

# Thermal and Mechanical Properties for Binary Blends of Metallocene Polyethylene with Conventional Polyolefins

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**ABSTRACT:** The thermal and mechanical properties for four binary blends, high-density polyethylene (HDPE)–metallocene polyethylene (MCPE), polypropylene (PP)–MCPE, poly(propylene-*co*-ethylene) (CoPP)–MCPE, and poly(propylene-*co*-ethylene-*co*-1-butene) (TerPP)–MCPE were investigated to compare the compatibility and molecular micromechanism of the blends. We report in this work all the blend systems that are thermodynamically immiscible but mechanically compatible which have been understood by their thermal and mechanical behaviors. A lower content of MCPE (up to 50%) in PP–MCPE, CoPP–MCPE, and TerPP–MCPE blends showed discernibly two  $\beta$  transitions, whereas  $\beta$  relaxation was shifted to a lower temperature with the MCPE content in the HDPE–MCPE system. These results conclude that the degree of compatibility in the HDPE–MCPE blend is the largest among the blend systems that we have studied, which also can be explained in terms of the similar chemical structure of polyolefins. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2441–2450, 1998

**Key words:** compatibility; binary blends; metallocene polyethylene; conventional polyolefins; Ziegler–Natta catalyst

## INTRODUCTION

Compatible polymer blends provide opportunities of attaining advantageous mechanical properties which are averages of and sometimes superior (i.e., synergistic effect) to those available with the individual component polymers. However, in the case of incompatible polymer blends, the mechanical properties are lower than their weight-average values. In general, polymer pairs are immiscible. Fortunately, however, even phase-separated blends proved to be mechanically compatible, provided, of course, there exists adequate ad-

hesion between the phases. Many of the polymer blends have successfully found commercial applications although they are, in fact, not miscible, for example, high-impact polystyrene (HIPS) and the acrylonitrile–butadiene–styrene terpolymer (ABS). It is well known that polyethylene and polypropylene form a mechanically compatible blend, whereas polyolefin and nylon 6 form mechanically incompatible ones, although both types of blends are thermodynamically immiscible. So, the former types of the blend are much more industrially important than are the latter ones.

Polyolefins are the prime polymers in the industrial field. A vast amount of the blends in linear low-density polyethylene (LLDPE) with conventional polyolefins has been used commercially in the agricultural application and packaging industry as a form of extrusion-blown film. LLDPE

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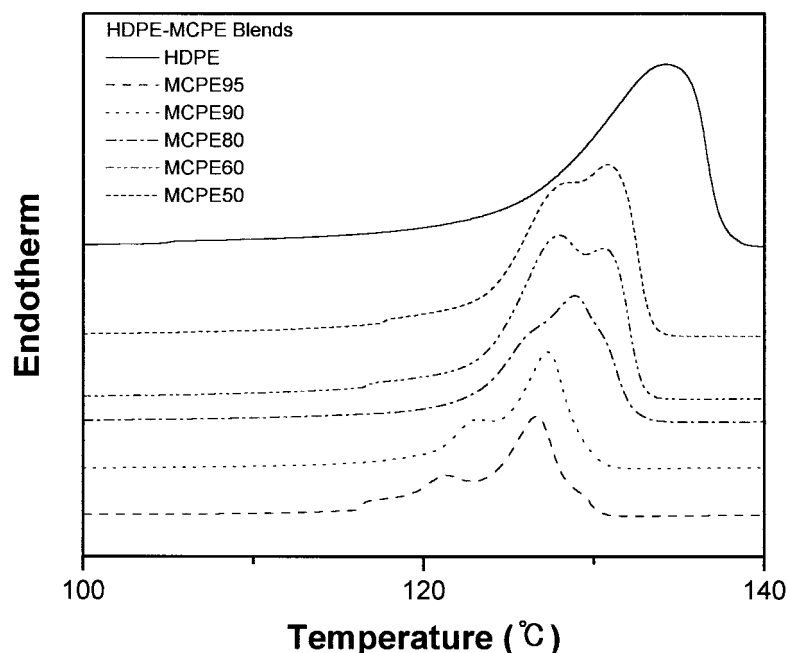
**Table I** Characterization Data of the Polymer Used in This Study

Characterization Data	Sample				
	MCPE	HDPE	PP	CoPP	TerPP
Supplier	DuPont Dow	SK Corp.	SK Corp.	SK Corp.	SK Corp.
Grade name	Engage 8200	7200	H730F	R141N	T131N
MI (g/10 min)	5	5	3.5	6	5
Density (g/mL)	0.87	0.968	0.9	0.898	0.919
Comonomer wt %	24,1-octene	—	—	3.4, ethylene	2.5, ethylene, 5,1-butene
$M_n \times 10^4$	8.29	2.68	11	7.47	9.83
$M_w \times 10^5$	1.73	2.6	4.76	4.22	4.44
PDI	2.09	9.71	4.33	5.65	4.52
$T_m$ (°C)	58.2	134	159.8	144, 152.9	134.1, 153.4
$T_c$ (°C)	40.1	112.7	109.4	99.6	89.6
$\Delta H_m$ (J/g)	19.7	183.2	83.1	57.2	47.1
$\Delta H_c$ (J/g)	24.8	187.6	87.9	66.1	54.6

