

CHAPTER V

RESULTS AND DISCUSSION

5.1 Characterization of catalyst synthesized

5.1.1 Morphology of fresh catalysts and spent catalysts at various reaction times

In this thesis, spent catalyst represents both catalytic coke and deteriorative catalyst, while fresh catalyst represents catalyst before reaction. The characterization of synthesized catalysts was studied using SEM. SEM micrographs of fresh catalyst and spent catalysts at various reaction times are shown in Figure 5.1. Micrographs of the spent catalysts showed that the surface was covered with filamentous coke, in contrast to the clean surface seen in fresh catalysts.

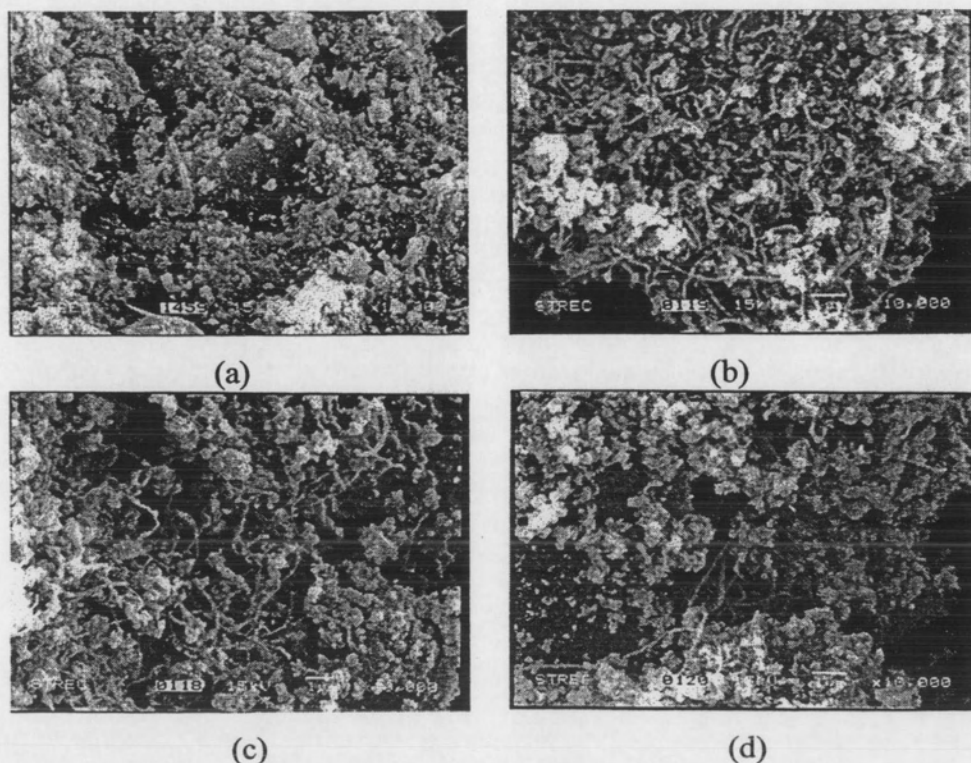
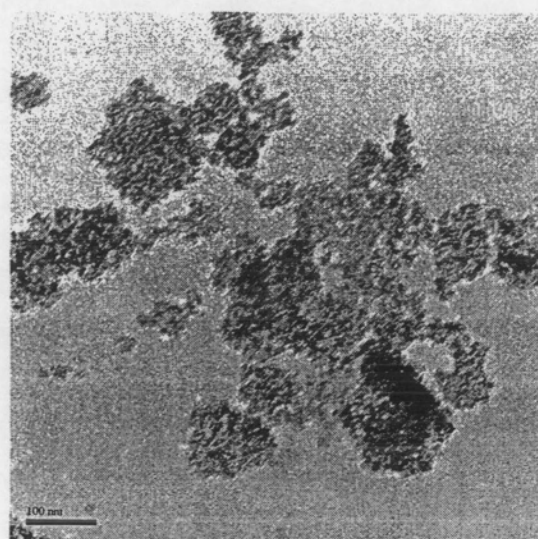
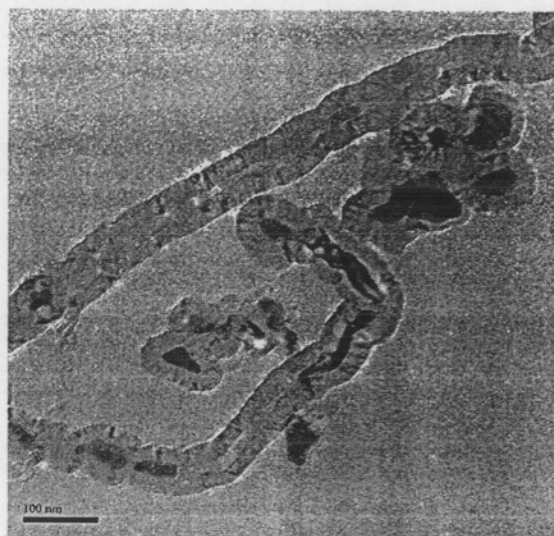


