonitrile content have a lower compressive yield stress than that by CTBN with 30% acrylonitrile content. At 5 and 10 vol% of CTBN with 15% AN, the compressive yield stress was reduced by 14 and 35 % while the compressive yield stress of the system with CTBN with 30% AN was reduced by 16 and 28 % respectively. Although the compressive moduli of epoxy with either CTBN are close, it can be seen from Figure 4.3 that the CTBN with 30% AN has a better resistance to permanant deformation than the CTBN with 15% AN.

As shown in Figure 4.3, the sequence of the ability of rubber to decrease the yield stress of epoxy is titanate treated NBR < NBR < CTBN with 30% AN < CTBN with 15% AN respectively. It should be noted that the treated NBR, NBR and the CTBN with 30% AN reduce the yield stress at a rate close to each other. Thus it is difficult to conclude which type of rubber exhibits greater ability to decrease the yield stress.

The effect of the various types of rubber and the rubber content on the compressive fracture strain of rubber-filled epoxy system is shown in Figure 4.4.

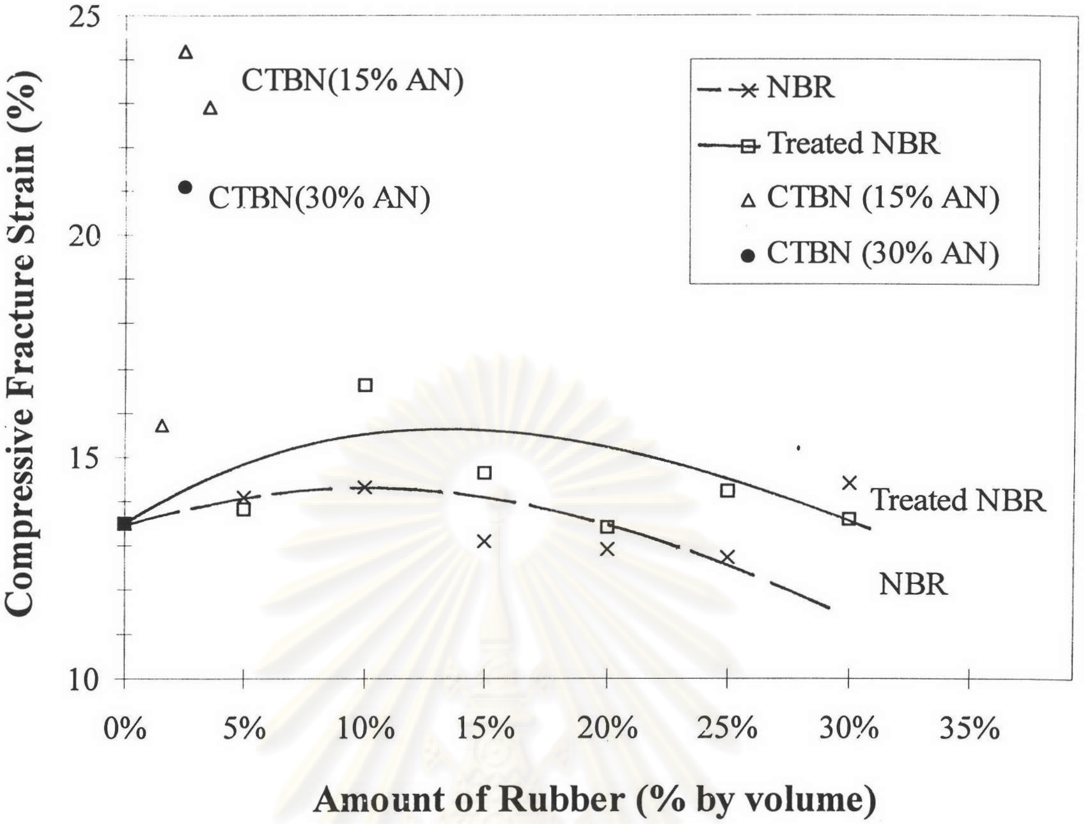

Figure 4.4: Compressive fracture strain for various types of rubber-filled epoxy system.

For various types of rubber-filled epoxy system as shown in Figure 4.4, it is apparent that the fracture strain tends to scatter and does not exhibit a consistant trend for all four types of rubber. In the case of CTBN-filled epoxy system, both types of CTBN show an increase in the fracture strain at a very low percent of rubber, i. e. less than 5 vol%. When the percent of rubber is increased up to 5 % by volume or higher, the value of the fracture strain can not be measured because the test sample did not break. Instead, it got buckled and sprang out of the compression test fixture. The CTBN-filled epoxy has good compressive property.

For both the untreated NBR and the treated NBR-filled epoxy systems shown in Figure 4.4, the fracture strain of both types of rubber-filled epoxy tends to increase when the volume percent of NBR used was less than 10 % by volume. However, it tends to decrease again when the amount of NBR is greater than 10 vol%. The plot in Figure 4.4 evidently shows that the treated NBR exhibits higher value of fracture strain than that of the NBR at every level of rubber content. When compared with the pure epoxy, the compressive fracture strain of the NBR-filled epoxy system with 15 and 25 % by volume of rubber was reduce by 3.7 and 6.6 %. The compressive fracture strain of the treated NBR-modified epoxy was increased by 7.7 and 4.8 % respectively. The results clearly show that treated NBR-filled epoxy system can deform more than the untreated NBR-filled epoxy system.

4.1.2 Tensile Test

Tensile test is one of the most useful test frequently conducted to investigate the mechanical properties of polymers. It is very similar to the compression test except that the load for the tensile test is applied in the opposite direction to that of the compression test. In this experimental work, the pure epoxy was tested to compare its tensile properties with the rubber-filled epoxy. The results of the tensile test as received are shown in Figure 4.5. The tensile properties obtained for each rubber-modified epoxy system were averaged from results generated by eight individual tests.

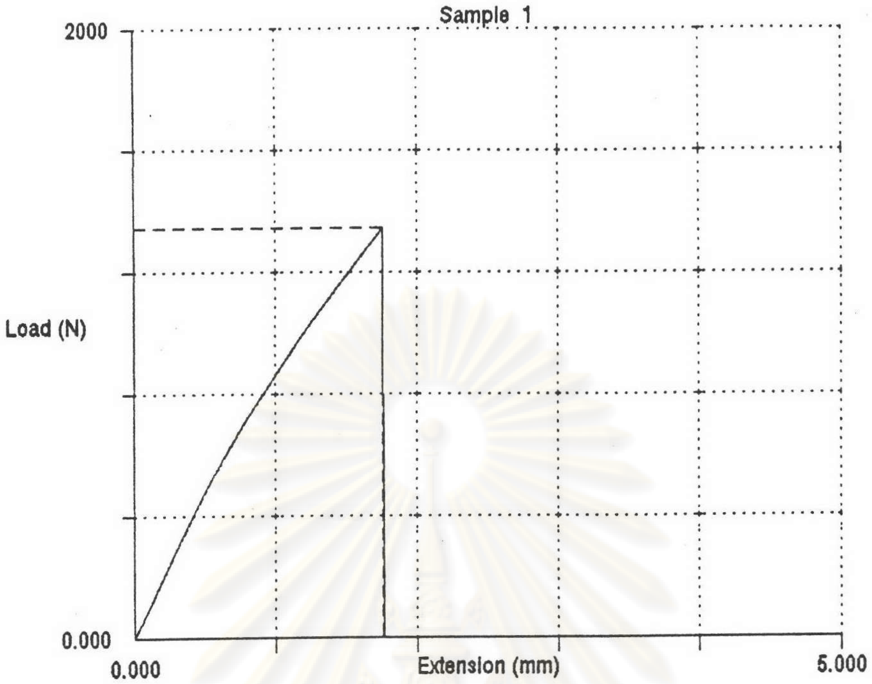

Figure 4.5: The load-deformation curve of 2.5 % CTBN (30% AN)-filled epoxy system from the tensile test.

The fact that the specimen within the test gauge was in the form of a regtangular piece and that epoxy is hard and brittle thermoset means that the tensile deformation cannot be obserbed clearly even when the tensile test was conducted to fracture.

The effect of the various types of rubber and the rubber content on the tensile modulus of the rubber-filled epoxy system is shown in Figure 4.6.

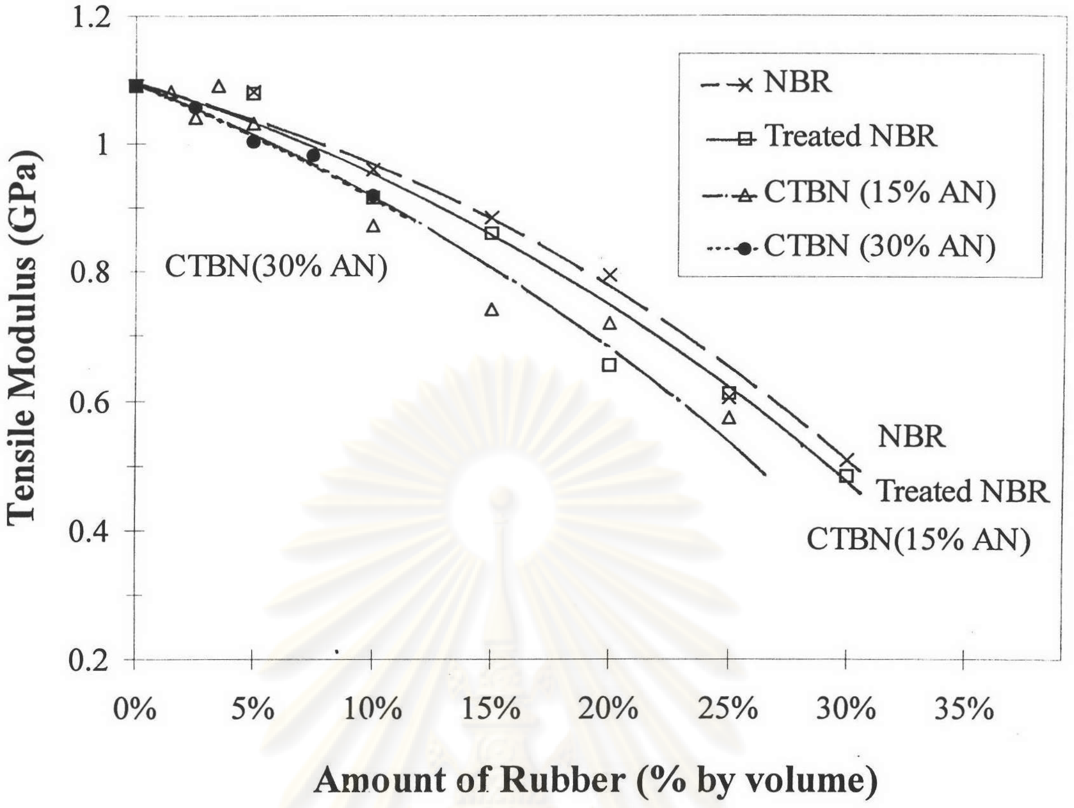

Figure 4.6: Tensile modulus for various types of rubber-filled epoxy systems.

The plot In Figure 4.6 shows that the amount of rubber-filled epoxy resin has a significant effect on the modulus of the composites. All types of rubber-filled epoxy system depict a decrease in the tensile modulus with an increase in the rubber content. This is resulted from the toughness of the rubber phase dispersed in the epoxy resin which can absorb the load applied to the samples. The rubber-filled epoxy system deform more easily than the pure epoxy system.

A comparison between the untreated NBR and the treated NBR-filled epoxies reveals that the tensile modulus of the treated NBR is lower than that of the untreated one. This result depicts a trend identical to that of the compressive modulus from the compression test. It verifies the effect of the titanate coupling agent in improving the surface adherance between the NBR rubber and the epoxy resin. The pure epoxy resin possesses a tensile modulus of 1.1 GPa. With 10, 20 and 30 vol% rubber added to the epoxy, the tensile modulus of the NBR-filled epoxy system can be reduced by 12, 27 and 53 % while the tensile modulus of the treated NBR-filled epoxy system can be reduced by 16, 40 and 56 % respectively. A similar conclusion can be made as in the case of the compression test, i.e., the titanate coupling agent is capable of reducing the tensile and the compression moduli of the NBR-filled epoxy systems.

For the CTBN-modified epoxy systems with 15 % and 30 % acrylonitrile content, the tensile moduli are lower than those modified by the untreated and treated NBR. When compare with the pure epoxy, the tensile modulus of the modified systems with 15 and 25 % by volume of CTBN with 15% acrylonitrile content were lowered by 32 and 47 % while those of the systems with 5 and 10 % by volume of CTBN with 30% acrylonitrile content were reduced by 8 and 16 % respectively. Furthermore, the tensile moduli of the CTBN-modified epoxy systems are all lower than those of the NBR-modified ones for the same amount of rubber added. The greater reduction of the tensile moduli in the CTBN-modified epoxy systems is believed to be due to the finer rubber particles dispersed throughout the epoxy resin. Microscopic observation by application of a scanning electron microscope reveals the average CTBN particle size for both 15 and 30 % acrylonitrile content to be about

1 to 20 μm. Figure 4.7 and 4.8 shows the CTBN particle size for the 15 and 30 % acrylonitrile-filled epoxy system respectively.

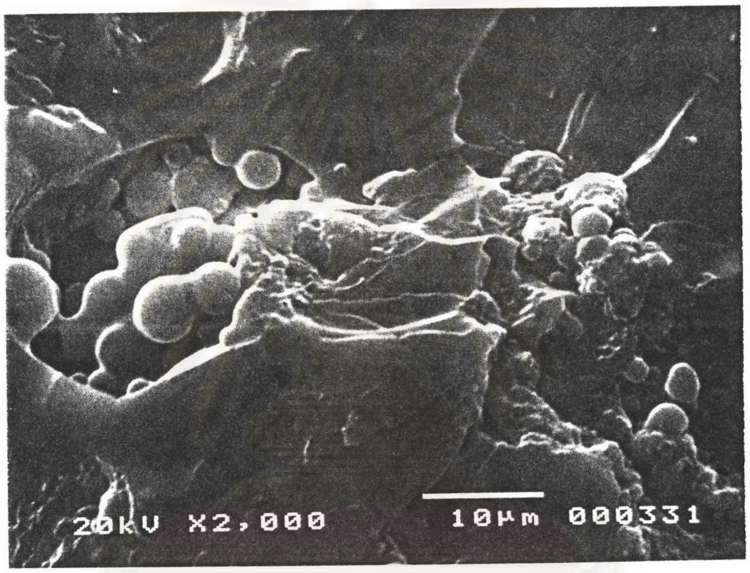

Figure 4.7: SEM photomicrograph of CTBN with 15% AN-filled epoxy system (2000X).

