Fracture Behaviors of Metallocene Catalyzed Polyethylene Elastomer Via Peroxide Crosslinking

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ABSTRACT: Peroxide cured metallocene catalyzed polyethylene (mPE) has been prepared to form an elastomer. mPEs with two different levels of comonomer contents have been cured with various amounts of dicumyl peroxide. "Threshold" fracture energy is roughly proportional to the reciprocal square root of Young's modulus. The values of tear strength are generally two orders of magnitude larger than the results from cutting measurements. The cutting strength of mPE vulcanizates gives an intermediate value compared with crystalline plastics and conventional elastomers and is comparable with other evaluations of cutting strength for different crosslinking types of mPE and different types of materials, which further signifies the importance of crystalline yielding even in the nano-fracture zone of deformation. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3791–3798, 2009

Key words: metallocene polyethylene; peroxide crosslinking; fracture behaviors; depth of flaw (natural flaw size)

INTRODUCTION

Thermoplastic elastomers (TPEs) generally exhibit elastomeric characteristics, yet can be easily processed as thermoplastics. Thus, TPEs have been used in numerous applications in the past.[1] Major classes of TPEs include block copolymers, blends of elastomers with thermoplastics, and metallocene polyethylene elastomer (mPE), among others. Most interestingly, mPE is not only treated as a TPE for processing convenience but also as a conventional elastomer for the requirement of low compression set. The successful development of mPE is considered to be one of the most significant achievements in recent years.[2–4] Tremendous work has been done to understand this unique polymer. This work is carried out to investigate the fracture behaviors of this peroxide-cured elastomer.

As mPE is a low-crystalline elastomer, several factors inclusive of crosslinking types, curing degree, crystallinity, and morphology can affect fracture behavior. For conventional elastomers without crystalline effect, the authors' earlier work has presented the role of the crosslinking types in providing strength to polybutadiene rubber and styrene-butadiene rubber (SBR) under a viscoelastic response.[5] Threshold fracture energy measured under a minimized energy dissipation condition is found to be proportional to the square root of number average molecular weight between crosslinks for a peroxide crosslinked elastomer.[5–7] The strength of material is generally governed by the effective crack tip diameter varied with a viscoelastic condition.[8] For crystalline material, enhanced energy dissipation from crystalline effect has to be considered. Highly crystalline material like high-density polyethylene (HDPE) has been studied to determine the fracture zone of deformation in an order of spherulite size and to elucidate the importance of crystalline region on the strength of materials.[9,10] To the authors' knowledge, except for those amorphous elastomers and conventional thermoplastics, there is limited literature available that discusses the aforementioned factors on the strength of this peroxide-cured crystalline elastomer. The study aims to apply the previous theories for a thorough study on this low-crystalline elastomer. Previous attempts to bring about the evolution of depth of flaw (natural flaw size) for silane-cured mPE, in comparison with other amorphous elastomers, showed a promising approach on the basis of an elaborate treatment.[11] Care should be taken to apply the basic assumption of the conventional elastomer possessing elasticity.

In this study, mPE with a different cured degree was imparted with peroxide. Both factors (crosslinking and crystallization) would affect the interfacial strength and ultimate properties of materials.[5,12] The recently developed correlation of tear strength and tensile strength for both conventional elastomers and silane-cured mPE elastomer[6,8,11] is applied to derive

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a corrected depth of flaw for this peroxide-cured mPE. The determination of effective crack tip diameter and threshold fracture energy is also used.[13–17] The cutting test to confine a crack tip is performed to elucidate the importance of crack tip diameter.[8,14,17] Several types of other polymers listed in the literature are summarized and compared to assess the effect of crystalline yielding and crosslinking types for mPE elastomers.

EXPERIMENTAL

Materials

The materials used in this study were mPEs. MPEs with a melt index of 1.0 were supplied from Dow Corporation under the trade name of EG8100 and EG8003 corresponding to octene comonomer contents (%) of 38 and 30, respectively. Dicumyl peroxide (DCP, Coin Akzo Nobel Co., Taipei, Taiwan) was the reagent used to impart curing on mPE.

Sample preparations

mPE with various dosages of peroxide (0.2, 0.5, 1, and 2 phr) was premixed using an internal mixer (Brabender 815,605, Plastograph) under 25 rpm and equilibrated for 10 min at 110°C. The dosage of peroxide incorporated was based on the weight of mPE. This low mixing temperature would prevent the scorch of mPE as well. The resulting batches were hot pressed to form a thin sheet in a compression molding machine. Curing was then effected at a prescribed temperature of 160°C for 35 min. Tensile test specimens complied with ISO-37 Type (III) standard were then prepared through a die cut. Trousers tear test specimens with a thickness of 1 mm were prepared with a backing cloth at one side and a center groove of 0.2 mm deep at both sides to guide crack propagation. Thus, the thickness that remained to be torn through was about 0.6 mm. Cutting test specimens with a thickness of 1 mm were also prepared with a backing cloth at one side to prevent an extension of sample legs under load.