Figure 5.1 SEM micrographs of (a) fresh catalyst (b) spent catalyst at 60 min (c) spent catalyst 80 min and (d) spent catalyst 100 min.

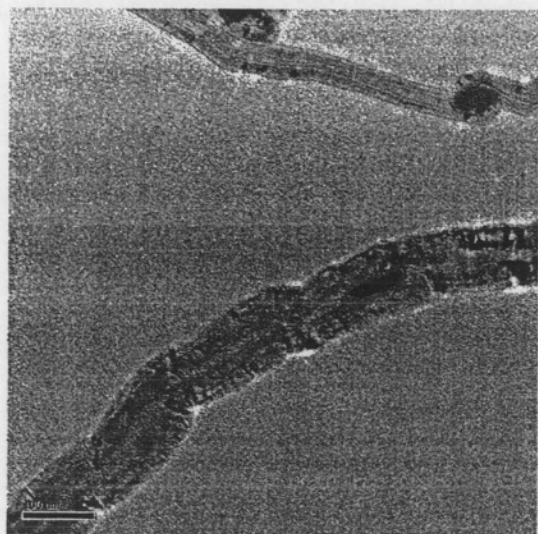
TEM micrographs of fresh catalyst and spent catalyst show in Figure 5.2. The micrographs show that the catalytic coke at reaction time 60, 80 and 100 min are rod-shaped with diameter about 68, 94 and 63 nm, respectively. The fresh catalyst is spherical in shape.



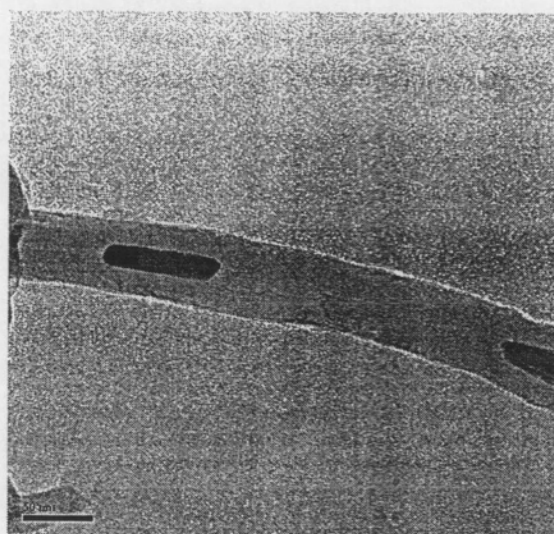
(a)



(b)



(c)



(d)

Figure 5.2 TEM micrographs of (a) fresh catalyst (b) spent catalyst at 60 min (c) spent catalyst 80 min and (d) spent catalyst 100 min.