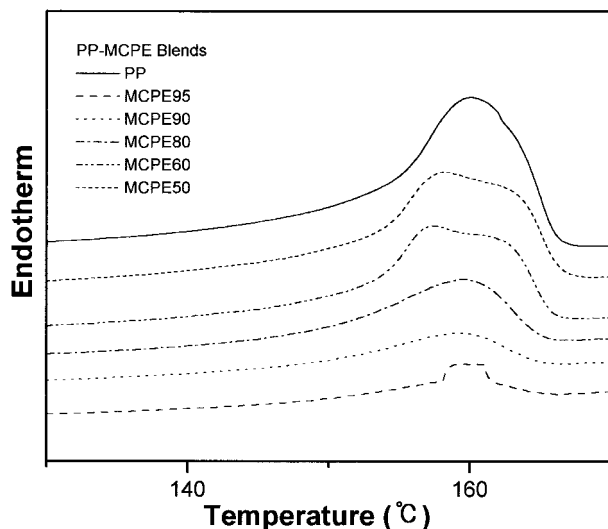
contains generally a 1-butene or 1-hexene or 1-octene comonomer controlled by the Ziegler–Natta catalyst. Recently, LLDPE is made with a higher percentage of the above-mentioned comonomer which is uniformly distributed using the metallocene catalyst. Although many research works<sup>1–5</sup> have already been done regarding LLDPE made by the Ziegler–Natta catalyst, study of the recently modified LLDPE made by the metallocene catalyst still needs to be done.

LLDPE produced by the latter method is generally known as a metallocene polyethylene resin or metallocene polyethylene (MCPE).

In recent literature,<sup>7–14</sup> there have appeared very interesting results regarding MCPE blends: The interfacial tension between MCPE and polypropylene (PP) is to be found very low, which indicates submicron dispersions of polyolefins being accomplished even with a high melt index of PP. So, MCPE may be used as a low-temperature im-



**Figure 1** Melting peak shape of HDPE in HDPE–MCPE blends in the second scan of DSC thermogram. The number indicates the percentage of MCPE in the blends.

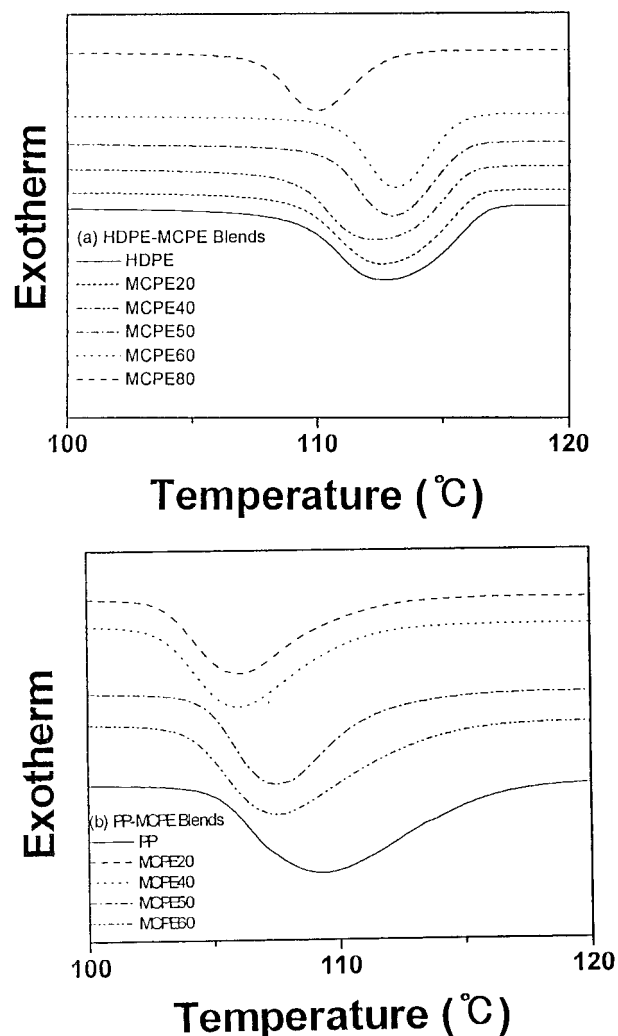


**Figure 2** Melting peak shape of PP in PP-MCPE blends in the second scan of the DSC thermogram. The number indicates the percentage of MCPE in the blends.

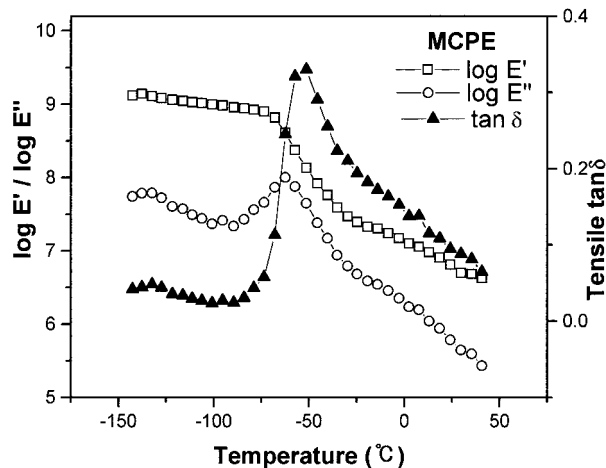
compact modification of PP.<sup>7</sup> MCPE exhibits broad  $\beta$  relaxation at subambient temperature measured by dynamic mechanical analysis and also shows a superior low-temperature impact property.<sup>8,9</sup> Blends of LLDPE containing a lower percentage of the 1-octene comonomer are found to be immiscible in crystalline regions, whereas solid-state phase behavior in amorphous regions depends upon the comonomer content.<sup>10,11</sup> High and low molecular weight high-density polyethylene (HDPE) made by the metallocene catalyst are found to be miscible themselves although they are different in molecular weight by rheological measurements.<sup>12,13</sup> Again, isotactic polypropylene (i-PP) forms a miscible blend with hexene-1-rich poly(ethylene-co-hexene-1) but not with ethylene-rich poly(ethylene-co-hexene-1) by their dynamic viscoelastic studies.<sup>14</sup>