Measurements

Thermal characterizations

Continuous extraction of cured samples in boiling p-xylene) (140°C) corresponding to ASTM D 2765-90 was carried out using a Soxhlet extraction method. The gel content was calculated by the ratio of the weight of dried insoluble samples to the weight of samples before swelling. The glass transition temperature (T_g) was determined via a dynamic mechanical analyzer (Perkin Elmer, Pyris Diamond) under a tension mode at a frequency of 1 Hz and at a heating

rate of 5°C/min from –80 to 30°C. The melting temperature (T_m) was measured using a DSC (DuPont, TA Q10) at a heating rate of 10°C/min from 5 to 120°C. The crystallinity was calculated by dividing the heat of fusion by the enthalpy required for 100% crystallinity equal to 289 J/g.[18] Thermogravimetric analysis (Perkin Elmer Pyris 1) was used to evaluate the thermal stability of the vulcanizates with the heating rate of 20°C/min from 40 to 800°C.

Mechanical tests

Tensile measurements were conducted based on ASTM-D638 at a crosshead speed of 20 cm/min under various test temperatures ranging from room temperature to 100°C using a Instron 4469. Tensile strength, elongation, and Young's modulus were recorded. Energy density (U_b) under a stress–strain curve was likewise determined. Trousers tear test was carried out in a similar condition to determine the fracture energy (G_c) for this type of vulcanizate, where

$$G_c = 2F/t \qquad (1)$$

where F is the minimum force required to propagate a crack and t is torn thickness.

The evaluation of effective edge crack depth (c) was calculated from the following equation[6,8]

$$G_c = U_b \times 2\pi c_o = U_b \times c \qquad (2)$$

where c_o is the depth of flaw (natural flaw size) and c is the effective edge crack depth. In this case, the effective edge crack depth is much larger than the crack tip diameter.

In addition, cutting test was also used to measure the fracture energy (G_c) using a razor blade at a cutting speed of 10 mm/min at approximately room temperature. The schematic sketch of the cutting test is shown in Figure 1. Pulling energy (P) and cutting energy (C) were calculated as follows[8,17]:

$$P = 2f_A(1 - \cos\theta)/t \qquad (3)$$
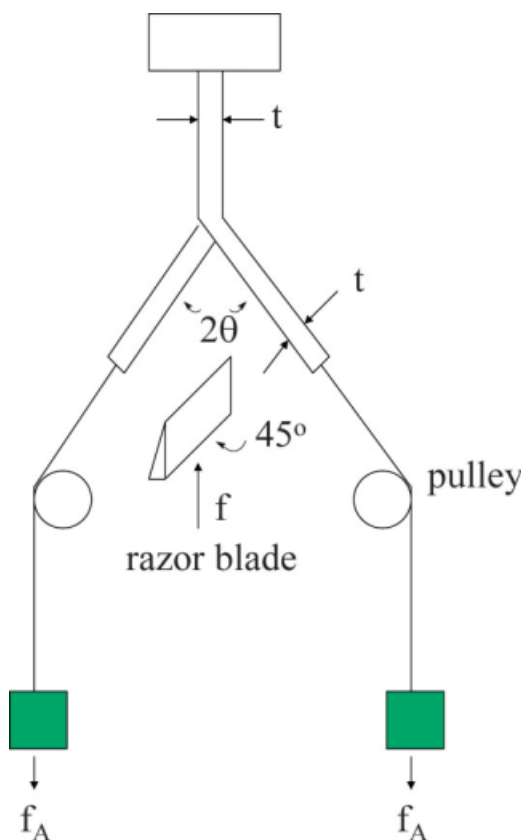
$$C = f/t \qquad (4)$$

where f_A is the load, f is cutting force, 2θ is angle between two legs, and t is cut thickness.