5.1.2 X-ray diffraction analysis

Figure 5.3 (a), (b) and (c) reveals the XRD pattern of spent catalysts at various reaction times that were recovered after the catalytic decomposition of methane reaction. The irreversible carbon that is deposited on the catalyst which is appeared in XRD pattern of the deactivate catalysts, indicates the methane decomposition to produce carbon. The reflections at $2\theta = 26.6^\circ$, 43.2° , 53.8° , and 77.7° are attributed to the graphitic carbon which appeared in almost all the deactivated catalysts [Venugopal. et al., 2007].

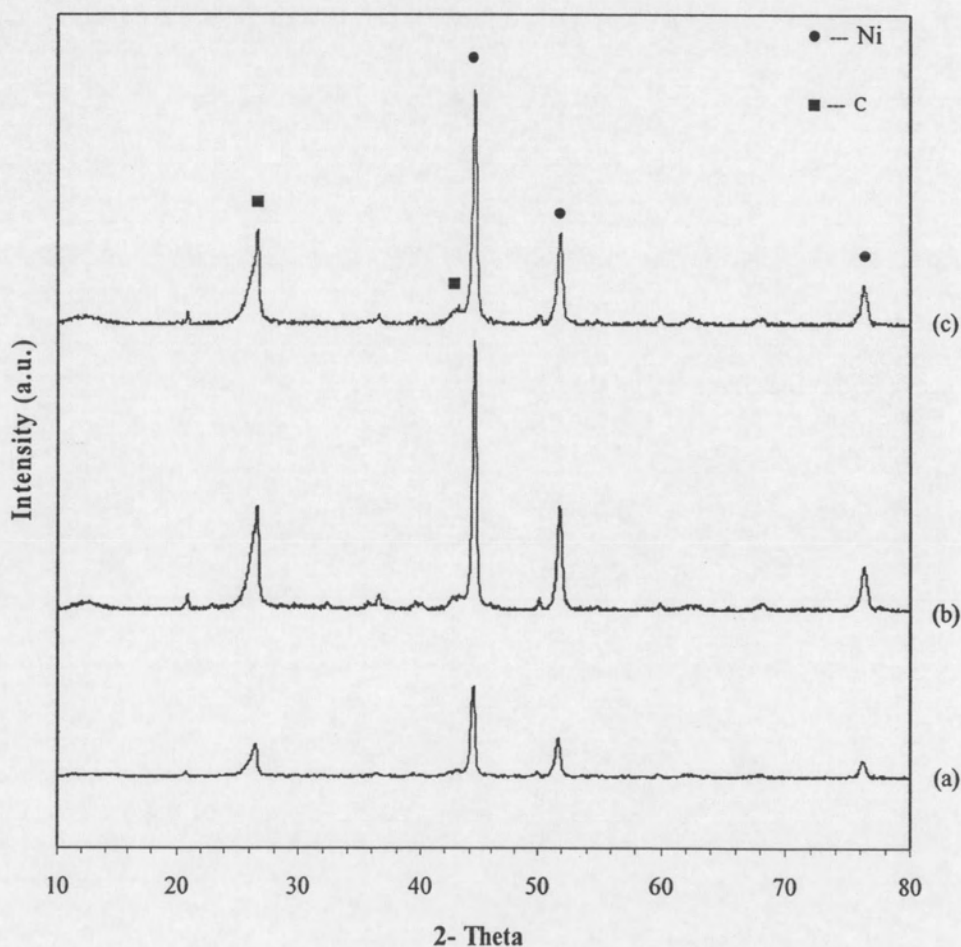


Figure 5.3 XRD patterns of (a) spent catalyst at 100 min (b) spent catalyst 80 min and (c) spent catalyst 60 min.