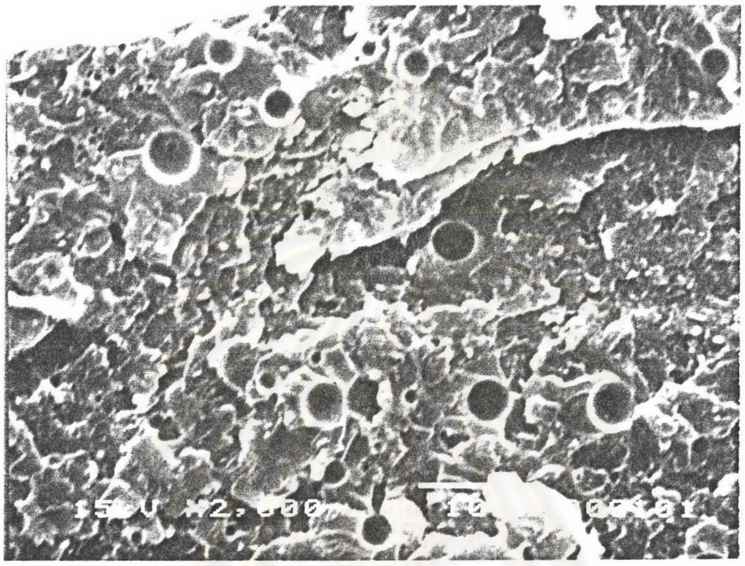

Figure 4.8: SEM photomicrograph of CTBN with 30% AN-filled epoxy system (2000X).

The NBR particles are much larger. Their average size varies from 100 to 200 μm. In addition, the CTBN is capable of interacting with the epoxy matrix upon solidification. Hence, better interfacial bonding is achieved in the CTBN-modified system. The tensile moduli for both types of CTBN are close to each other.

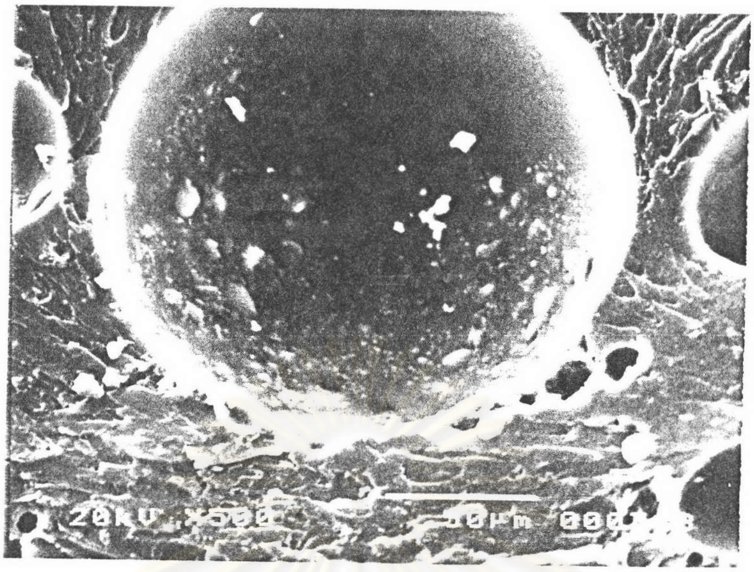

Figure 4.9: SEM photomicrograph of the untreated NBR-filled epoxy system (500X).

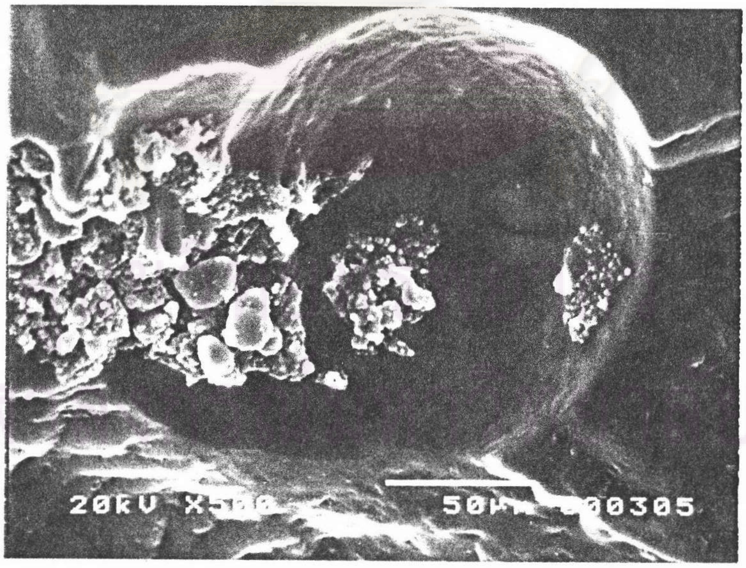

Figure 4.10: SEM photomicrograph of the titanate treated NBR-filled epoxy system (500X).

The sequence of the ability for rubber to decrease the tensile modulus of epoxy is NBR < treated NBR < CTBN with15% AN < CTBN with 30% AN respectively as shown in Figure 4.6. It is not yet obvious which type of CTBN, the 15% acrylonitrile or the 30% acrylonitrile yields lower tensile modulus.

The effect of the various types of rubber and the rubber content on the 0.2% offset yield stress of rubber-filled epoxy system is shown in Figure 4.11.

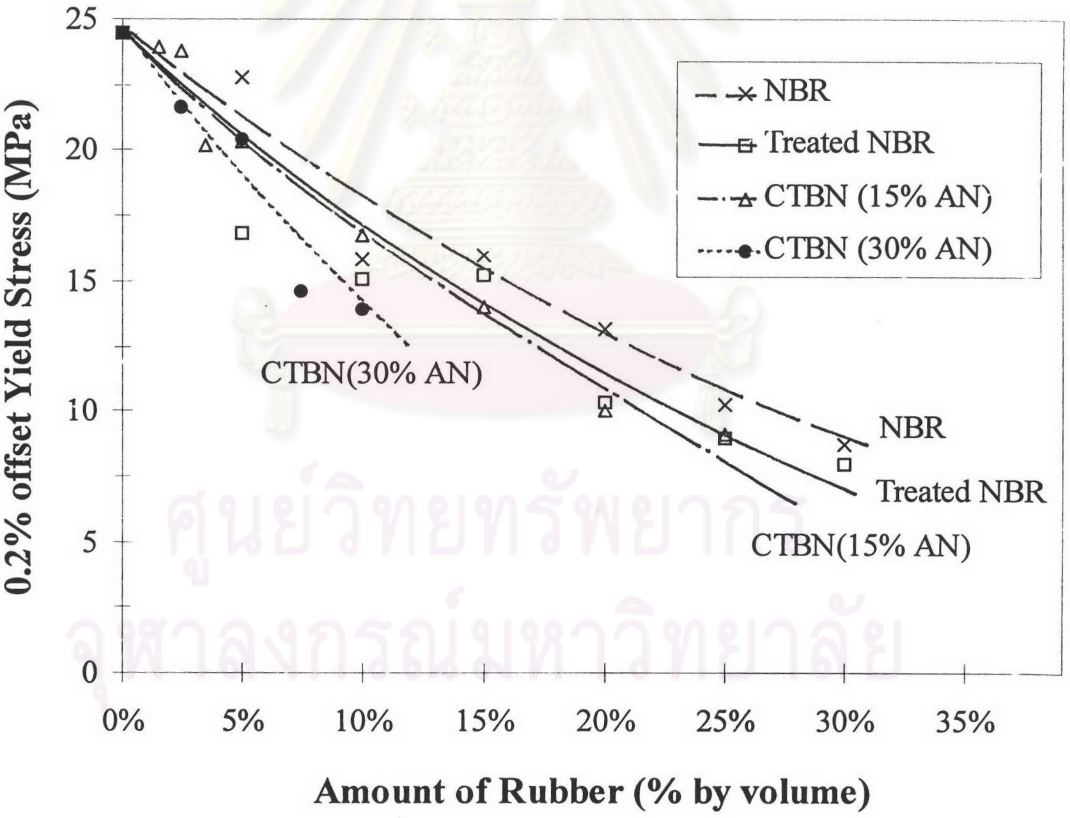

Figure 4.11: The 0.2% offset yield stress for the various types of rubber-filled epoxy systems.

As shown in the load-deformation curve in Figure 4.5, it is apparent that in the tensile test that most fracture did not occur within the gauge length. It tends to occur more at the end of the grip. Samples fractured at these locations, i.e. outside the gauge length, were all rejected. The yield stress and the fracture strain determined from these samples are incorrectly. Since the yield point on the stress-strain curves were not well-defined, the *0.2% offset yield stress* and the *0.2% offset yield strain* were investigated.

It is apparent for the various types of rubber-filled epoxy system that the 0.2% offset yield stresses for all types of rubber-filled epoxy systems decrease with an increase in the rubber content. This result can be explained in a similar manner to that in the compression test. The rubber filled in the epoxy resin behaves like a softening manner. The decrease in the 0.2% offset yield stress implies that the epoxy filled with rubber is softer and easier to deform than the pure epoxy.

A comparison of the untreated NBR and the treated NBR in Figure 4.11 reveals that the treated NBR system has a lower yield stress than that of the untreated NBR system. Pure epoxy has a 0.2% offset yield stress of 24.5 Mpa. For epoxy with 20 and 30 vol% rubber, the 0.2% offset yield stress of the treated NBR-filled epoxy system was reduced by 58 and 68 % while that for the NBR-filled epoxy system was reduced by 46 and 65 % respectively. It is evident that the titanate coupling agent helps the treated NBR-filled system to deform more easily.

For epoxy systems filled by the CTBN with the acrylonitrile content of 15% and 30%, Figure 4.11 also shows that the epoxy systems filled by CTBN with 30% acrylonitrile possess a lower 0.2% offset yield stress than those from the system filled by CTBN with 15% acrylonitrile. Compared with pure epoxy, it is found that the system with 5 and 10 vol% rubber have their 0.2% offset yield stress reduced by 17 and 31 % for CTBN with 15% acrylonitrile while the systems with the same amount of CTBN rubber but with 30% acrylonitrile have theirs reduced by 17 and 43 % respectively. The CTBN with 30% acrylonitrile cannot be applied at concentration greater than 10 % by volume because the extremely high viscosity of the system make it impossible to flow and be processed.

The sequence of the ability of rubber to decrease the 0.2% offset yield stress of epoxy is NBR < treated NBR < CTBN with 15% AN < CTBN with 30% AN respectively. Comparison between both types of CTBN cannot be made at concentrations greater than 10 vol% because the CTBN with 30% AN can not be processed at concentration greater than 10 vol%.

The effect of the various types of rubber and the rubber content on the 0.2% offset yield strain of rubber-filled epoxy system is shown in Figure 4.12

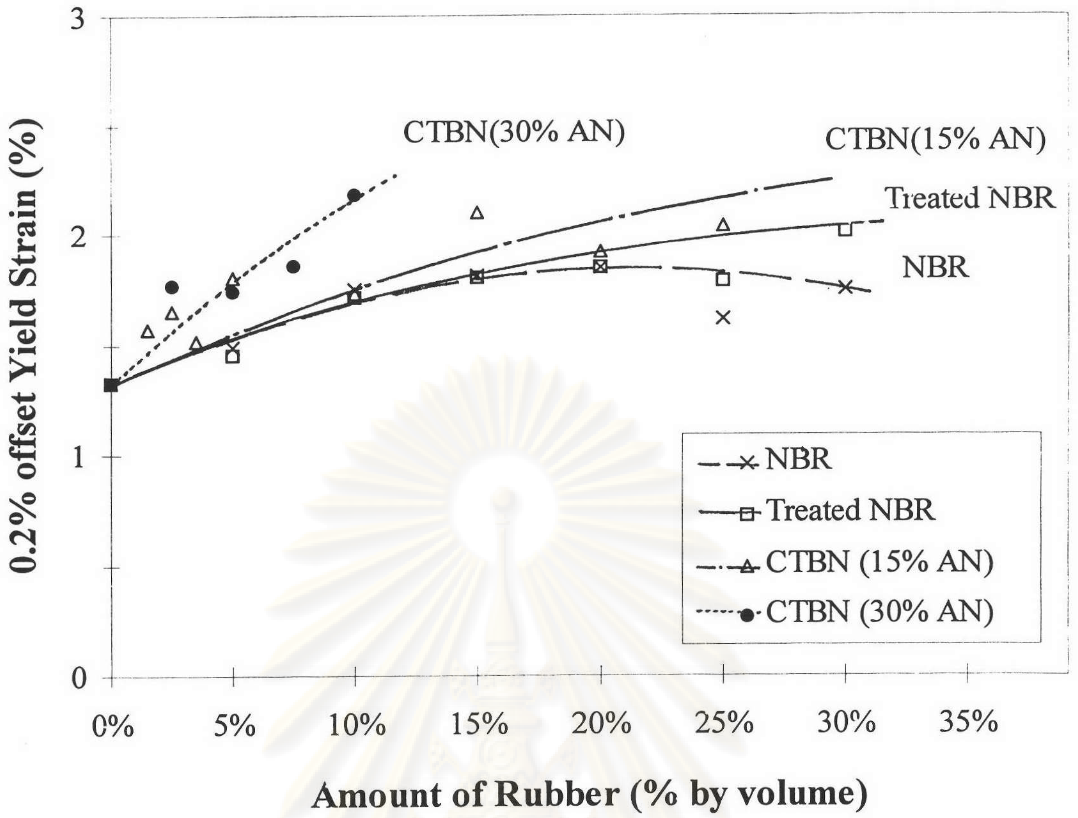

Figure 4.12: The 0.2% offset yield strain for the various types of rubber-filled epoxy systems.