By measuring the cutting force and angle, the fracture energy G_c was calculated from the sum of energies expended in both pulling and cutting, i.e.,

$$G_c = P + C \qquad (5)$$

RESULTS AND DISCUSSION

In this study, two types of mPEs have been investigated. A representative mPE 8003 was presented

Figure 1 Schematic sketch of cutting test. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

unless otherwise stated. The authors have no intention of comparing the strength of these two materials. The purpose of presenting two materials is to demonstrate the application of earlier theories for conventional elastomers (without crystalline effect) which has some limitations as applied to mPE vulcanizates with low crystallinity. Various types of properties including tensile strength, tear strength, and cutting strength were carefully correlated to derive the natural flaw size and effective crack tip diameters. In addition, the results of silane-cured mPE in the previous work were adapted for comparison in some cases.[11]

Thermal characterizations

Gel levels were measured for each resin cured under different peroxide concentrations. Figure 2 shows the gel contents for the two types of mPEs investigated in this study. As the dosages of peroxide increased, gel contents increased until they leveled off at higher amounts of peroxide. Maximum values of gel content were attained at 97.3% and 99.5% for mPE 8003 and mPE 8100, respectively. The differences in gel contents for both resins under the same peroxide levels were relatively small, but were higher than silane-cured mPE at 77.8% and 71.8%
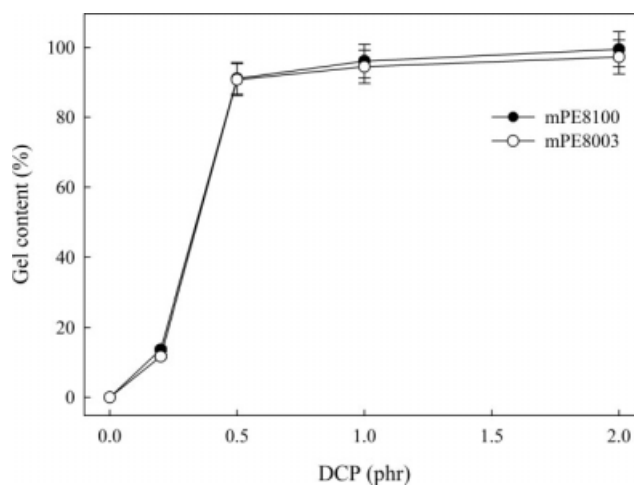
Figure 2 Gel contents of mPE 8100 and 8003 at various peroxide-curing degrees.

for mPE 8003 and mPE 8100, respectively.[11] As several factors including comonomer content, comonomer distribution, molecular weight distribution, polydispersity, etc., are involved in a complicated manner, a concrete explanation is not given here.

To investigate the effect of curing on the thermal behavior of mPE, the glass transition temperatures (T_g) based on tan δ curves recorded from a dynamic mechanical analyzer were evaluated and the results shown in Figure 3 for mPE 8003 vulcanizates. The glass transition temperatures remained largely unchanged in this investigated dosage levels. A similar behavior was found for mPE8100 vulcanizates. For a quick comparison, the melting temperature (T_m), the heat of fusion (ΔH), and the crystallinity assessed using differential scanning calorimetry are listed in Table I for mPE with various peroxide contents. It seemed that the melting temperatures
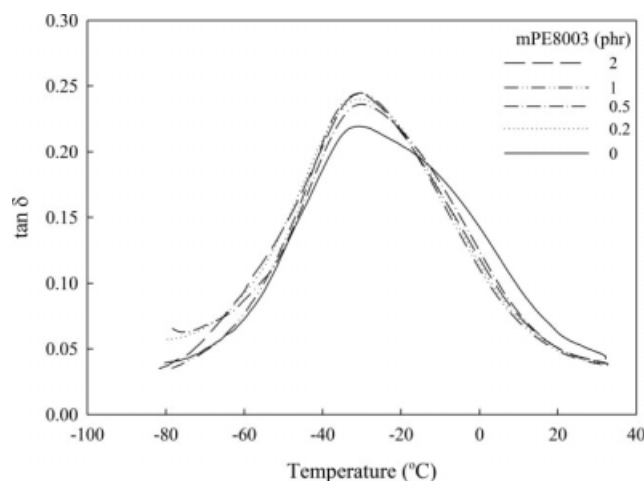
Figure 3 Typical tan δ curves recorded from the dynamical mechanical analyzer for mPE 8003 at various peroxide curing degrees.