From XRD results, the crystal size of the Ni particles and C particles can be estimated as presented in Table 5.1. The crystal size calculation method is mentioned in the appendix A. It can be seen that the crystal size of Ni particles increased with increasing reaction time but reaction time at 100 min crystal size of Ni particle will decrease. The crystal size of C particles decreased with increasing reaction time but reaction time at 100 min crystal size of C particles will increase. Carbon deposited is cracked due to reactant flow, which led to the crystal size reduction of C particles.

Table 5.1 Crystal size of nickel and carbon of spent catalyst by XRD

Material	Crystal size of Ni (nm)	Crystal size of C (nm)
Fresh catalyst	4	-
Spent catalyst 60 min	28	13.5
Spent catalyst 80 min	30.8	12.6
Spent catalyst 100 min	24.7	10.9

5.1.3 Weight of catalytic coke

The weight of catalytic coke deposited on the surface of catalyst which had been used for the methane decomposition for various reaction times were measured by TGA. The results are given in Table 5.2.

Table 5.2 Weight of coke deposited on surface of spent catalyst measured by TGA.

Sample	Weight of coke (wt%)
Spent catalyst 60 min	38.2
Spent catalyst 80 min	32.7
Spent catalyst 100 min	32.3

The spent catalyst at reaction time 60 min had the highest amount of coke deposit. The spent catalyst at reaction time 80 min and 100 min had the lowest amount of coke respectively. After long time operation, almost all of Ni active sites were covered by the carbonaceous components. Consequently, less carbon atom was adsorbed.

5.1.4 Surface area of fresh catalyst and spent catalysts

Table 5.3 shows BET surface area of fresh catalyst and spent catalyst. It was observed that the fresh catalyst had much greater surface area than the spent catalysts. In comparison to the spent catalyst, it can be seen that the surface area of the spent catalyst decreased with the increase of reaction times. The possible reason that accounts for the decrease of catalyst surface area at long reaction times might be because of the blocking of the pores of the catalyst. The blocking of the pores will result in decrease of the reactive surface area and will be the reason for deactivation of the catalyst at long reaction times.

Table 5.3 BET surface area of fresh catalyst and spent catalysts at various reaction times.

Sample	BET surface area (m ² /g)
Fresh catalyst	76.0
Spent catalyst 60 min	15.9
Spent catalyst 80 min	10.2
Spent catalyst 100 min	6.7

From results above we select synthesis spent catalyst at reaction time 60 min because it had the highest catalytic coke content and surface area. The surface area of the filler is an important factor influencing mechanical properties [Wu et al., 2005].

5.2 Characterization of polypropylene composites at various filler contents and filler types

5.2.1 Effects of filler contents and filler types on thermal properties of polypropylene composites

The effects of filler contents and filler types on the degradation temperature of all composites are shown in Figure 5.4. The degradation temperature was measured by TGA and was calculated at 5 % weight loss of composites. It can be seen that the degradation temperature decreased with increasing filler contents. It could be noticed that the thermal stability of pure PP was better than all composites.

In comparison to the fresh catalyst/PP composites and spent catalyst/PP composites, the spent catalyst/PP composites had the higher thermal stability than fresh catalyst/PP composites. This might be because of the difference between compositions of the filler that affected the stability. Usually spent catalyst will have more carbon deposit while fresh catalyst will not have. Moreover the size of the filler might affect the stability. Spent catalyst usually has larger sizes and because of the size this filler is harder distributed through the matrix than fresh catalyst. In other aspect, the agglomeration of the fresh catalyst also response for the poor migration in the matrix, so the degradation temperature will be lower.