For the various types of rubber-filled epoxy systems as shown in Figure 4.12, it is apparent that the 0.2% offset yield strain for all types of rubber-filled epoxy increases with an increase in the rubber content. This result is due to the toughness of the rubber phase dispersed in the epoxy resin. The rubber phase tends to impart the toughness property and consequently make the epoxy system toughener and easier to deform.

The epoxy systems with titanate-treated NBR have higher yield strains than those with untreated NBR. Pure epoxy has a yield strain of 1.3%. For epoxy with 20 and 30 vol% rubber, the yield strain of untreated NBR system can increase by 40 and 32 % while those of the treated NBR system increase by 40 and 52 % respectively. This is because the titanate coupling agent is capable of improving the interfacial bonding between the treated NBR and the epoxy matrix. Consequently, more extension is observed in the treated NBR systems.

For the CTBN-modified epoxy, Figure 4.12 shows that the system with 30% acrylonitrile content exhibits a higher yield strain than that with 15% acrylonitrile content. With 2.5 and 10 vol% CTBN, the yield strain of the systems with 30% acrylonitrile have their yield strain increased by 34 and 65 % while the one with 15% acrylonitrile have theirs increase by only 25 and 31 % respectively. This is because CTBN with 30% acrylonitrile solidified to smaller particles than those from the CTBN with 15% acrylonitrile. The smaller particle size leads to a higher deformation in the modified epoxy.

The sequence of the ability of the rubber to increase the 0.2% offset yield strain is NBR < treated NBR < CTBN with 15% AN < CTBN with 30% AN.

4.1.3 Izod Impact Test

Izod impact tests measure the energy expended upto failure under conditions of rapid loading. Information obtained from impact tests may be used to determine whether a given plastic has sufficient energy-absorbing properties to be useful for a particular application.

The effect of various types of rubber and the rubber content on the Izod impact strength of the rubber-filled epoxy systems is shown in Figure 4.13.

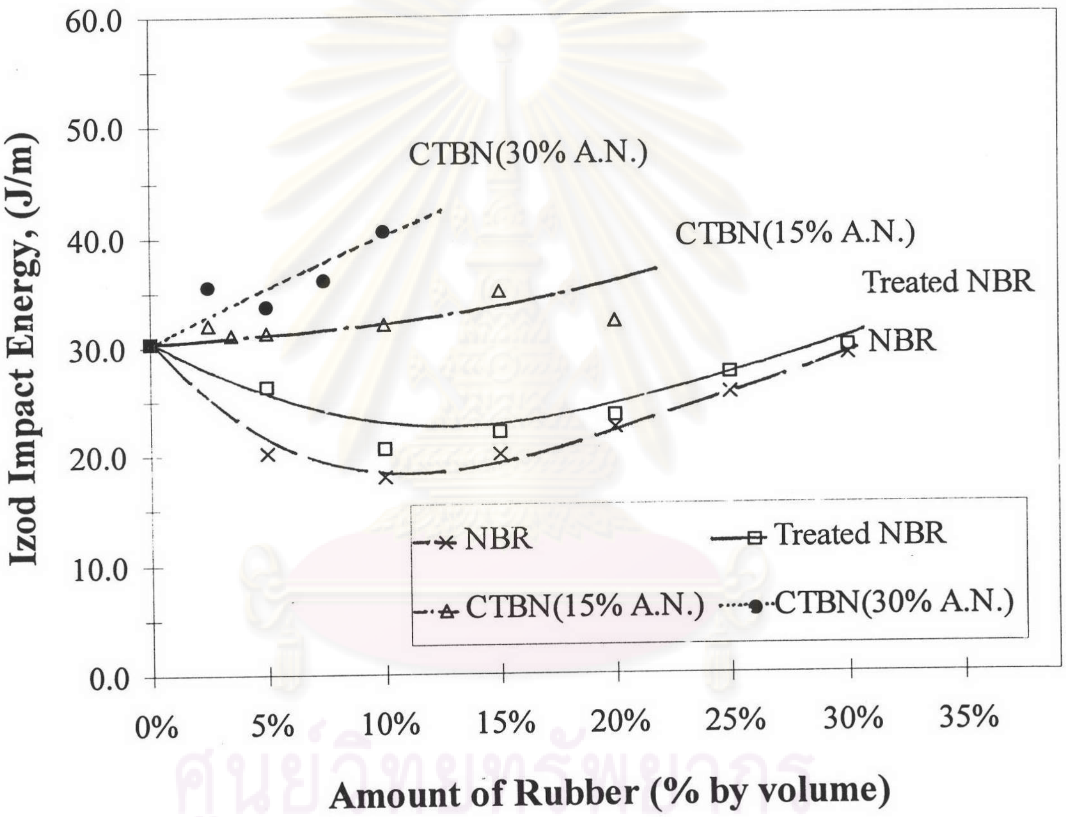

Figure 4.13: The Izod impact strength for various types of rubber-filled epoxy systems.

The Izod impact energy for all amount of the untreated NBR and the treated NBR systems is lower than that of the pure epoxy. The pure epoxy resin possesses an impact energy of 30.4 J/m. The impact energy tends to decrease when the amount of NBR and treated NBR filled in the epoxy is less than 10% by volume. Beyond 10 vol%, the impact energy was found to increase. With 10, 20 and 30 vol% of rubber added to the epoxy, the impact energy of the NBR-filled epoxy system can be reduced by 41, 26, 4 % while those for the treated NBR-filled epoxy system can be reduced by 32, 22 and 2 % respectively. This is due to the large particle size and the non-reactive surface of the NBR and the treated NBR. Althought coupling agent is used to treat the surface of the NBR, the impact energy did not increase that much. When the amount of the NBR was low, crack was initiated easily and it propagated rapidly because the NBR rubber particle was quite large. They ranged from about 100-300 μm. However, when the amount of the rubber was raised to more than 10 vol%, more work was required for crack to propagate and deviate around part of the rubber particles.

For CTBN-filled epoxy system, it was found that the impact energy for CTBN with 15% acrylonitrile system increases slower than that from the CTBN with 30% acrylonitrile system. However, both types of CTBN show an increase in the impact energy with an increase in the amount of rubber. The CTBN particle ranged from about 1-20 μm, they were much smaller than the NBR. The smaller particle size means crack has to deveiate evenn more than that in the system with the larger ones. More energy was dissipated while crack propagated. Hence, greater energy was required to break the specimen with CTBN finer particles.

In this experimental work, It can be concluded that CTBN(30% AN) has the most effectively increase the impact energy. Pure epoxy has an impact energy of 30.4 J/m. With CTBN with 30% AN by 5 and 10 vol%, the impact energy of the CTBN modified system was increased by 11 and 33 %. For CTBN with 15% AN, the impact energy was raised by 3 and 5.4 %.

4.1.4 Falling weight test

In the falling weight impact test, a circular disc of material is impacted by a metal dart with a hemi-spherical tip. The result of the falling weight test is shown by a plot between the force and the displacement curve as illustrated in Figure 4.14. The energy requried in this test can be calculated as the area under the curve. The tests are carried out either at conditions where the impact energy is far in excess of that required to break the specimen or at a low level of impact energy so that damage tolerance and the possible initiation of a crack can be observed. Besides, the falling weight test can also yield the deformation upon fracture while Izod impact test gives only the impact strength and the impact energy.

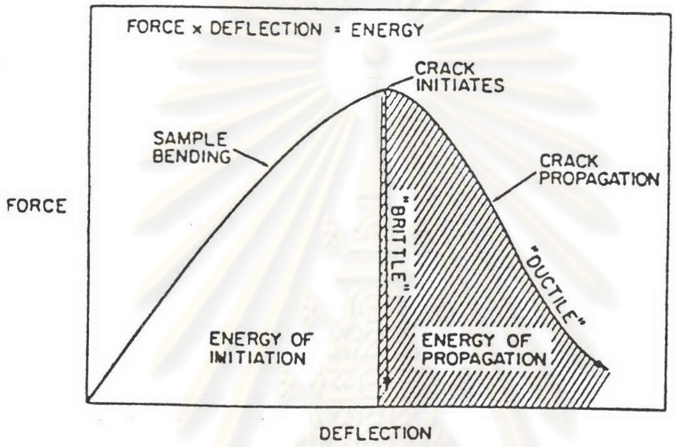

Figure 4.14: Schematic representation of the force-displacement curve from the falling weight test for brittle and ductile fracture.

In the present work, the effect of the various types of rubber and the rubber content on the energy of the rubber-filled epoxy systems is shown in Figure 4.15.

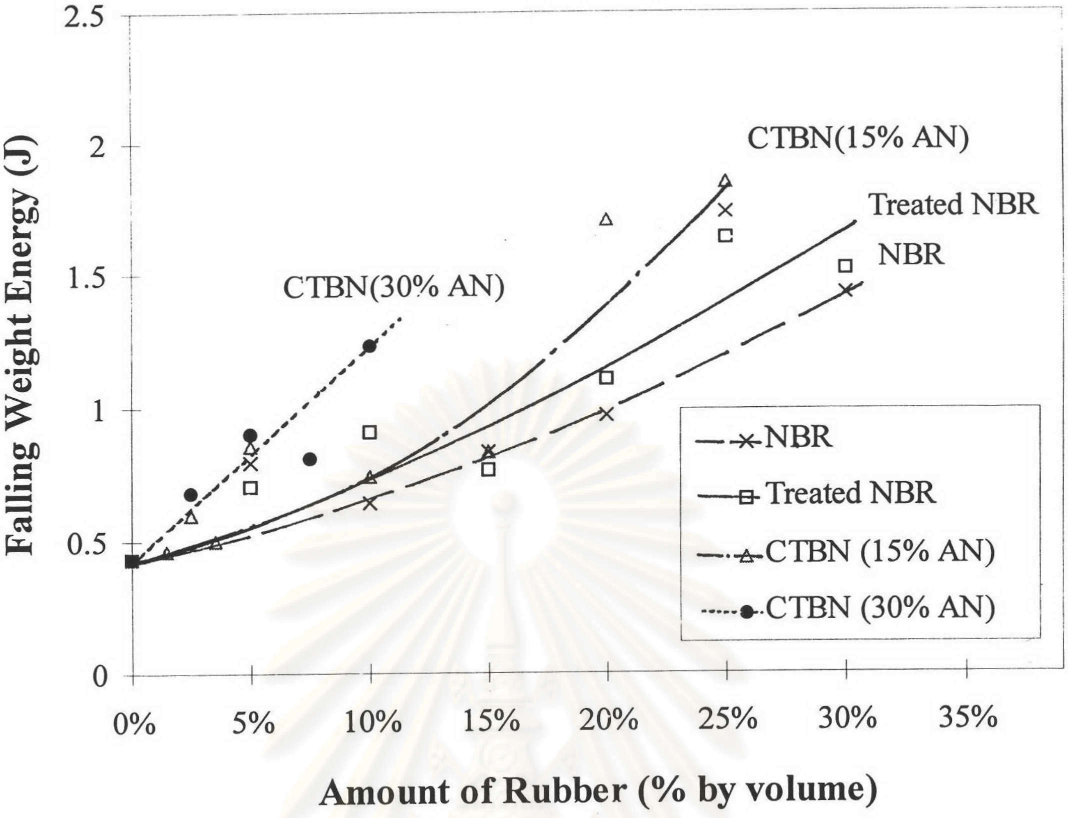

Figure 4.15: The energy obtained from the falling weight tests for various types of rubber-filled epoxy systems.

For the various types of rubber-filled epoxy systems, it is apparent that the energy for all types of rubber-filled epoxy increases with the rubber content. Thus, the rubber which is dispersed in the epoxy resin can obviously increase the toughness of the epoxy.

A comparison between the untreated NBR and the treated NBR shows that the energy of both the untreated NBR and the treated NBR-modified epoxy was enhanced. However, the treated NBR has a higher energy than that of the untreated NBR. Pure epoxy possesses a energy of 0.43 J. The epoxy with 20 and 30 vol% of the untreated NBR-filled epoxy can have their energy increase by 158 and 258 % while those of the NBR-filled epoxy can increase 128 and 237 % respectively. This is because the titanate coupling agent treated on the surface of the NBR had reacted and form some interfacial bonding with the epoxy matrix. When the metal dart dorpped and impacted the sample, the treated NBR-filled epoxy can absorb more energy than the untreated NBR ones. The area under the curve which represent the energy absorbed by the treated NBR-filled epoxy is greater than that of the untreated NBR.

For CTBN-modified epoxy systems whth 15% and 30% acrylonitrile content, the energy of the epoxy modified by the CTBN with 30% acrylontrile is higher than that by the CTBN with 15% acrylonitrile content. When compare with pure epoxy, the energy of modified systems with 2.5 and 10 vol% of CTBN with 15% acrylonitrile were increased by 41 and 74 % while those of the system modified by the CTBN with 30% acrylonitrile content were increased by 59 and 188 % respectively. This can be explained in term of the rubber particle size. The CTBN with 30% acrylonitrile content solidified to smaller particles and yielded greater surface area for interfacial bonding between the rubber and the epoxy matrix than the CTBN with 15% acrylonitrile content. Hence, higher energy was required to break the specimen.

The sequence of the ability of various types of rubber to increase the energy of epoxy is NBR < treated NBR < CTBN with 15% AN < CTBN with 30% AN respectively.

The effect of the various types of rubber and the rubber content on the deformation of the rubber-filled epoxy systems is shown in Figure 4.16.