After the systematic investigations regarding the miscibility and processability of LLDPE made by the Ziegler-Natta catalyst with other conventional polyolefins in this laboratory,<sup>15-21</sup> we are presently interested in examining the thermal, mechanical, viscoelastic, and morphological behaviors of MCPE blended with conventional polyolefins, for example, HDPE, PP, poly(propylene-co-ethylene) (CoPP), and poly(propylene-co-ethylene-co-1-butene) (TerPP). PP exhibits many advantageous properties, for example, low density, low material cost, relative high thermal sta-

bility, resistance to chemical attack, easy processing, and recyclability. However, it has some limitations in terms of the production of foam due to the weak melt strength and melt elasticity compared to other plastics. It is well known that the PP copolymer with a low content of  $\alpha$ -olefin had a better surface and cell state than those with pure PP. An attempt to mix the PP copolymer with MCPE was carried out to determine the structure-properties relationship of the blend. In this article, we present evidence that all the blends become immiscible by both thermal and mechanical studies and the extent of compatibil-



**Figure 3** Representative crystallization peak shape of conventional polyolefin in the second scan of the DSC thermogram of higher content of MCPE. The number indicates the percentage of MCPE in the blends: (a) for HDPE-MCPE; (b) for PP-MCPE.



**Figure 4** Representative curve of ( $\square$ ) storage modulus  $E'$ , ( $\circ$ ) loss modulus  $E''$ , and ( $\blacktriangle$ ) tensile  $\tan \delta$  as a function of temperature of pure MCPE.

ity of the HDPE–MCPE blends are the largest compared to the other three systems. Work is currently in progress for the rheological and morphological characterization of the blends, which will be published in a separate communication.

## EXPERIMENTAL

### Materials and Blend Preparation

The polymers used in this study are commercial grades and are chosen based on a similar melt-flow index value. MCPE based on the 1-octene comonomer is the product of DuPont Dow Elastomers, Wilmington, DE, (USA), by the grade name Engage 8200. HDPE, CoPP, which is a copolymer of propylene and a lower percentage of ethylene, and TerPP, which is basically a terpolymer of propylene and a lower percentage of both ethylene and 1-butylene, are products of SK Corp., Ulsan, (Korea). The density, melt flow index (MI), and composition of the comonomer (weight percentage) were provided by the manufacturer. Information on these polymers is given in Table I.

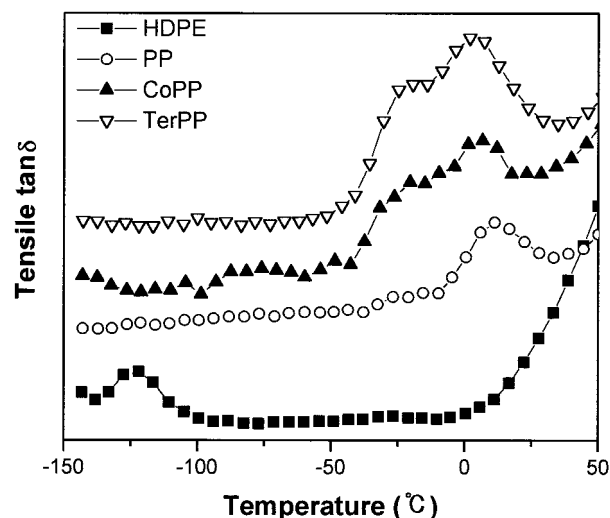
MCPE with each of HDPE, PP, CoPP, and TerPP was melt-blended in proportion to the weight ratio: 95/5, 90/10, 80/20, 60/40, 50/50, 40/60, 20/80, 10/90, and 5/95. A twin-screw extruder (Brabender PL 2000) was used at a counterrotating mode with a high mixing condition. The temperature profiles were 190, 200, and 210°C for the feed zone, the compression zone, and

the metering and die end, respectively. The screw speed was held at 50 rpm and extruded materials were pelletized after passing through cold water at 25°C. All the pure polymers were also processed under the same conditions to give them the identical thermal history as that of the blends. The resin pellets were melt-pressed in a Carver laboratory hot press at 190°C for 5 min under about  $2 \times 10^4$  Pa and allowed to cool under a normal atmosphere. The specimens were prepared in the desired dimension for the instrumental measurements.