TABLE I
Thermal Analysis of mPE with Different Peroxide Contents

mPE types	Peroxide (phr)	T_g (°C)	T_m (°C)	ΔH (J/g)	Crystallinity (%)
mPE 8003	0.0	−30.7	78.3	51.8	17.9
	0.2	−30.5	78.1	50.8	17.6
	0.5	−30.5	77.4	50.5	17.5
	1.0	−30.5	76.9	50.1	17.5
	2.0	−30.4	76.4	48.8	17.2
mPE 8100	0.0	−38.0	62.0	27.1	9.4
	0.2	−37.8	61.3	27.0	9.3
	0.5	−37.6	60.9	26.6	9.2
	1.0	−37.6	60.7	25.2	8.8
	2.0	−37.4	59.4	25.0	8.8

decreased from 78.3°C to 76.4°C with increasing curing degree. This is probably so because the restricted molecular chain tended to disrupt the molecular packing within mPE, which caused the entropy to increase. This increase would reduce the melting temperature based on the thermodynamic point of view. Additionally, no notable differences are found on the effect of the degree of cure on melting behavior and crystallinity. Thus, for mPE with low crystallinity, only the limited effects of curing degree was observed.

"Threshold" fracture energy

The tensile strength of mPE 8003 elastomer at various peroxide-curing degrees under different test temperatures is depicted in Figure 4. Tensile strength, as expected, decreased from 27.9 ± 1.1 MPa at 25°C to 0.5 ± 0.04 MPa at 100°C from a viscoelastic point of view. As for the effect of curing degree, tensile strength varied slightly with increasing the levels of peroxide concentrations at all test temperatures. In this case, when the crystalline region of mPE melted at test temperature approaching 80°C, tensile strength tends to increase, and the

values at low peroxide levels were not measurable. If one considered the previous changes in crystallinity to be marginal, then the current results would represent the sole effect of curing degree, especially at the temperature above melting temperature of mPE. As a matter of fact, when the tensile strength was measured at test temperature above 80°C, the phenomena became more obvious.

To further compare the strength of this material, the tear strength, which measures fracture energy, is evaluated. Figure 5 illustrates the tear strength of a representative vulcanizate (mPE 8003) at various dosages of curing under different test temperatures. A significant drop of tear strength in temperature from above 60°C close to the melting temperature of mPE 8003 approximately 80°C was observed. At a specific temperature, tear strength continued to decrease with increasing degree of crosslinking. Some data points were not available due to the melting of materials with low degree of cure at the temperatures above 80°C. Again, if one could leave out the effect of marginal change in crystallinity, the sole effect of curing degree can be seen to be clearly dominant in tear strength.
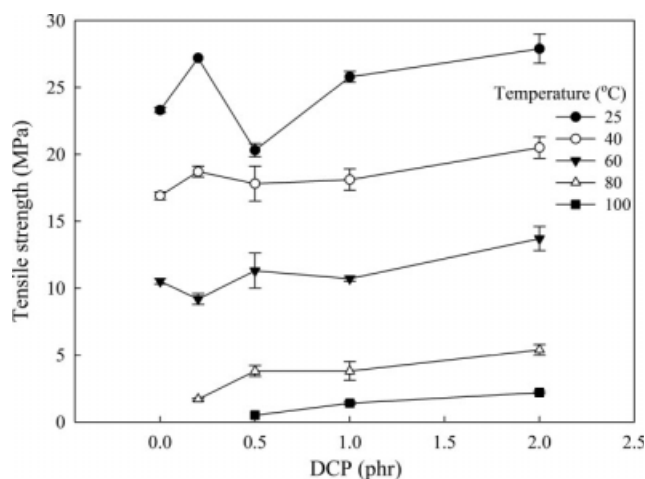

Figure 4 Tensile strength of mPE 8003 at various peroxide-curing degrees under different test temperatures.
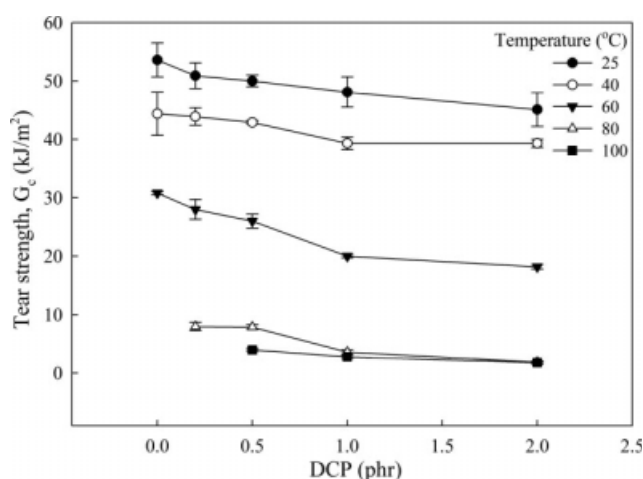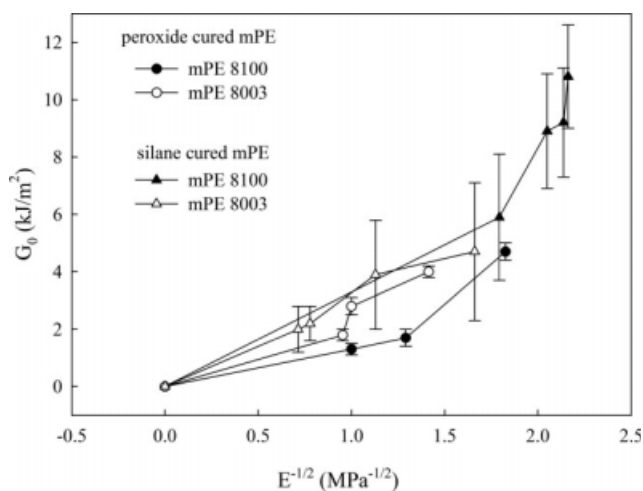