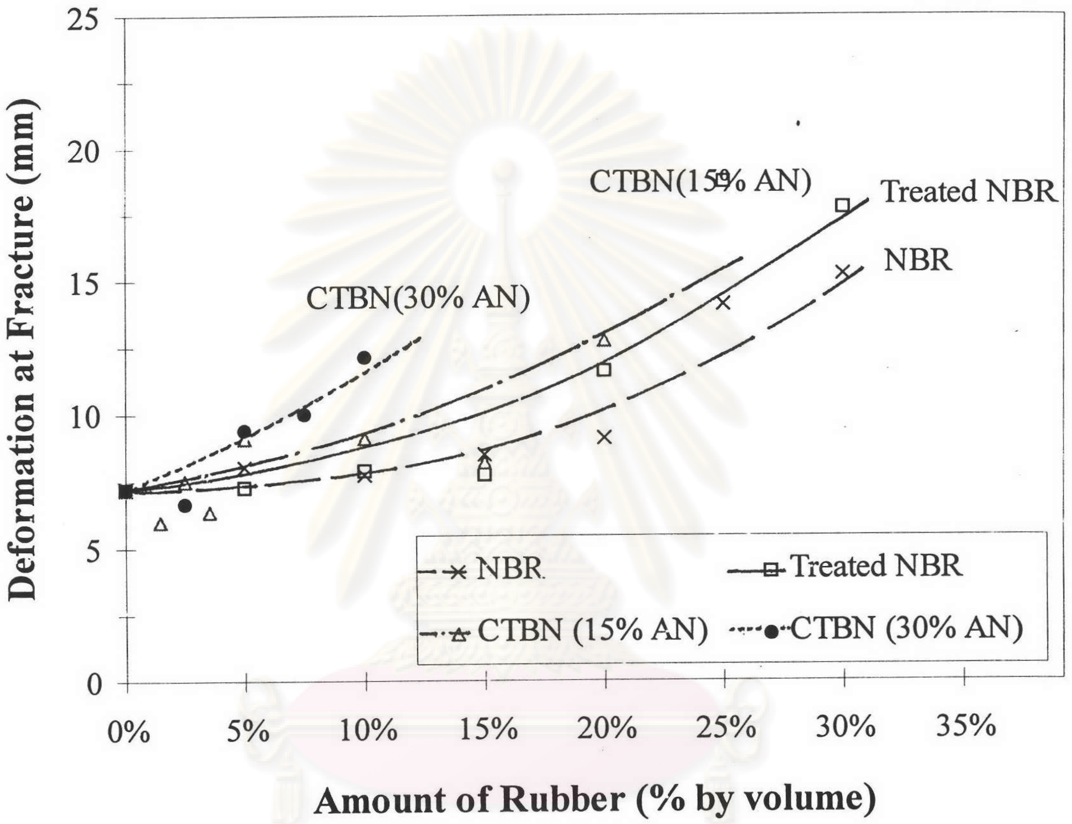

Figure 4.16: The deformation for various types of rubber-filled epoxy system.

For various types of the rubber-filled epoxy systems, it is apparent that the deformation for all types of rubber-filled epoxy increases with the rubber content. This can be explained in terms of the energy dissipation. When rubber is filled in the epoxy matrix, the rubber phase is the important part to absorb and dissipate the energy applied and increase the deformation of the modified epoxy. As shown in Figure 4.16, the more rubber content filled in the epoxy, the greater will be the deformation.

A comparison of the untreated NBR and the treated NBR shows the treated NBR to have undergone more deformation than the untreated one. The pure epoxy system posesses a deformation of 7.2 mm which is equivalent to a strain of 240% of the specimen thickness. With 20 and 30 vol% rubber added to the epoxy, the deformation of the treated NBR-filled epoxy system was increased by 60 and 144 % while the deformation of the untreated NBR-filled epoxy system were increased by only 25 and 110 % respectively. Thus, the titanate coupling agent is capable of increasing the deformation and fracture energy of the treated NBR-filled epoxy systems.

For the CTBN-modified epoxy systems with acrylonitrile content of 15% and 30%, when compare with the pure epoxy, the deformation of the modified systems with 20 and 30 vol% of CTBN with 30% acrylonitrile content was increased by 30 and 67 % while the deformation of the epoxy modified by CTBN with 15% acrylonitrile content was increased to only 26.3 and 27 % respectively.

The sequence of the ability of the rubber to increase the deformation of epoxy is NBR < treated NBR < CTBN with 15% AN < CTBN with 30% AN respectively.

4.1.5 Double Torsion Test

The double torsion test is one type of tests used to evaluate the energy required to break a material. This energy is known as the fracture toughness. In the present work, the effect of various types of rubber and the rubber content on the stress intensity factors (K_{IC}) of the rubber-filled epoxy systems are illustrated in Figure 4.17.

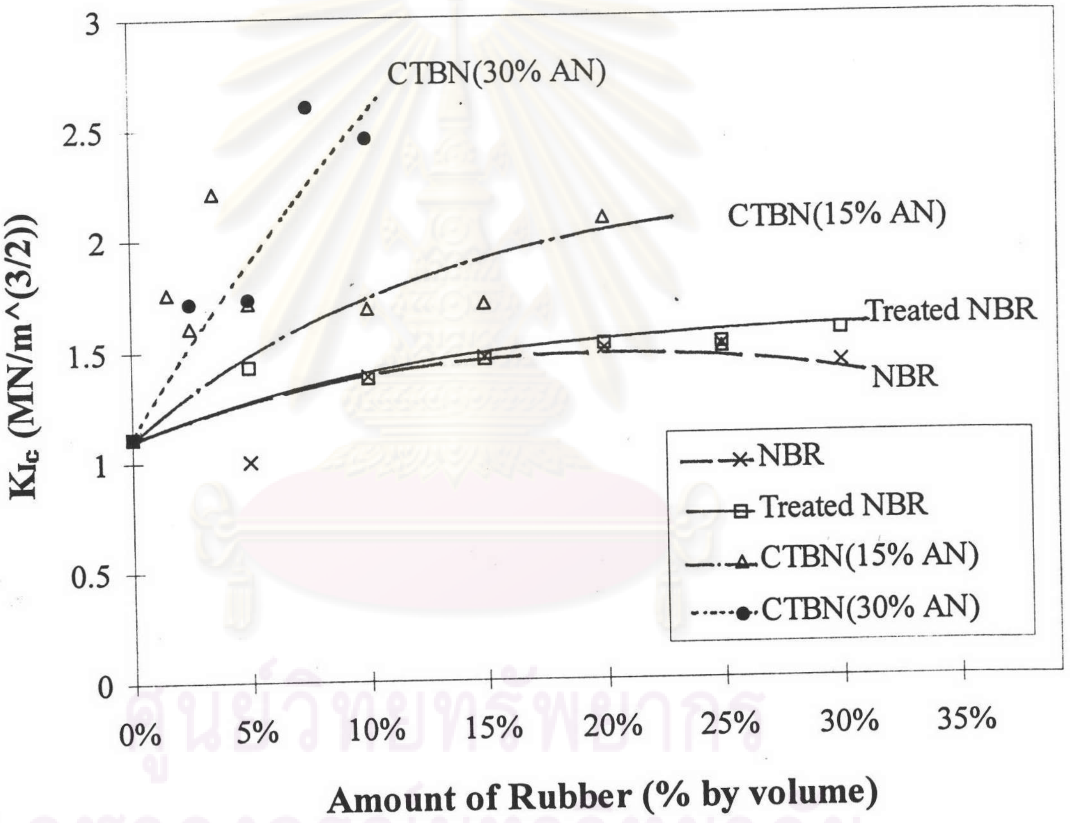

Figure 4.17: The stress intensity factor for the various types of rubber-filled epoxy systems.

Figure 4.17 illustreates an increase in the stress intensity factor (K_{Ic}) with the rubber content. The stress field around a sharp crack in a linear elastic material can be uniquely defined by a parameter named the stress-intensity factor, K. Fracture occurs when the value of K exceeds some critical value, K_C. Thus K is a stress field parameter independent of the material whereas K_C, often referred to as the fracture toughness, is a measure of the material property. The results of the present research show an increase in the stress intensity factor with the rubber content. This implies that the epoxy is toughened by the amount of rubber filled into it.

The sequence of the ability of rubber to increase the stress intensity factor is NBR < treated NBR < CTBN with 15% AN < CTBN with 30% AN respectively. A comparison between the untreated NBR and the treated NBR shows that both had almost the same value of stress intensity factor. The treated NBR shows slightly higher stress intensity factor which may be due to the effect of the titanate coupling agent. Figure 4.17 also illustrates that both types of CTBN result in greater levels of stress intensity factor than the NBR. The smaller particle size of the CTBN system leads to a greater interfacial adhesion between the CTBN particles and the epoxy matrix.

From the stress intensity factor, the fracture energy (G_{IC}) can be evaluated as shown in Equation (4.1).

$$G_C = [(1-\nu^2)/E]*K_{Ic}^2 + [(1-\nu^2)/E]*K_{IIc}^2 + [(1+\nu)/E]*K_{IIIc}^2 \quad (4.1)$$

or epuivalently

$$G_C = G_{Ic} + G_{IIc} + G_{IIIc} \tag{4.2}$$

For Mode I fracture

$$G_{IC} = (K_{IC})^2/E \tag{4.3}$$

E is the modulus of elasticity. The specimens tested by double torsion technique in the present work failed in mode I manner. Hence, Equation (4.3) can be applied throughout the present work.

The effect of various types of rubber and the rubber content on the fracture energy of the rubber-filled epoxy system is shown in Figure 4.18.

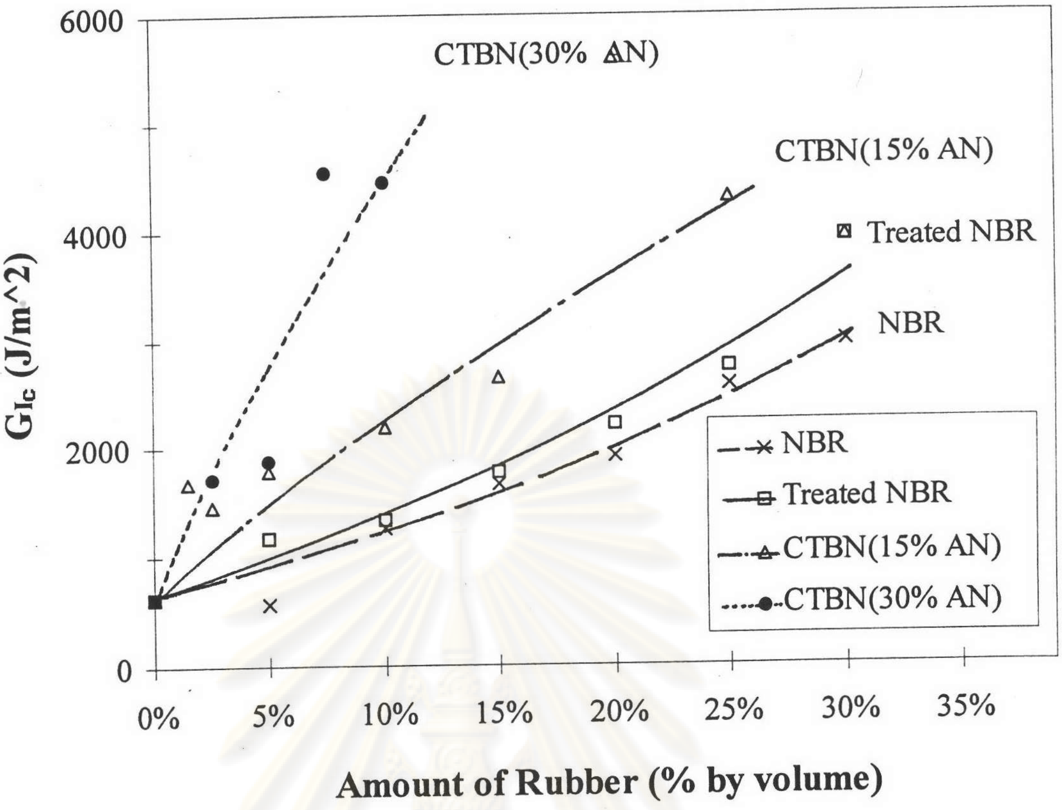

Figure 4.18: The fracture toughness for various types of rubber-filled epoxy systems.

The fracture energy for all types of rubber-filled epoxy increases with the rubber content. The sequence of the ability of rubber to increase the fracture energy is NBR < treated NBR < CTBN with 15% AN < CTBN with 30% AN respectively.

A comparison between the NBR and the treated NBR shows a higher fracture energy in the treated NBR-modified epoxy. Pure epoxy system has a fracture energy of 1074 J/m^2. With 20 and 30 vol% rubber added to the epoxy, the fracture energy of the treated NBR-filled epoxy was increased by 259 and 543 % while that of the NBR-filled epoxy was increased by 213 and 385 % respectively.

For CTBN-modified epoxy systems with acrylonitrile content of 15% and 30%, when compare with the pure epoxy, the fracture energy of the systems modified by 5 and 10 vol% of CTBN with 30% acrylonitrile content was increased by 205 and 625 % while that of the systems modified by 5 and 10 vol% of CTBN with 15% acrylonitrile content increased by 192 and 257 % respectively.

4.2 SAMPLE CHARACTERIZATION

4.2.1 Density test

In the present work, rubber which has the density about 0.95 g/cc, is dispersed in the epoxy resin. The density of the epoxy resin is about 1.2 g/cc. Consequently, two limiting densities for the rubber-filled epoxy systems are 0.9 and 1.2 g/cc. The important part of this test is the accuracy in the calibration of the density column.

Figure 4.19 illustrates a decreasing trend of the density of the rubber-modified epoxy with the rubber content. The reduction in the density tends to follow the *Rule of Mixture*. Scattered values from the ideal line calculated from the *Rule of Mixture* arise possibly due to the operator's error in this experiment. The use of an extremely long column may reduce such error.