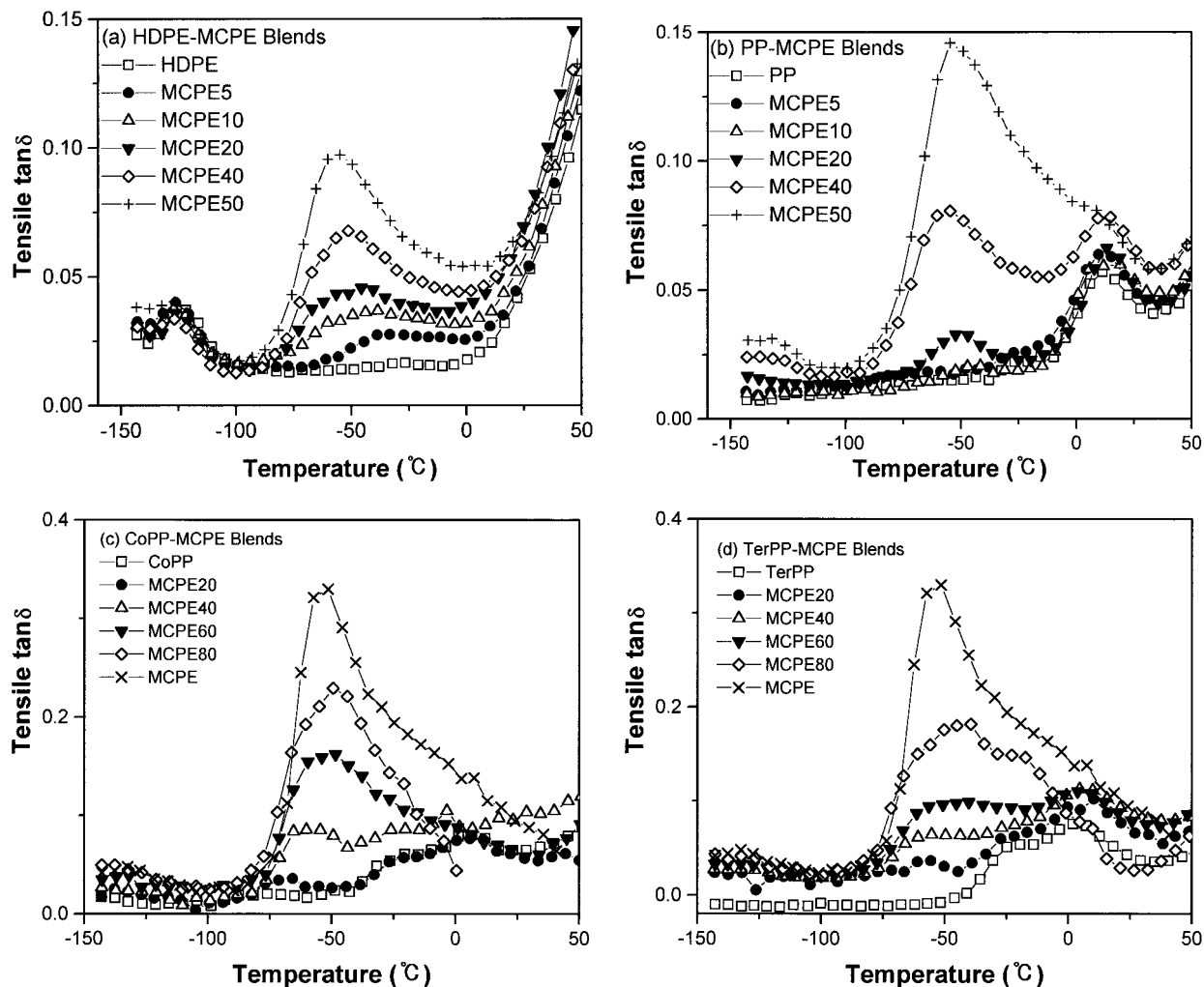
### Measurements and Instrumental Analysis

Molecular weights of the polymers were measured by a Waters GPC 150C at 140°C using 1,2,4-trichlorobenzene as a solvent and polystyrene was used as a standard. The number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and polydispersity index (PDI,  $M_w/M_n$ ) were calculated from the GPC curves. The molecular weight characterization data of the polymer used are listed in Table I.

The melting and crystallization behaviors of the blends were examined by a Perkin–Elmer DSC-7. Indium and zinc were used for the calibration of the melting peak temperature and the enthalpy of fusion. The samples were scanned up to 180°C at a heating rate 10°C/min, annealed for 5 min, and cooled to 50°C at a cooling rate of 10°C/min and again rescanned at the same rate and



**Figure 5** Tensile  $\tan \delta$  spectra versus temperature of ( $\blacksquare$ ) pure HDPE, ( $\circ$ ) PP, ( $\blacktriangle$ ) CoPP, and ( $\nabla$ ) TerPP.



**Figure 6** Tensile  $\tan \delta$  spectra of pure polyolefin and its blends. The number indicates the percentage of MCPE in the blends: (a) for HDPE–MCPE; (b) for PP–MCPE; (c) for CoPP–MCPE; (d) for TerPP–MCPE.

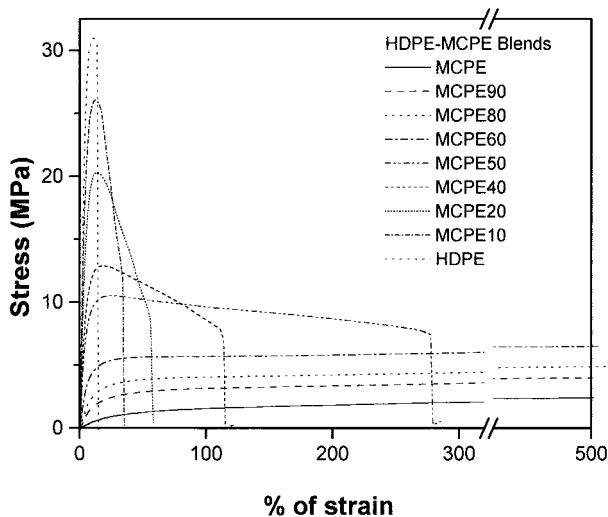
temperature interval. For pure MCPE, as a special case, the cooling temperature was 0°C but the other parameters were identical. The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), heat of fusion ( $\Delta H_m$ ), and heat of crystallization ( $\Delta H_c$ ) were calculated from the second scan of the DSC thermogram. The thermal characterization data of the pure polymer are also shown in Table I.