Figure 5 Tear strength of mPE 8003 at various peroxide curing degrees under different test temperatures.

Figure 6 Threshold fracture energy plotted against reciprocal square root of modulus (results of silane-cured mPE were adopted from Ref. 11).

As crystalline regions also affect the strength of materials aside from the crosslinking phenomena mentioned earlier, an attempt to rule out this effect was made to deliberately increase test temperatures above the melting temperature of mPE. With this arrangement, the effect from crystal deformation of mPE on tear strength was minimized. Fracture energy dropped significantly up to one tenth of the values obtained at room temperatures. Contributions to the low strength of fracture energy came only from the crosslinking effect at high temperature.

Based on the theory developed by Lake and Thomas[13] for an elastomer, the threshold fracture energy of an elastomer with C—C, C—O—C, and C—O—O—C crosslinks wherein energy dissipation was minimized is linearly proportional to the square root of molecular weight between crosslinks. According to the theory of elasticity, the molecular weight between crosslinks is reciprocal to modulus. Young's modulus was determined at the highest temperature) (100°C) available for mPE 8003; some of the results at higher temperature were not available due to a low degree of cure that can cause the melting of materials. Representative results at the highest temperature, termed threshold fracture energy, were plotted against the reciprocal square root of modulus, shown in Figure 6. The theoretical infinite E at the origin represents an infinite amount of crosslinking degree, which leads to the numbers of molecular bonds or molecular weight between crosslinks reaching a simple C—C bond level. An infinite small value of fracture energy can be deduced.[13] It is to be noted that the quoted values at the origin are not measured values, but theoretical numbers. It seemed that a linear relationship exists at this temperature under reduced dissipation for both resins cured under peroxide and silane. A

slight deviation at the lower modulus region has been explained in the previous work on silane-cured mPE[11] as the degree of cure for Si—O—Si crosslinks was still not high as compared with these C—C, C—O—C, or C—O—O—C crosslinks types induced by peroxide curing. A small portion of uncured molecular chain may flow significantly at high temperature, which makes the current theory invalid. This theory is based on the assumption that all the bonds of one molecule between crosslink points must be stressed to break a single bond. It is implied that the less the amount of crosslinks in an elastomer, the higher is the value of fracture energy. This accounts for the results of tear strength in Figure 5.
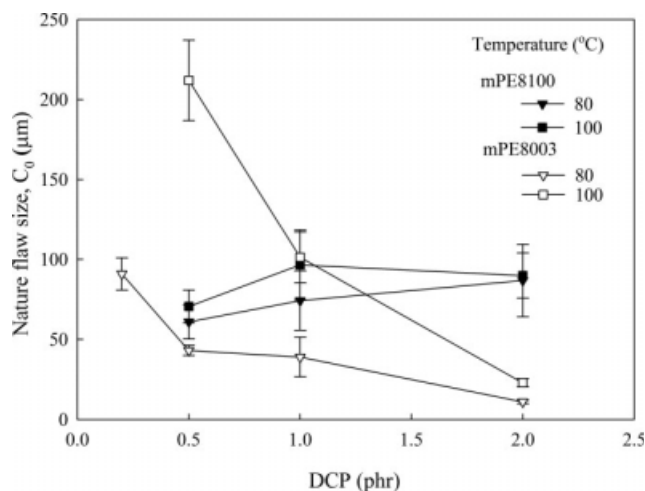
Corrected depth of flaw (natural flaw size): a correlation between tensile strength and tear strength

By determining the relationship of tensile strength to tear strength, energy density is calculated and shown in Figure 7. Based on the results at room temperature, energy density did not vary greatly with increasing peroxide concentrations, except that of mPE 8100 at high dosages of peroxide. In addition, the values of mPE 8003 were slightly higher than those of mPE 8100. When a comparison was made at different temperatures, energy density decreased with test temperatures due to the aforementioned explanations in Figure 4.