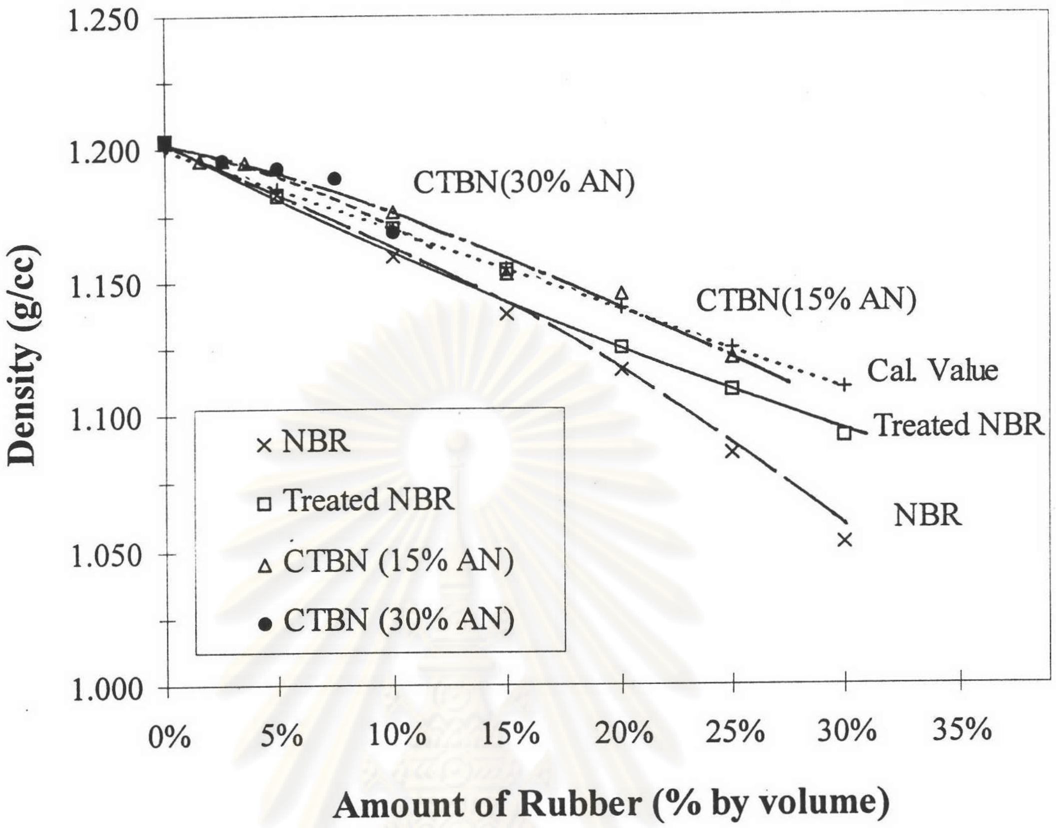

Figure 4.19: The density for various types of rubber-filled epoxy systems.

For the NBR-filled epoxy system shown in Figure 4.19, an increase in the NBR content from 5, 10, 15, 20, 25 and 30 % results in decrease in the density by 1.7, 3.6, 5.4, 7.1, 9.7 and 12.5 % respectively in comparison with that of the pure epoxy. The deviation of the results obtained from the calculated values based on the *Rule of Mixture* is most prominent in the case of NBR. This is possibly due to the fact that the NBR solid particles tend to form agglomerated upon dispersion in epoxy. Air or voids might have been entrapped or created in this NBR agglomerates and consequently the density of the NBR-filled epoxy system is reduced. The greater the amount of NBR, the more possibility of air or voids be created in the agglomerates.

For the treated NBR-filled epoxy system shown in Figure 4.19, an increase in the treated NBR content from 5, 10, 15, 20, 25 and 30 % results in an decrease in the density by 1.5, 2.7, 4.1, 6.1, 7.8 and 9.2 % respectively in comparison with that of the pure epoxy.

For the CTBN with 15% acrylonitrile content or CTBN (15% AN)-filled epoxy system shown in Figure 4.19, an increase in the CTBN content from 1.5, 2.5, 3.5, 5, 10, 15, 20, and 25 % results in an decrease in the density by 0.6, 0.6, 0.7, 0.8, 2.2, 3.6, 4.8 and 6.8 % respectively in comparison with that of the pure epoxy.

For the CTBN with 30% acrylonitrile content or CTBN (30% AN)-filled epoxy system shown in Figure 4.19, an increase in the CTBN content from 2.5, 5, 7.5 and 10 % results in an decrease in the density factor by 0.6, 0.8, 1.2 and 2.8 % respectively in comparison with that of the pure epoxy.

4.2.2 Dynamic Mechanical Thermal Analysis (DMTA) Test

Many important synthetic polymers consist of long, flexible chains of very high molecular weight. In many cases, individual chains are randomly coiled and intertwined with no molecular order or structure. Such a physical state is termed *amorphous*. Below a certain temperature called a glass-transition temperature (T_g), long-range cooperative motions of individual chains cannot occur; however, short-range motions involving several contiquous groups along the chain backbone or substituent group are possible. Such motions are called secondary-relaxation processes and it can occur at temperatures as low as 70 K. The glass-transition temperature can be determined by a wide range of techniques for example in the measurement of volume (dilatometry), specific heat (calorimetry) and mechanical properties and particularly the modulus through test such as the dynamic mechanical analysis.

The DMTA test is capable of measuring viscoelastic properties of polymer such as the storage modulus (G') and the loss tangent (tan δ). These properties can be plotted against the temperature. The value of the glass transition temperature (T_g), the bending modulus in the rubbery state, the molecular weight between crosslinks (M_c) and the strand density or the crosslink density of polymer can be evaluated from these property-temperature curves. Figure 4.20 illustrates an example of the dynamic mechanical curves.

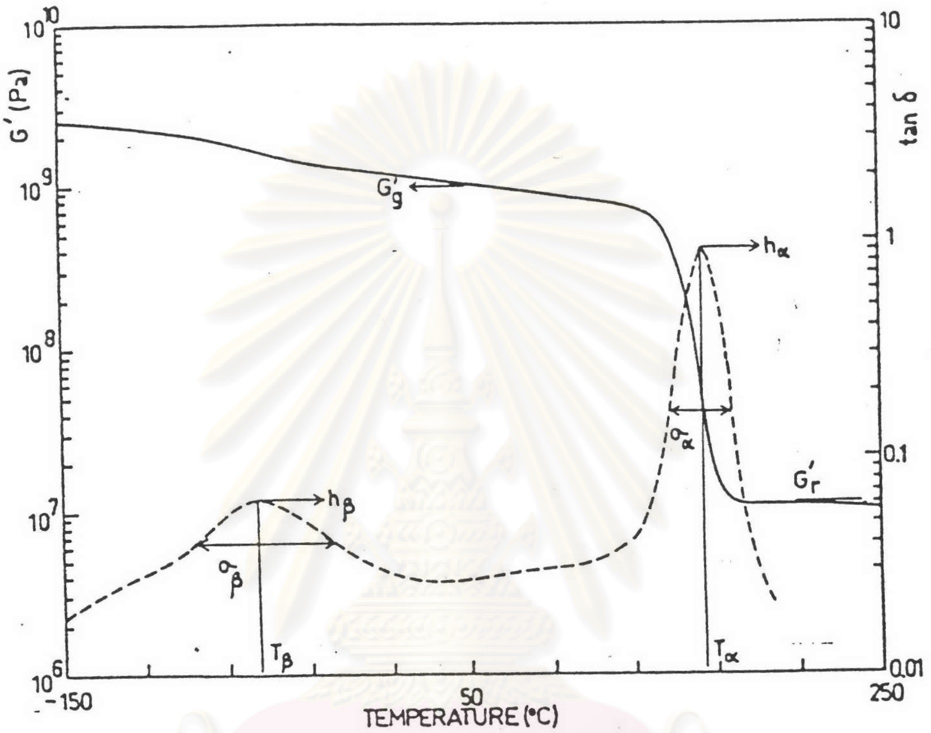

Figure 4.20: The dynamic mechanical spectrum (storage modulus G' and loss factor tan δ plotted against the temperature at 10 Hz) for the 100/180 DGEBA-DDA network. The system was cured for 1 hr at 100 °C and 1 hr at 180 °C.

In the present DMTA work, dynamic properties such as the bending modulus (E') and the loss factor (tan δ) were obtained as plots against the temperature. The glass transition temperature of the epoxy and the rubber can be defined and located as illustrated in Figure 4.21.

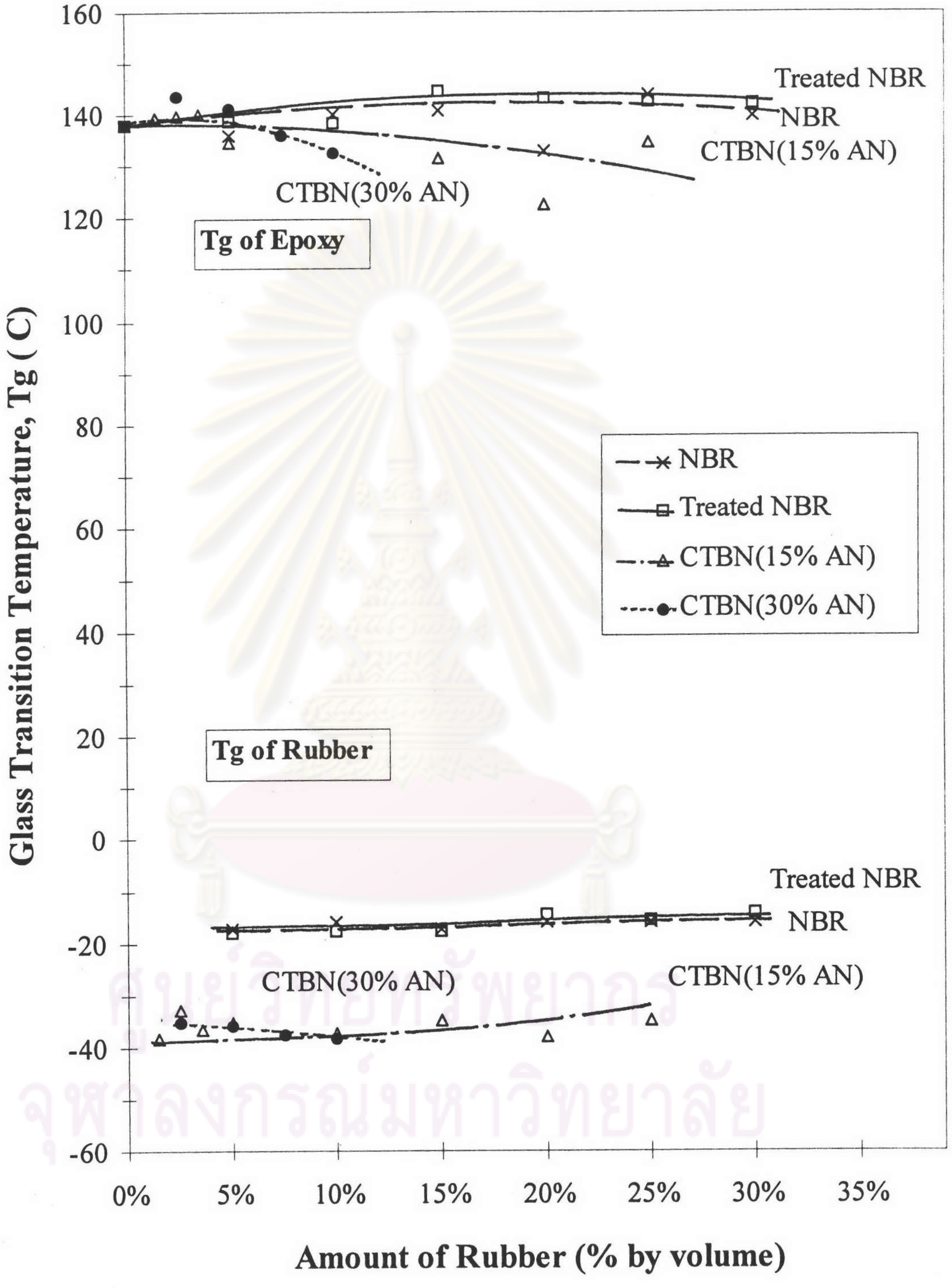

Figure 4.21: Glass transition temperature of epoxy, untreated and treated NBR and CTBN with 15 and 30 % acrylonitrile.

Figure 4.21 shows the difference between the T_g of pure epoxy system and the T_g of the rubber-filled epoxy systems. For untreated NBR and treated NBR-filled epoxy system, the glass transition temperature of the epoxy therein is increased with the rubber content. Pure epoxy has a T_g of 138 °C. An addition of 10 vol% NBR can increase T_g of epoxy to 139.9 °C while 10 vol% of the treated NBR-filled epoxy can increase the T_g of the epoxy to 138.5 °C. The increase in the glass transition temperature of epoxy is due to the presence of the NBR particles which tend to interrupt the vibrational motion of the epoxy chains. NBR particles makes it more difficult for the chains to vibrate. A higher T_g of epoxy is thus observed.

For CTBN-filled epoxy systems, the glass transition temperature of epoxy decreases as the CTBN concentration is increased. Figure 4.21 shows that T_g of the CTBN with 30% AN tends to decrease more than that of the CTBN with 15% AN. For example, 15 vol% CTBN(15% AN)-filled epoxy can decrease the T_g of the epoxy to 132 °C while only 5 vol% CTBN(30% AN)-filled epoxy can decrease the T_g of the epoxy to 136 °C. These reductions in the T_g are about 4.4 and 1.5 % respectively.

The glass transition temperature of the rubber was observed over two ranges, one for the untreated NBR and treated NBR and the other for the CTBN with 15 and 30 % acrylonitrile. The T_g for the first one did not change when the rubber content was increased. But for CTBN modified epoxy system, the T_g of the rubber increased slightly when the rubber content was raised. This can be due to the compatibility between the epoxy resin and the CTBN. However, it must be noted that for both types of CTBN, the T_g of the CTBN itself is about -37 °C. This T_g of the CTBN lies very close to the β peak of the epoxy as shown in Figure 4.20. Hence, the value of T_g of the CTBN rubber may not be accurately defined because of the difficulty due to the overlap of the two peak in the DMTA scan.