The  $\beta$  relaxation was measured by using a Polymer Laboratories DMTA Mk III in the range  $-145^\circ\text{C}$  to  $T_m - 10^\circ\text{C}$ , and the tensile mode at a constant frequency of 1 Hz and at a heating rate of  $2^\circ\text{C}/\text{min}$  was applied. All the specimens were

rectangular-shaped in a 10-mm-gauge length, 5-mm width, and about 0.5-mm thickness.

The mechanical properties were measured using an INSTRON 4465 universal testing machine with a crosshead speed of 200 mm/min and at ambient temperature. All the specimens were dumbbell-shaped in a 25-mm-gauge length, 6-mm width, and about 1.6-mm thickness. Mean averages of the different tensile parameters were obtained from 10 specimens of each sample.

The impact energy was measured by a Tinius Olsen impact tester at the notched mode. All the specimens for the notched Izod impact strength tests have a dimension of  $80 \times 10 \times 4$  mm. The



**Figure 7** Representative stress–strain curve for the HDPE–MCPE system. The number indicates the percentage of MCPE in the blends.

experiment was repeated five times with each sample and the impact energy was averaged.

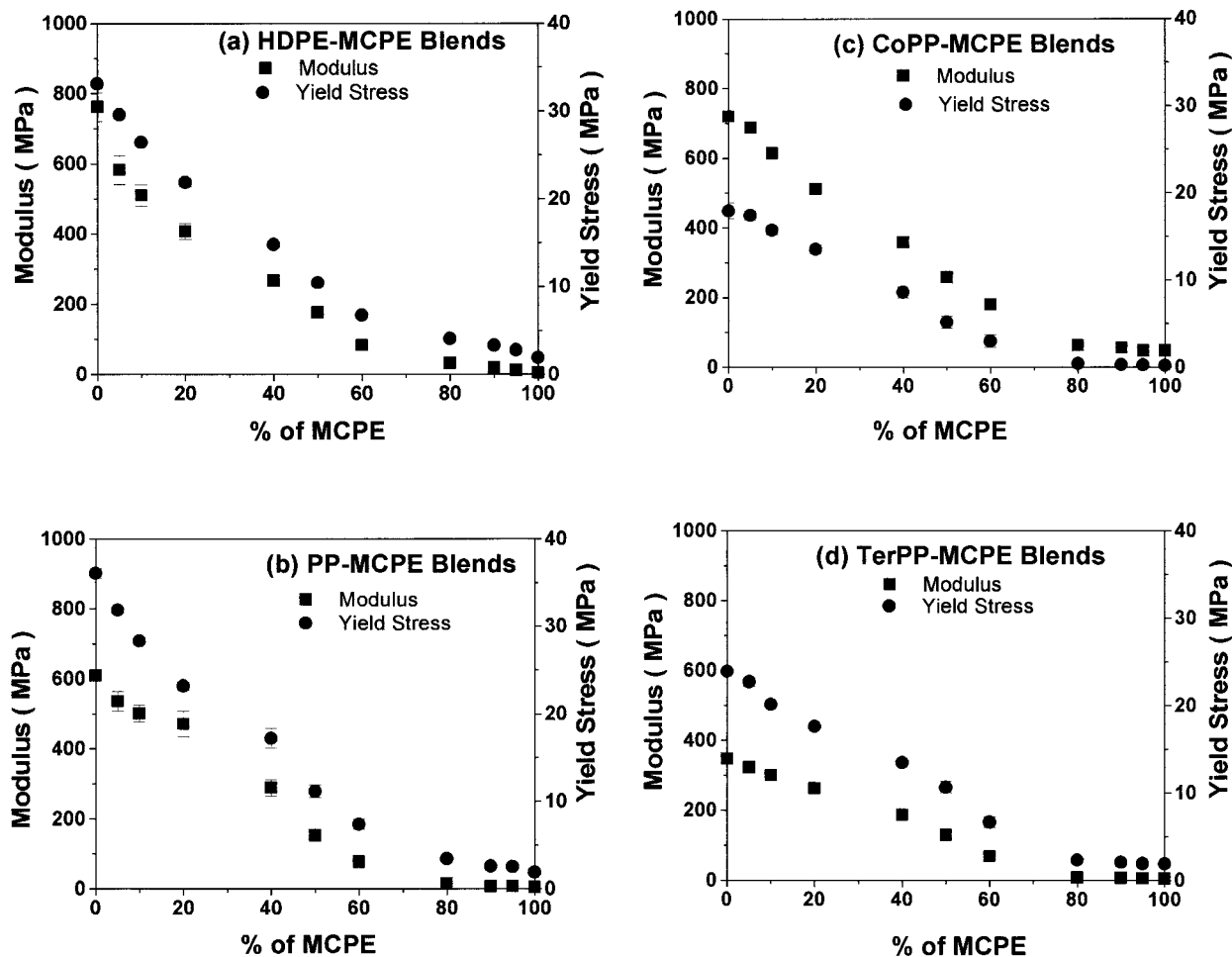
## RESULTS AND DISCUSSION

In our present investigated polyolefin blend systems, the DSC measurement indicates that all the blends are immiscible in the crystalline regions due to the existence of two distinct melting points that correspond to those of the individual components. The depression of the melting point is maximum for the HDPE–MCPE system compared to the other three blend systems, which implies that the interaction between the polymer segments of the HDPE and MCPE are maximum. The melting peak shape of HDPE in HDPE–MCPE blends and PP in PP–MCPE blends are shown in Figures 1 and 2, respectively. HDPE has a low weight average molecular weight and the polydispersity index value is also large. So, there is a larger number of low molecular weight polymers for HDPE than for PP. During crystallization, MCPE affects only the HDPE crystal where two-dimensional nucleation with diffusion-controlled growth occurs but not the PP crystal where two-dimensional nucleation takes place with linear growth. So, fractionation takes place in the case of the HDPE–MCPE blend (as shown in Fig. 1) only, which also indicates better interaction between HDPE and MCPE. In the case of the CoPP–MCPE and TerPP–MCPE systems, the melting peak shape