To further understand the details of fracture phenomena for this vulcanizate, the previous theory was tested by deducing the depth of flaw (natural flaw size) from energy density and tear strength according to eq. (2); this is shown in Figure 8. These values decreased slightly with increasing peroxide
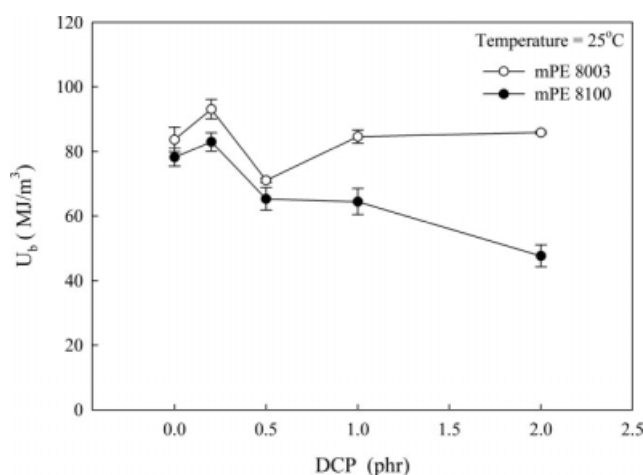
Figure 7 Energy density of mPE with different peroxide contents at 25°C.

Figure 8 The depth of flaw (natural flaw size) of mPE with different peroxide contents at various temperatures.

concentrations and tended to level off at a peroxide concentration above 1 phr. Likewise, when the comparison was made at varying temperatures, the values of depth of flaw were seen to vary widely. This is contradictory to the physical sense of the depth of flaw, wherein the value should be independent of test temperature. The reason that may account for this observation is that the application of theory becomes invalid when materials lose their elasticity.

Both crystalline domains and low degree of cure resulting in the loss of elasticity would be major limitations of previous theory as mentioned in our other study.[11] Thus, at 0 phr of curing, the deviation from elastic behavior is noticeable. The corrected average depth of flaw should be determined at a relatively higher curing degree and lower crystalline effect. In the silane-cured system, the maximum curing degree was low, so the previous comparison was made below the melting temperature of resin to treat the crystalline region as pseudo-crystallinks. In this case, as the peroxide curing degree was high, the comparison was made above the melting temperature to eliminate the crystalline effect. Hence, to account for the experimental errors obtained when measuring the strength of materials, all test temperatures above 80°C at peroxide dosage levels from 1 to 2 phr were taken into consideration. The corrected average depth of flaw was found to be within the range of 65 ± 33 μm. These values were slightly higher than those derived from the silane-cured system (40.5 ± 11.0 μm)[11] and the natural flaw size of 40 ± 20 μm obtained from several different approaches.[16] This implies that the application of the previous theory for conventional elastomer (without crystalline effect) to these developed low-crystalline vulcanizate materials still requires further modification to fulfill the basic assumption of elasticity.

Effective diameters of fracture zone

To further give an insight on the fracture phenomena for the vulcanizate, the following is presented. The effective diameters of fracture zones deduced from intrinsic energy density and tear strength according to the following equation ranged from 10.7 to 0.4 μm for mPE8003, and from 10.2 to 0.3 μm for mPE8100. This was observed in test temperatures between room temperature and 100°C, if one takes intrinsic strength as 5 GJ/m^3 as stated in the literature.[8,13,17,19] This correlation was established by Rivlin and Thomas.[6]

$$G_c = U_t \times d \tag{6}$$

where U_t is the energy density at the crack tip and is an intrinsic strength of material, and d is the crack tip diameter. The results at room temperature for both resins are illustrated in Figure 9. Effective crack tip diameters ranged from 10.7 to 9.0 μm for mPE8003 and from 10.2 to 8.3 μm for mPE8100 at room temperature. The crack tip diameters slightly decreased with increasing peroxide contents. Similar treatments on the fracture zone were compared, giving an effective diameter of 15 μm for HDPE and 18 μm for low-density polyethylene (LDPE).[10]