From the dynamic mechanical test, another significant property can be evaluated, the molecular weight between crosslink or M_c. The molucular weight between crosslinks shows whether the molecular weight of the pure epoxy between each crosslinking point is high or low. High M_c means the epoxy has low density of crosslinks which results in high movement of the epoxy chains. Generally, polymer which has high M_c shows better properties in softening, deformation and flow of molecular chains.

An analysis on the molecular weight between crosslinks can be done by application of the *Statistical Theory Of Rubber Elasticity* under the condition that makes the polymer most elastic and rubber-like. The molecular weight between crosslinks can be found by the use of the relationship shown in Equation 4.4(12):

$$\mathrm{Log}\,(G'/3) = 6 + (293\rho/M_c) \tag{4.4}$$

G' is the bending modulus. In the present work the value of G' was found at 200 °C. The term ρ is the density of the corresponding rubber-modified epoxy systems and the M_c is the molecular weight between crosslinks.

The bending modulus for the rubber-modified epoxy with various types and concentrations of rubber is shown in Figure 4.22.

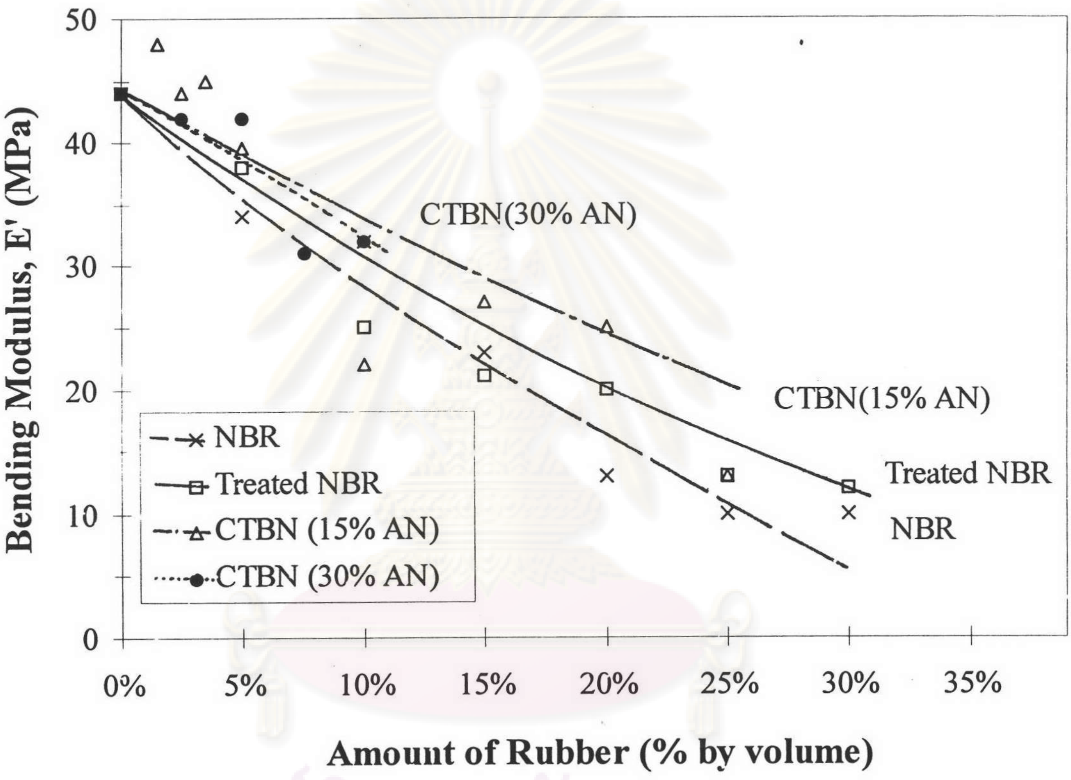

Figure 4.22: Bending moduli for various types and concentrations of rubber-filled epoxy systems.

This study found that the bending moduli for all types of rubber tend to decrease with the rubber content. This means that the rubber-filled epoxy system is more flexible than pure epoxy. The sequence of the ability of rubber to decrease the bending modulus of epoxy from low to high is CTBN with 30% AN < CTBN with 15% AN < treated NBR < NBR respectively.

Figure 4.22 shows that the rate of decreasing in bending modulus of the treated NBR is smaller than that of the untreated NBR. For pure epoxy, the bending modulus is 44 MPa but when 5 and 30 vol% untreated NBR is dispersed in the epoxy, the bending modulus is decreased to 34 MPa and 10 MPa respectively. For the treated NBR-filled epoxy system, an increase in the treated NBR content from 5 to 30 % results in a decrease in the bending modulus by 18 and 73 % respectively.

For CTBN-modified epoxy systems with 15% acrylonitrile, a decrease in the CTBN content from 1.5, 2.5, 3.5, 5, 10, 15, 20 and 25 % results in a decrease in bending modulus by 1.1, 1.8, 4.5, 9, 23, 34, 43 and 50 % respectively.

For CTBN-modified epoxy systems with 30% acrylonitrile, a decrease in the CTBN content from 2.5, 5, 7.5 and 10 % results in a decrease in the bending modulus by 4.5, 7, 15 and 20 %.

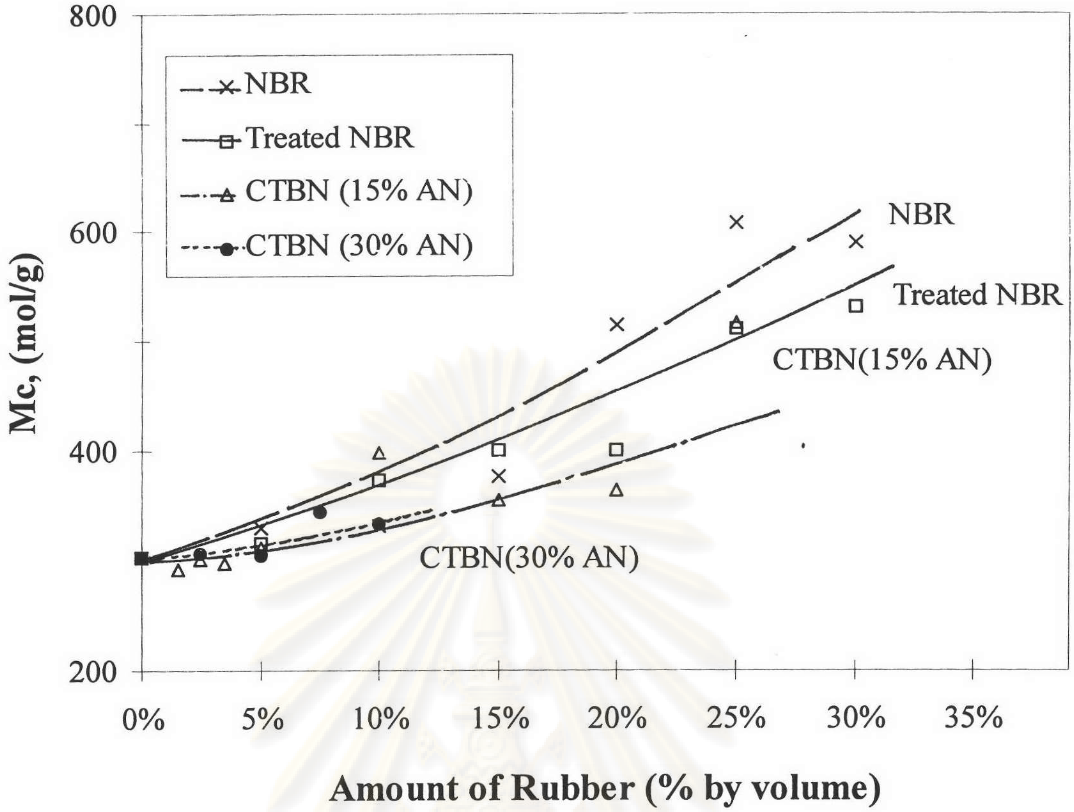

Figure 4.23: Molucular weight between crosslinks for various types of rubber-filled epoxy systems.

From Figure 4.23, it is apparent that molecular weight between crosslinks for all types of rubber-filled epoxy systems tends to increase with the rubber content. Pure epoxy has a molecular weight between crosslinks of 302 g/mol. Increasing the amount of CTBN with 15% AN, treated NBR and NBR rubber to 20 vol% can cause the molecular weight between crosslinks to increase to 390, 470 and 525 g/mol. This is equivalent to an increase by 29, 56 and 74% respectively. Also implied in Figure 4.23 is the sequence of the ability of rubber to increase the molecular weight between crosslinks. The order of the ability is CTBN with 15% AN < CTBN with 30% AN < treated NBR <

NBR respectively. In the case of CTBN with both 15% AN and 30% AN, the rate of increasing the molecular weight between crosslinks are closed to each other.

The strand density of the epoxy resin can also be found according to Equation 4.5.

$$\nu = G'/(K_B T) \qquad (4.5)$$

The term G' is the bending modulus at the temperature that the epoxy is in its rubber-like state. The term ν is the strand density. It is defined as the number of crosslinking chains per unit volume. Boltzmann's constant is represented by K_B in Equation 4.5; its value is $13.8*10^{-24}$ J/mol and T stands for the absolute temperature that induce the epoxy to be in its rubber-like state.

The strand density implies whether the epoxy resin has low or high degree of crosslinks. High strand density is related to high degree of crosslinks. Lower strand density relates more to the softening of epoxy.

The effect of various types of rubber and the rubber content on the strand density of rubber-filled epoxy systems is shown in Figure 4.24.

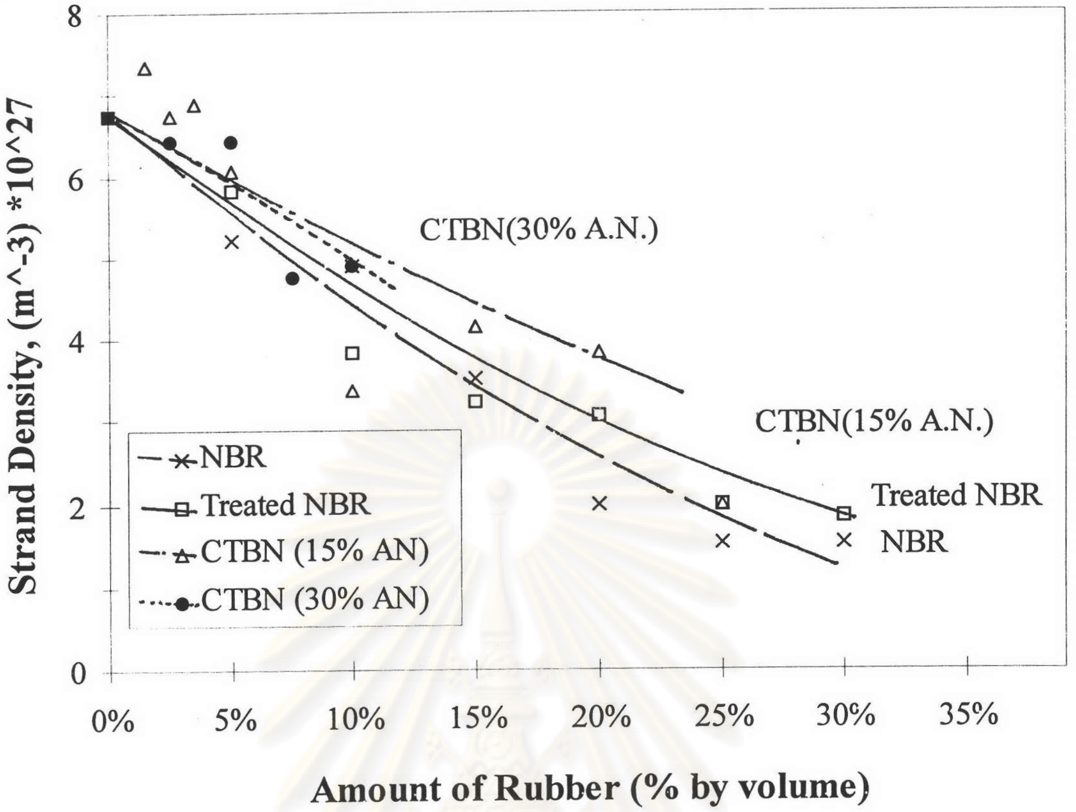

Figure 4.24: The strand density for various types of rubber-filled epoxy systems.

From Figure 4.24, it is apparent that the strand density of the rubber-filled epoxy systems decreases when the rubber content is increased. This is because the presence of the rubber particles in the epoxy matrix can interupt the crosslinking reaction between the epoxy and the curing agent.

The sequence of the ability of the rubber to decrease the strand density is CTBN with 15% AN < CTBN with 30% AN < treated NBR < NBR respectively. In fact, the rates of decreasing for CTBN with 15% AN and CTBN with 30% AN are close to each other. The rate of decreasing the strain density for CTBN is lower than that for the treated NBR and the untreated NBR because CTBN particles can react with epoxy molecules while treated NBR and untreated NBR hardly react or does not react with epoxy at all.

For NBR-filled epoxy systems, an increase in NBR content from 5, 10, 15, 20, 25 and 30 % results in a decrease in the strain density by 24, 41, 56, 68, 77 and 82 % respectively.

For treated NBR-filled epoxy system, an increase in treated NBR content from 5, 10, 15, 20, 25 and 30 % results in a decrease in the strain density by 19, 35, 49, 59, 68 and 74 % respectively.

For CTBN(15% AN)-filled epoxy system, an increase in CTBN content from 1.5, 2.5, 3.5, 5, 10, 15, 20 and 25 % results in a decrease in the strain density by 2.9, 6, 9, 12, 25, 40, 50 and 57 % respectively.

For CTBN(30% AN)-filled epoxy system, an increase in CTBN content from 2.5, 5, 7.5 and 10 % results in a decrease in the strain density by 10, 16, 27 and 29 % respectively.