of CoPP or TerPP in the blend remains the same as that of pure polymer, that is, it is not affected by MCPE. In contrast, the crystallization peak of polyolefin is observed as very sharp in all the systems. The crystallization peak shapes of blended MCPE with HDPE and PP are shown in Figure 3(a,b), respectively. The crystallization peak of polyolefin (i.e., HDPE or PP) is shifting toward low temperature as the MCPE proportion increases due to the latter component acting as a polymeric diluent of the blend.

A representative DMTA spectrum trace of the tensile storage modulus  $E'$ , tensile loss modulus  $E''$ , and tensile  $\tan \delta$  versus temperature for MCPE are shown in Figure 4. MCPE exhibits a broad  $\beta$  relaxation at about  $-55^\circ\text{C}$  (peak position of tensile  $\tan \delta$ ) which may arise due to the segmental motion of the 1-octene comonomer. HDPE does not show any  $\beta$  relaxation as also observed by other researchers,<sup>22,23</sup> PP shows it at  $12^\circ\text{C}$ , whereas Amash and Zugenmaier<sup>24</sup> noticed it at  $8^\circ\text{C}$ , CoPP shows it at  $5^\circ\text{C}$ , and TerPP shows it at  $2^\circ\text{C}$  as depicted in Figure 5. For CoPP and TerPP, these transitions probably originated from that of PP. It is seen from this display that the  $\tan \delta$  peak has a doubling shape for CoPP and TerPP, which is may have arisen from the ethylene comonomer and from ethylene and 1-butene, respectively. The  $\beta$  relaxation shifted to higher temperature with MCPE in the HDPE–MCPE blend containing a lower content of MCPE [in Fig. 6(a)]. However, a lower content of MCPE in the PP–MCPE, CoPP–MCPE, and TerPP–MCPE blends show two discernible  $\beta$  transitions [in Fig. 6(b–d)]. The  $\beta$  transitions (i.e., glass transition temperature) for the latter three blend systems indicated that the blend components are immiscible in the amorphous region also. So, the HDPE–MCPE system becomes more compatible than the PP–MCPE, CoPP–MCPE, and TerPP–MCPE blends. This result can be explained in that MCPE and HDPE are very similar in structure; thereby, they are more compatible than are the other systems.

A representative stress–strain curve for the HDPE–MCPE blend is depicted in Figure 7. As expected, both modulus and yield stress decrease with the MCPE content in all the blend systems as shown in Figure 8(a–d). Although the modulus and yield stress are measured for all the systems, the tensile strength at break and elongation at break cannot be measured when blends contain higher than 80% of MCPE as well as pure MCPE. The tensile strength at break for the HDPE–