To further confine the crack tip diameters at a nanoscale using a sharp razor blade, the cutting strength was evaluated. A typical curve of cutting strength for mPE8003 at 2 phr of peroxide is shown in Figure 10. A negative slope of −1 is successfully drawn to obtain the cutting strength of 719 ± 51 J/m^2, which was dramatically lesser than the tear strength 45.1 ± 2.9 kJ/m^2.
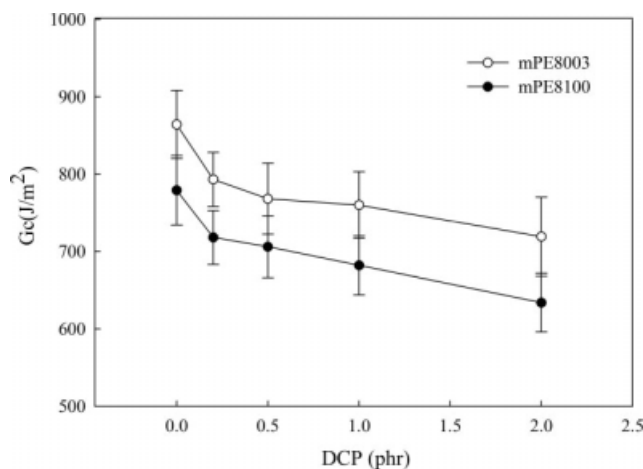
More measurements for comparison of cutting strength were carried out to reduce macroyielding effect for two types of mPE vulcanizates. The results
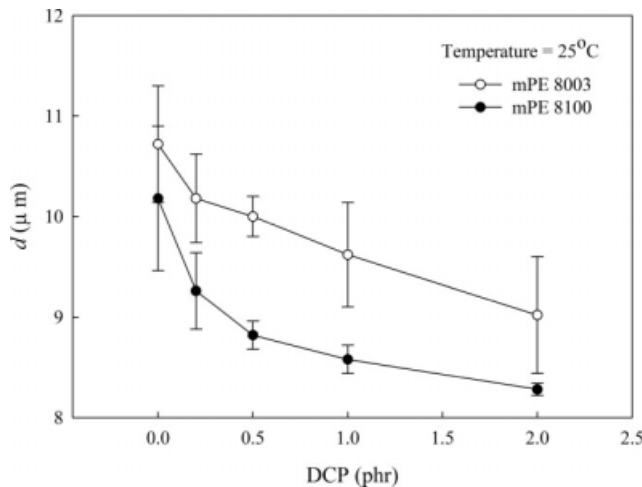
Figure 9 The effective crack tip diameter of mPE with different peroxide contents at 25°C.
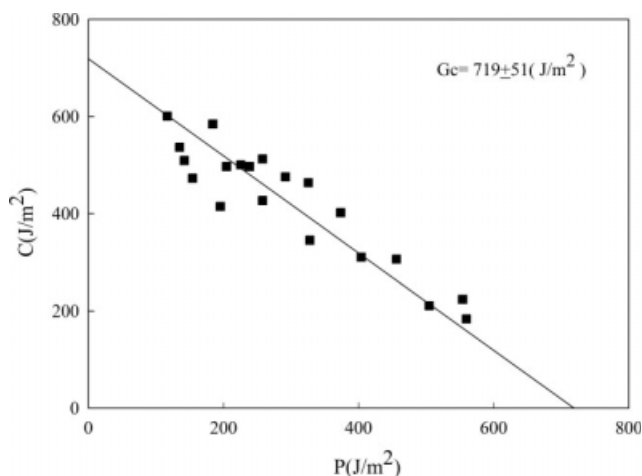
Figure 10 Cutting strength of mPE8003 (2 phr peroxide) at 25°C.

Figure 11 Cutting strength of mPE at various peroxide contents at 25°C.

are depicted in Figure 11. The lowest value attained is approximately 634 ± 38 J/m^2. The cutting strength decreases slightly as seen in the authors' other work.[8] As the peroxide concentrations seem to be saturated at higher levels, only marginal difference is observed. These values are not previously evaluated in the literature, but are found to be comparable with other methods of evaluation of cutting strength for different types of materials, e.g., HDPE,[10] SBR,[8] styrene–butadiene–styrene (SBS),[19] polypropylene/ethylene propylene diene monomer thermoplastic vulcanizate (PP/EPDM TPV),[14] and silane-cured mPE[11] (Table II). Lower values of cutting strength are normally observed in conventional elastomers without crystalline effect, such as silicon rubber and SBR. Higher values of cutting strength for crystalline materials (LDPE and HDPE) indicate that the crystalline yielding effect still dominate the

strength of material even when using a blade to reduce the zone of deformation. TPE (SBS and mPE) belong to the intermediate order of cutting strength. Cutting strength also slightly decreases with increasing degree of cure, which is demonstrated using cured mPE and SBS.