4.2.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry or DSC is a thermal analysis instrument that can be used to test many plastics. The DSC has been used to determine the transition temperature and the heat flow associated with material transition as a function of time and temperature. It also provides quantitative and qualitative data on the endothermic (heat absorption) and the exothermic (heat evolution) processes of materials during physical transitions. This information helps in identifying the processing and end-use performance of the tested polymers.

One important transition property of plastic which can be tested with the DSC is the glass transition temperature (T_g). Figure 4.25 shows the glass transition temperature for various types of rubber-filled epoxy systems.

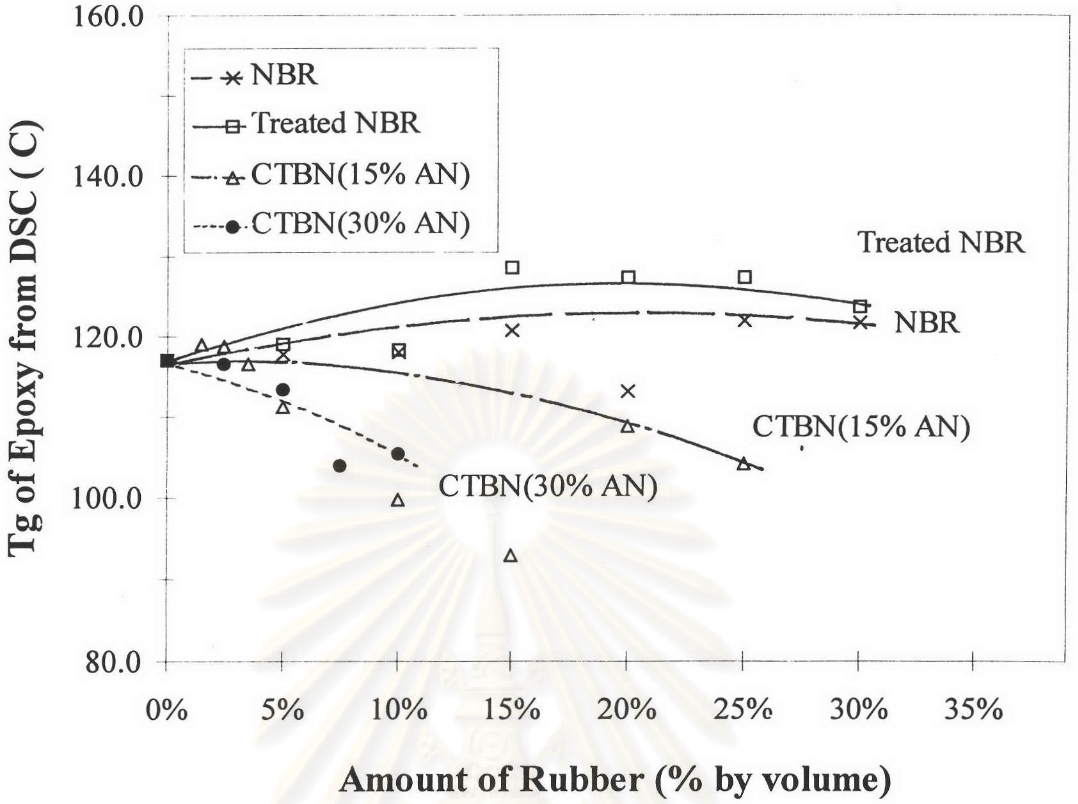

Figure 4.25: The glass transition temperature from the DSC test for various types and concentrations of rubber-filled epoxy systems.

The glass transition temperature found in the DSC test is not identical in value as that obtained in the DMTA test. This is because both equipments have a different rate of heating. Pure epoxy in the DMTA test has a T_g of 138 °C but in the DSC, the T_g was found to be 117 °C.

For DSC test, when NBR and treated NBR is filled in epoxy resin, the glass transition temperature of the epoxy tends to increase with the rubber content. But when CTBN with 15% AN and CTBN with 30%

AN is filled in epoxy, the glass transition temperature tends to decrease. Untreated and treated NBR both have very large particle size. Hence they tend to interupt the reaction of crosslinking between the epoxy resin and the DETA curing agent. Hence the T_g tends to increase. However, the T_g of the CTBN-filled epoxy resin shows a decrease with increase CTBN content because CTBN particles was capable of reacting with epoxy resin. Interfacial bonding was developed and hence the epoxy resin with DETA and the CTBN system are considered partially compatible. Consequently, the T_g for CTBN-filled epoxy system is decreased.

For untreated NBR-filled epoxy system, an increase in NBR content from 5, 10, 15, 20, 25 and 30 % results in an increase in the T_g by 1.7, 2.6, 4.3, 4.7, 4.7 and 4.9 % respectively.

For treated NBR-filled epoxy system, an increase in treated NBR content from 5, 10, 15, 20, 25 and 30 % results in an increase in the T_g by 3.4, 6, 8.5, 9, 8.5 and 7.7 % respectively.

For CTBN(15% AN)-filled epoxy system, an increase in CTBN content from 1.5, 2.5, 3.5, 5, 10, 15, 20 and 25 % results in a decrease in the T_g by 0.4, 0.4, 0.9, 1.3, 3.8, 6.8, 9.4 and 11.1 % respectively.

For CTBN(30% AN)-filled epoxy system, an increase in CTBN content from 2.5, 5, 7.5 and 10 % results in a decrease in the T_g by 0.9, 3.8, 6.8 and 9.8 % respectively.

4.2.4 Fractographic Studies

The study of the fracture surface of the rubber-filled epoxy systems are shown in their fractographs in Figures 4.26 to 4.38.

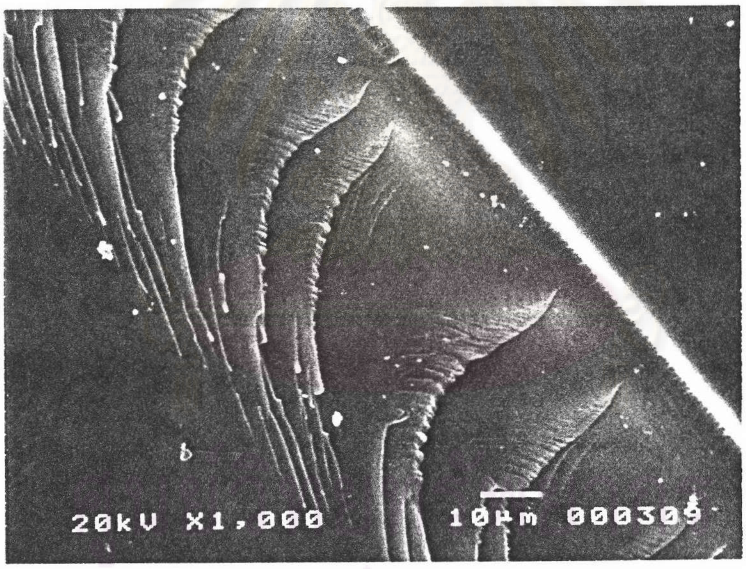

Figure 4.26: SEM photomicrograph of pure epoxy (1000X).

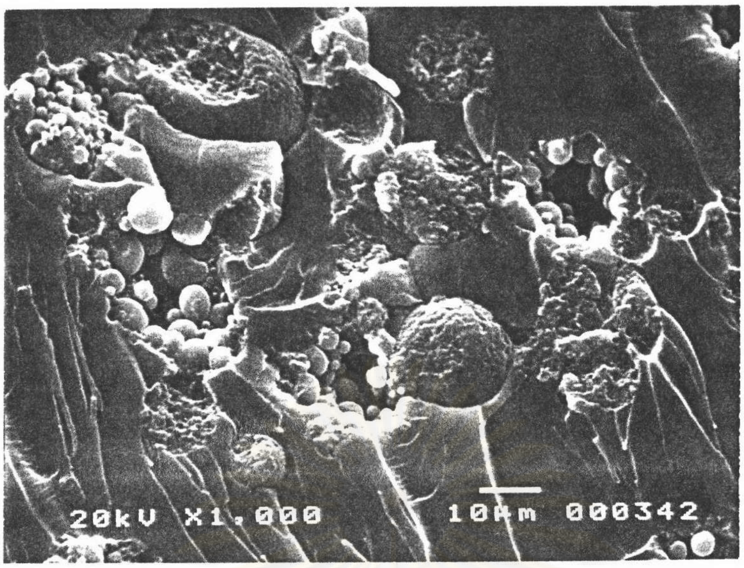

Figure 4.27: SEM photomicrograph of 10 vol% CTBN with 15% acrylonitrile-filled epoxy system (1000X).

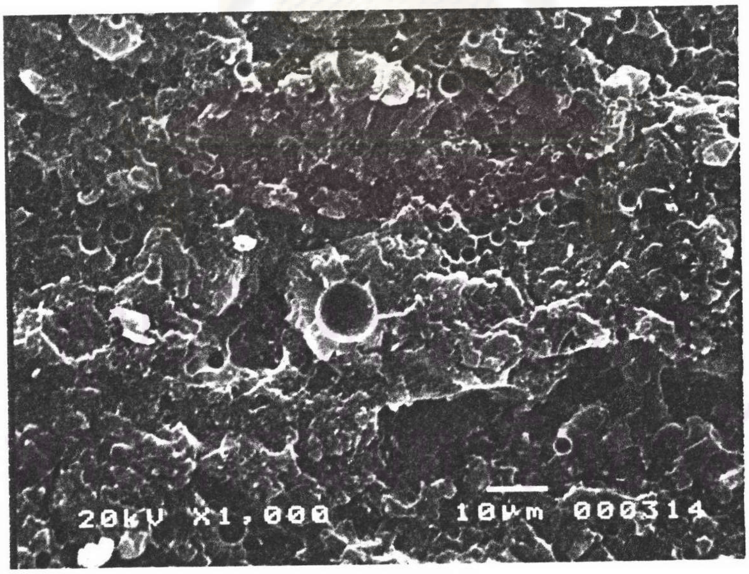

Figure 4.28: SEM photomicrograph of 10 vol% CTBN with 30% acrylonitrile-filled epoxy system (1000X).

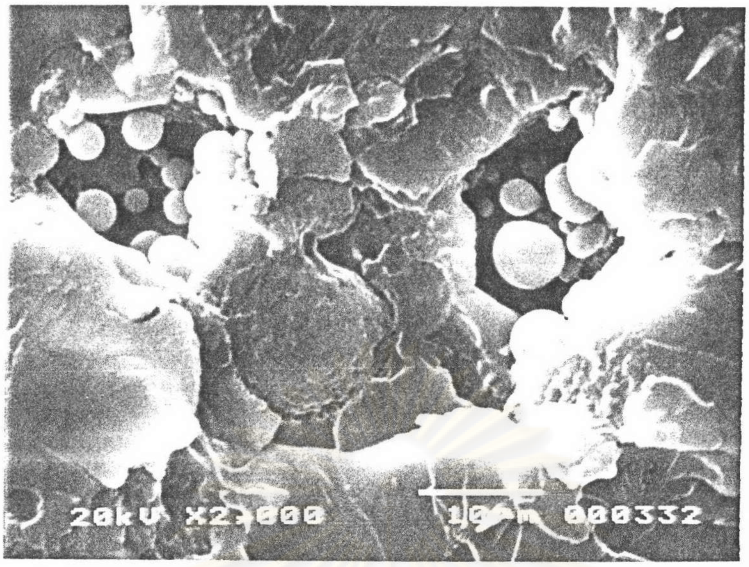

Figure 4.29: SEM photomicrograph of 10 vol% CTBN with 15% acrylonitrile-filled epoxy system (2000X).

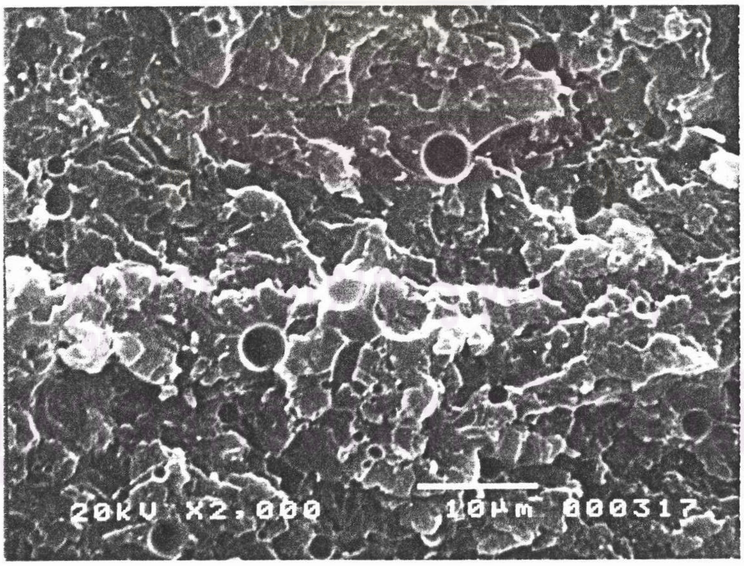

Figure 4.30: SEM photomicrograph of 10 vol% CTBN with 30% acrylonitrile-filled epoxy system (2000X).

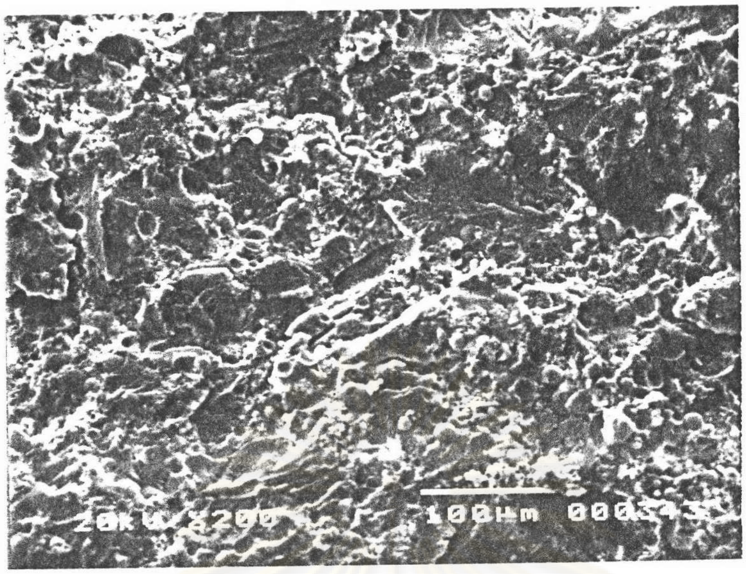

Figure 4.31: SEM photomicrograph of 20 vol% CTBN with 15% acrylonitrile-filled epoxy syste (200X).