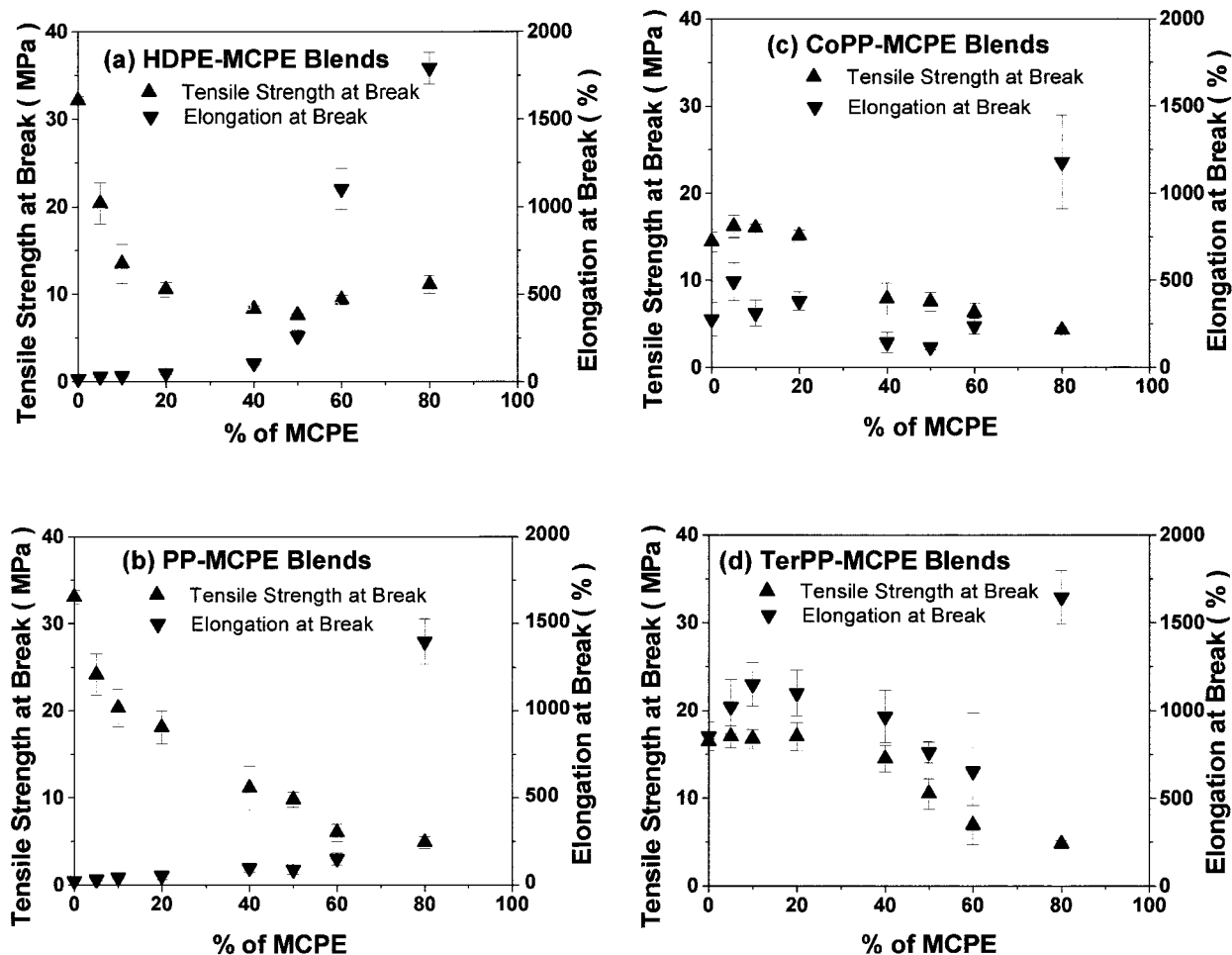


**Figure 8** Variation of (i) tensile modulus and (ii) tensile yield stress for pure polyolefin and their blends: (a) for HDPE–MCPE; (b) for PP–MCPE; (c) for CoPP–MCPE; (d) for TerPP–MCPE.

MCPE system decreases exponentially up to about 20% MCPE and then is independent with further MCPE as shown in Figure 9(a), whereas for the PP–MCPE blend, it decreases exponentially [shown in Fig. 9(b)]. For the CoPP–MCPE and TerPP–MCPE systems, the tensile strength at break is almost constant to about 20% MCPE and then decreases linearly with the MCPE content as shown in Figure 9(c) and (d), respectively. On the other hand, the elongation at break increases linearly to about 50% of MCPE and then abruptly increases with MCPE for HDPE–MCPE and PP–MCPE. For the CoPP–MCPE and TerPP–MCPE systems, the elongation at break may be divided into three regions depending upon the MCPE content: (i) CoPP- or TerPP-rich phase ( $\text{MCPE} \leq 20 \text{ wt } \%$ ), (ii) the intermediate phase ( $30 < \text{MCPE} < 70 \text{ wt } \%$ ), and (iii) MCPE-rich

phase ( $\text{MCPE} \geq 80 \text{ wt } \%$ ). In region (i), elongation at break slightly increases; in region (ii), it dramatically dropped; and in region (iii), the elongation at break value is very large.

The results of the impact test with three different temperatures are displayed in Table II. At room temperature and also at  $-27^\circ\text{C}$ , the order of the impact energy for the pure polymer is  $\text{HDPE} < \text{PP} < \text{CoPP} < \text{TerPP} < \text{MCPE}$ . The blends of HDPE–MCPE, PP–MCPE, CoPP–MCPE, and TerPP–MCPE containing 40, 80, 60, and 50% MCPE content, respectively, are not broken at  $-27^\circ\text{C}$ . So, 40% MCPE in the HDPE–MCPE blend has the largest impact energy among the systems due to the blend not being broken. The impact test data at  $-27^\circ\text{C}$  are also depicted in Figure 10. The HDPE–MCPE and TerPP–MCPE blends, both containing 50% MCPE, are not bro-



**Figure 9** Variation of (i) tensile strength at break and (ii) tensile elongation at break for pure polyolefin and their blends: (a) for HDPE–MCPE; (b) for PP–MCPE; (c) for CoPP–MCPE; (d) for TerPP–MCPE.

ken at  $-27^{\circ}\text{C}$ . So, we measured the impact energy of all the four above-mentioned blends containing 50% MCPE at  $-60^{\circ}\text{C}$ . In the case of pure MCPE, the impact energy could not be measured although the temperature was lowered to  $-60^{\circ}\text{C}$ . As expected, the impact energy increases with MCPE content in the blend, although the standard deviation of our data is very large. Within the experimental error, the order of the impact energy for the pure polymer is as follows: TerPP > CoPP > PP > HDPE, whereas for the blend containing 40% MCPE (at least or above), the order of the notched Izod impact energy is as follows: HDPE–MCPE > TerPP–MCPE > CoPP–MCPE > PP–MCPE. Although pure HDPE has the lowest impact energy, the blends exhibit the maximum impact energy among the other three blend systems. We conclude from these results that the interfa-

cial tension (i.e., adhesion between the two micro-phase domains) between MCPE and HDPE are strong compared to the others, that is, MCPE blended with PP, CoPP, and TerPP.