It can be noted that cutting test does reduce the zone of deformation to a certain degree when compared with tear measurements. If one takes intrinsic strength as 5 GJ/m^3 from the literature,[8,13,17,19] the effective diameter would seem to range from 0.17 to 0.14 μm for mPE8003 vulcanizate, and 0.16 to 0.13 μm for mPE8100. These values are close to the estimated blade diameter of approximately 0.1 μm at room temperature under controlled settings and are about two orders of magnitude smaller than the results from tear measurements. Apparently, these values are a measure of the extent of plastic yielding

TABLE II
Cutting Strength of Various Types of Polymers

Polymer types	Examples	G_c (J/m^2)	References
Conventional elastomer	Silicon rubber	70	10
	Styrene–butadiene rubber (high styrene content) crosslinked with 0.5 phr DCP	250 ± 15	8
	Styrene–butadiene rubber (high styrene content) crosslinked with 2.5 phr DCP	140 ± 10	8
Thermoplastic elastomer	SBS copolymer	570 ± 20	20
	SBS crosslinked with 0.1 phr DCP	375 ± 12	20
	PP/EPDM (Santoprene)	970 ± 65	14
	Two metallocene PEs (mPE) with different crystallinity	$908 \pm 62, 783 \pm 82$	11
	Two mPEs crosslinked with 3 phr silane	$571 \pm 29, 541 \pm 57$	11
	Two mPEs crosslinked with 2 phr peroxide	719 ± 51 634 ± 38	This work
Semicrystalline plastics	LDPE	1000 ± 200	10
	HDPE	4000 ± 500	10

around the tear tip, and compatible observations are reached for this prepared vulcanizate.

Energy dissipation: a comparison of tear strength and cutting strength

As reported in the authors' previous study, the higher the energy dissipation, higher is the strength.[5] Strength is predominately governed by the energy dissipation process, such as viscoelastic process (testing speed and temperature), crystalline yielding effect, crosslink types, etc., which in turn determines the magnitude of effective crack tip diameter. The small difference in the test speeds for the low T_g polymers for both tests was neglected based on the previous work on other systems involving a wide range of speed and temperature.[5,8] For instance, tear strength at 10 mm/min for mPE 8003 (0 phr) at 25°C is 48.1 ± 5.6 kJ/m^2, which is only approximately 10% difference in comparison with that at 20 cm/min. Most importantly, the difference in tear strength and cutting strength lies in the zone of fracture deformation (i.e., crack tip diameter, d) attained for different loading behavior. For tear test, the crack tip is not confined; instead it depends on the blade tip diameter as seen in cutting test. Even in the case of threshold fracture energy (the lowest measurable tear strength) for mPE vulcanizates, the values are in an order of kilo Joules per square meter and are still higher than those values equal to a few hundred Joules per square meter obtained at cutting test (Figs. 5 and 11).

As discussed earlier, the blade tip diameter is 0.1 μm. The fracture zone of deformation attained for tear measurement for low crystalline is still higher than that for the cutting measurement. On the other hand, the threshold fracture energy was lower than that of cutting strength for highly crosslinked SBR without crystalline effect as observed in the previous study.[8] Those differences are again attributed to the energy dissipation process. A high crosslinking degree of elastomer without crystalline yielding effect gives low fracture energy. The mPE vulcanizates, which possess a low crystalline yielding effect, still conferred high fracture energy, unless a limited controlled crack tip diameter is enforced as seen in the cutting measurement. The types of crosslinks were not dominant when comparing carbon–carbon related bonds with siloxane crosslinks in the previous study. Strength of materials was clearly dominated by the crystalline yielding effect, rather than by viscoelastic effect, even in this nanofracture zone of deformation.

CONCLUSIONS

Peroxide-cured mPE has been prepared to form a vulcanizate. With regards to the effect of curing degree, tensile strength is seen to have varied slightly with increasing levels of peroxide concentrations at all test temperatures. Tear strength generally decreases with reduced energy dissipation at a higher degree of cure. A careful measurement is made to eliminate the crystalline effect at the temperatures above melting temperature of mPE to represent the sole effect of curing degree. Representative results at the highest temperature termed threshold fracture energy seem to be linearly proportional to the reciprocal square root of modulus under reduced energy dissipation for both resins. The effective diameters of fracture zones deduced from intrinsic energy density and tear strength measure a few micrometer at room temperature. The cutting strength of mPE vulcanizates gives an intermediate value when compared with crystalline plastics and conventional elastomer. Those values are generally two orders of magnitude smaller than the results obtained from tear measurements. The strength of materials is clearly dominated by the crystalline yielding effect, rather than by viscoelastic effect and crosslink types, even in this nanofracture zone of deformation for low-crystalline mPE vulcanizates.

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