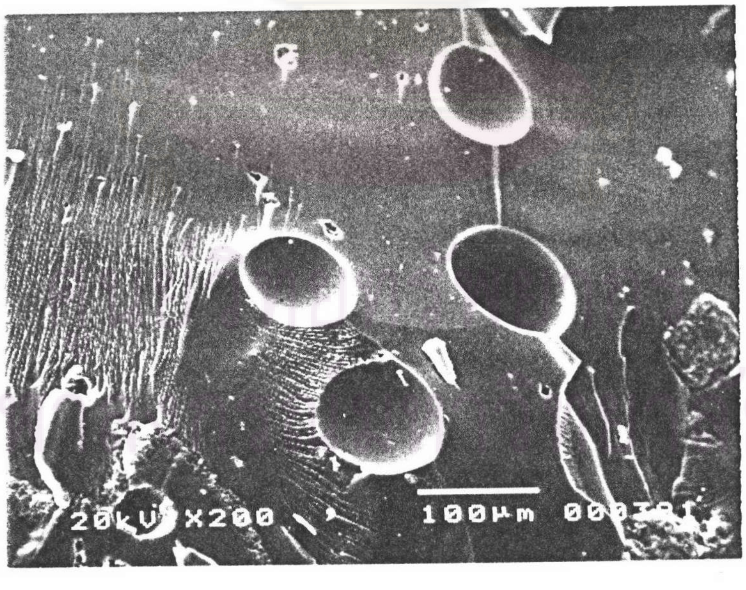

Figure 4.32: SEM photomicrograph of 20 vol% NBR-filled epoxy system (200X).

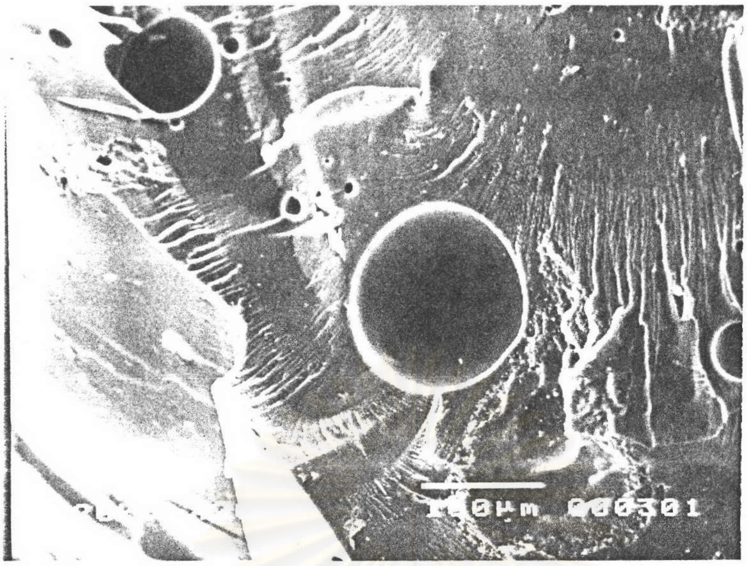

Figure 4.33: SEM photomicrograph of 20 vol% treated NBR-filled epoxy system (200X).

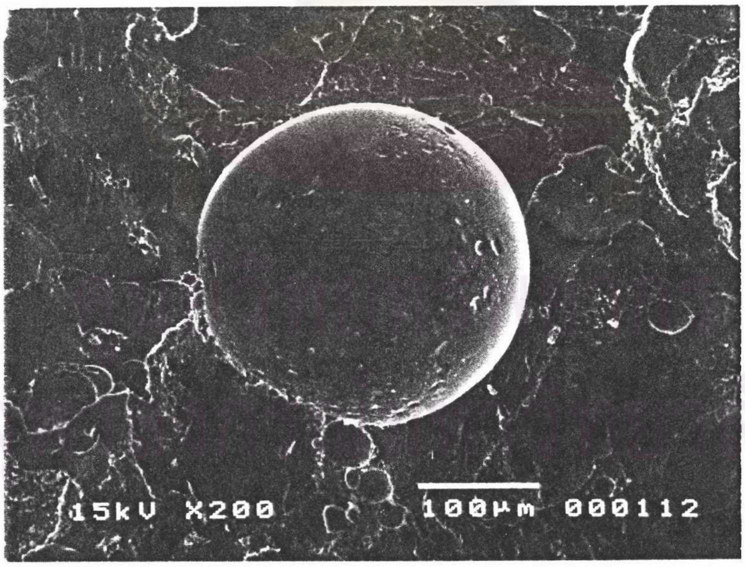

Figure 4.34: SEM photomicrograph of the hole from NBR-filled epoxy system (200X).

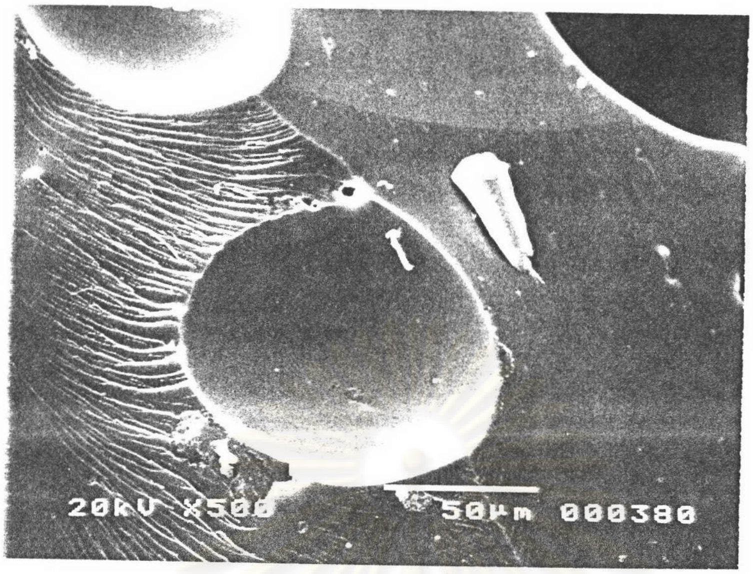

Figure 4.35: SEM photomicrograph of the hole from NBR-filled epoxy system (500X).

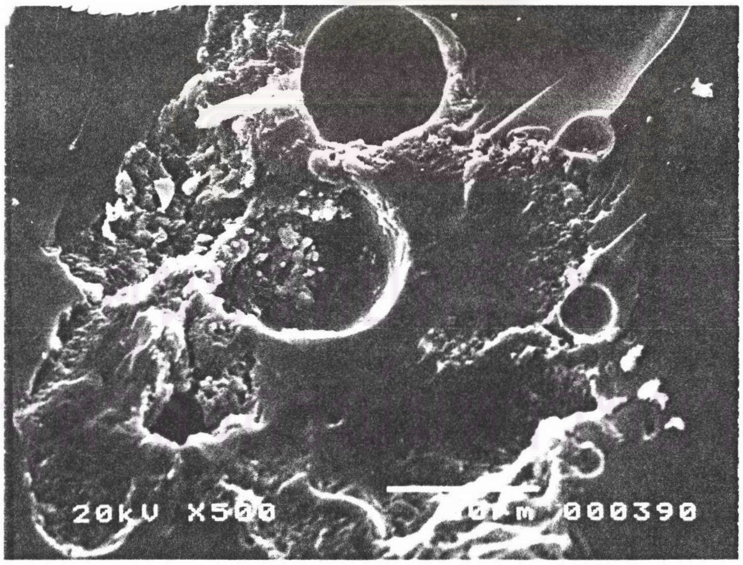

Figure 4.36: SEM photomicrograph of the hole from treated NBR-filled epoxy system (500X).

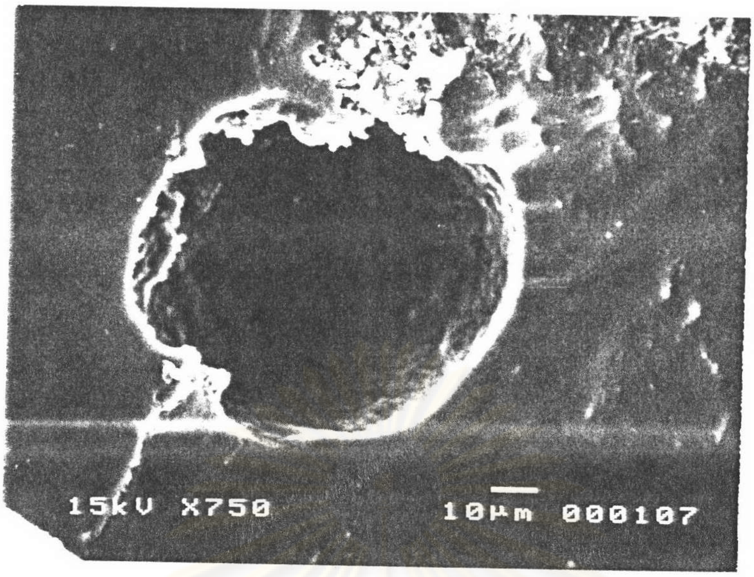

Figure 4.37: SEM photomicrograph of the hole from treated NBR-filled epoxy system (750X).

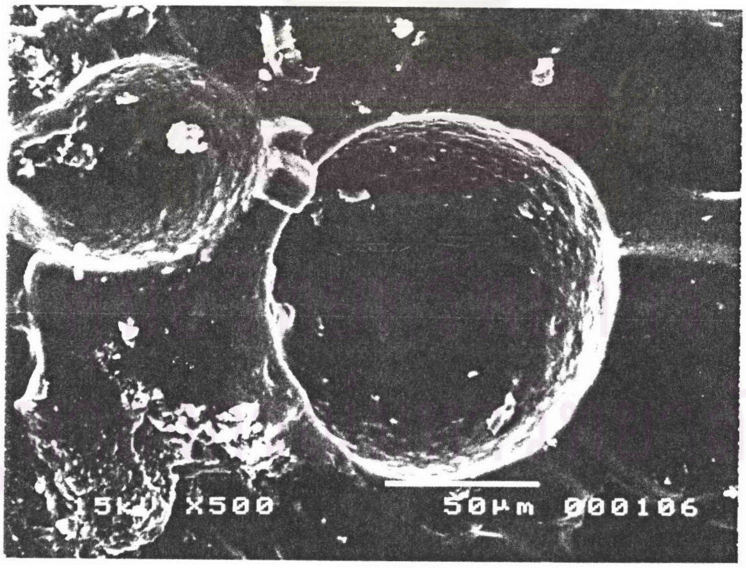

Figure 4.38: SEM photomicrograph of the hole from treated NBR-filled ,epoxy system (750X).

Figures 4.26 to 4.28 compare the surface of pure epoxy, CTBN with 15% acrylonitrile-filled epoxy and CTBN with 30% acrylonitrile-filled epoxy. Pure epoxy undergoes brittle fracture and its fracture surface is flat and smooth. The CTBN with 15% acrylonitrile-filled epoxy has a rougher surface than that of the pure epoxy. The CTBN particles fall within the range of 2-20 μm. The CTBN with 30% acrylonitrile-filled epoxy has the roughest surface and its particle size lies in the range of about 0.5-5 μm. It is apparent from Figures 4.27 and 4.28 that the dispersion of the CTBN with 30% acrylonitrile-filled epoxy is better than that of the CTBN with 15% acrylonitrile-filled epoxy. Smaller particle size from CTBN with 30% acrylonitrile can be dispersed more readily and throughly than those from CTBN with 15% acrylonitrile-filled epoxy which tend to form aggromerate.

Figure 4.29 and 4.30 also compare the CTBN with 15% acrylonitrile-filled epoxy system and the CTBN with 30% acrylonitrile-filled one but at a higher magnification. It can be seen clearly that the fracture surface of the CTBN with 30% acrylonitrile-filled epoxy system is much rougher than that of the CTBN with 15% acrylonitrile-filled one. This is the reason why CTBN with 30% acrylonitrile-filled epoxy is much tougher than CTBN with 15% acrylonitrile.

Figures 4.31 to 4.33 show a comparison of the fracture surface between the CTBN with 15% acrylonitrile-filled epoxy system, NBR-filled and the treated NBR-filled one. It is seen that the fracture surface of CTBN with 15% acrylonitrile-filled epoxy system is much rough than the others. This supports the results that CTBN with 15% acrylonitrile-filled epoxy system is tougher than NBR and treated NBR-filled epoxy systems. The surface of the NBR and treated NBR-filled epoxy systems do not exhibit any significant difference. Both of NBR and treated NBR-filled epoxy systems are more brittle than the CTBN-filled ones.

Figures 4.34 and 4.35 show the hole which occured after the NBR particle from NBR-filled epoxy system had fallen out of the fracture surface. The surface of the hole is flat and smooth. This implies that very little or no interfacial bonding between the NBR particle and the epoxy matrix occurs.

Figures 4.36 to 4.38 show the hole which occured after the treated NBR had fallen out of the surface. It can be seen that some parts of the NBR rubber particles still bonded at the surface of the epoxy matrix. The surface of the hole is not completely flat and smooth. Instead, it is rough which implies that some plastic deformation had taken place during fracture. This clearly verifies that the NBR which had been treated on the surface with the titanate coupling agent forms some interfacial bonding with the epoxy matrix. However, the bonding is still not strong enough to prevent the NBR particle from falling out of the matrix.