The melt miscibility of polyolefin is a rare occurrence. To achieve miscible systems, it is thus required that the heat of mixing ( $\Delta H_m$ ) should be exothermic, which occurs when there exist specific interactions such as hydrogen bonding, donor–acceptor interaction, and charge-transfer complex between the blend components. For a very similar structural polymer,  $\Delta H_m$  is almost zero, so that the overall negative Flory–Huggins interaction parameter  $\chi$  is expected. In general, the melt miscibility of branched and linear PE depends upon the branch content.<sup>25</sup> When the branch content is low (i.e., <4 branches/100 backbone carbon), the melt state becomes homogeneous, whereas when



**Table II** Results of Notched Izod Impact Energy (J/m) at  $-27^{\circ}\text{C}$ 

MCPE (%)	HDPE–MCPE	PP–MCPE	CoPP–MCPE	TerPP–MCPE
0	10.3 $\pm$ 2.06	10.59 $\pm$ 1.27	12.36 $\pm$ 0.88	14.12 $\pm$ 0.49
	10.0 $\pm$ 0.39 <sup>a</sup>	20.3 $\pm$ 3.92 <sup>a</sup>	24.03 $\pm$ 4.71 <sup>a</sup>	29.32 $\pm$ 8.53 <sup>a</sup>
5	14.12 $\pm$ 1.96	11.18 $\pm$ 1.08	12.26 $\pm$ 0.49	21.58 $\pm$ 8.92
10	20.3 $\pm$ 2.06	13.73 $\pm$ 2.06	20.1 $\pm$ 5.0	24.32 $\pm$ 1.08
20	34.81 $\pm$ 2.06	23.54 $\pm$ 0.69	35.44 $\pm$ 3.73	37.36 $\pm$ 8.73
40	Not broken	25.0 $\pm$ 1.08	38.5 $\pm$ 6.77	72.57 $\pm$ 4.12
50	Not broken	35.31 $\pm$ 2.75	51.0 $\pm$ 6.96	Not broken
	29.42 $\pm$ 4.51 <sup>b</sup>	9.61 $\pm$ 2.65 <sup>b</sup>	20.59 $\pm$ 2.75 <sup>b</sup>	24.71 $\pm$ 6.37 <sup>b</sup>
60	Not broken	90.22 $\pm$ 6.08	Not broken	Not broken
80	Not broken	Not broken	Not broken	Not broken
90	Not broken	Not broken	Not broken	Not broken
100			Not broken <sup>b</sup>	

<sup>a</sup> At  $23^{\circ}\text{C}$ .<sup>b</sup> At  $-60^{\circ}\text{C}$ .

the branch content is high (e.g.,  $> 8$  branches/100 backbone carbon), then the blends form a phase separation. Recently, a large negative Flory–Huggins interaction parameter  $\chi$  was found in a small-angle neutron scattering (SANS) experiment for a blend containing PP.<sup>26</sup>

In our present blend systems containing MCPE, basically, LLDPE is similar to the HDPE structure, that is, the ethylene unit. CoPP and TerPP contain mainly a propylene unit. So, as expected, all our investigated systems become thermodynamically immiscible. Due to a similar structure, MCPE is more compatible with HDPE

than is PP, CoPP, and TerPP. Among the three latter blend systems, on the basis of structure similarity with MCPE, there is speculation that the order of compatibility, that is, the microheterogeneous phase domains, is TerPP–MCPE  $>$  CoPP–MCPE  $>$  PP–MCPE. The morphology of the tensile fractured surface as observed by scanning electron microscope (SEM) photographs indicate that all the blends are heterogeneous and the order of the domain sizes in the two-phase micrographs are as follows<sup>27</sup>: HDPE–MCPE  $>$  TerPP–MCPE  $>$  CoPP–MCPE  $>$  PP–MCPE.

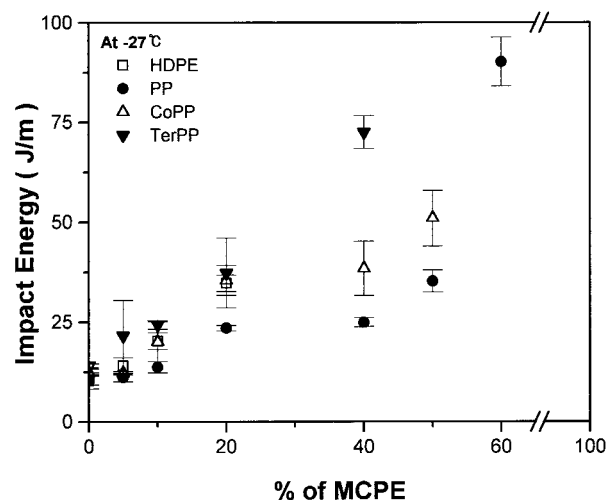
## CONCLUSIONS

Metallocene polyethylene (MCPE) blends with HDPE, PP, CoPP, and TerPP are thermodynamically immiscible but mechanically compatible. The degree of compatibility is the largest for the HDPE–MCPE blend system compared to the other three blend systems: PP–MCPE, CoPP–MCPE, and TerPP–MCPE, which reminds us of the old idea that “like dissolves like” is also valid in the polyolefin blends.

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**Figure 10** Variation of notched Izod impact energy with MCPE content at  $-27^{\circ}\text{C}$ : ( $\square$ ) for HDPE–MCPE; ( $\bullet$ ) for PP–MCPE; ( $\triangle$ ) for CoPP–MCPE; ( $\blacktriangledown$ ) for TerPP–MCPE.

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