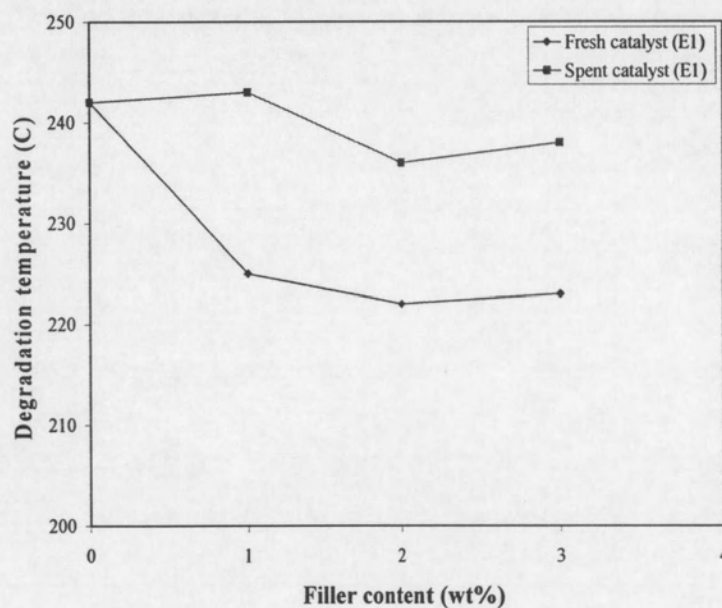


Figure 5.4 Degradation temperatures of the fresh catalyst/PP composites and spent catalyst/PP composites at various filler contents.

Table 5.4 shows glass transition temperature and melting temperature of pure PP and composites at various filler contents and filler types. The obtained results showed that the melting temperature and glass transition temperature were not significantly changed when spent catalyst filler were incorporated in the polymer matrix. In the other hand, the melting temperature decreased when fresh catalyst was incorporated in the polymer matrix, but glass transition temperature was not

significantly changed. The decrease in crystalline melting temperature of the matrix might result from the agglomeration of the fresh catalyst which reduced the interfacial bonding between fillers and the matrix at the interfaces [Kim et al., 2006].

Regarding the effect of the filler content on the melting temperature and glass transition temperature, no significant differences were observed.

Table 5.4 The variation of T_g and T_m of pure PP and composites at various filler contents and filler types.

Material	T_g (°C)	T_m (°C)
Pure PP	-8.8	160.0
PP-Spent catalyst 1% (E1)	-8.1	161.4
PP-Spent catalyst 2% (E1)	-8.1	161.3
PP-Spent catalyst 3% (E1)	-8.0	161.4
PP-Fresh catalyst 1% (E1)	-10.8	155.3
PP-Fresh catalyst 2% (E1)	-10.2	156.6
PP-Fresh catalyst 3% (E1)	-8.9	157.9

5.2.2 Effects of filler contents and filler types on mechanical properties polypropylene composites

The effect of filler contents and filler types on mechanical properties of all composites was tested under tension mode, which were reported in terms of tensile strength, Young's modulus, elongation at break and area under tensile stress-strain curve. Tensile strength was used to indicate the strength of composites. Young's modulus was used to indicate the stiffness of composites which was determined by

the first linear slope of stress-strain curves. Elongation at break was defined as strain at the rupture of the specimen. Area under tensile stress-strain curve was used to indicate the toughness of composites.

The effect of filler contents and filler types on tensile strength, Young's modulus, elongation at break and area under tensile stress-strain curve of all composites at various filler contents are shown in Figure 5.5-5.8. From Figure 5.5, it can be seen that the tensile strength was consistent with increasing filler content, due to the polar nature of filler and non-polar nature of polymer causes the poor interaction and dispersion between filler and polymer which may hardly effect on the tensile strength [Premalal et al., 2002; Suarez et al., 2003; Yang et al., 2006; Rattanasom et al., 2007].

From Figure 5.6, it can be seen that Young's modulus of spent catalyst/PP composites increased with increasing filler content. This may be due to the increased interfacial area in the composite with filler, with promotes the stress transfer efficiency with in small strain range [Wu et al., 2005]. Moreover, it may be caused the brittle characteristics of fillers.

Figure 5.7 and 5.8 present that elongation at break and area under tensile stress-strain curve of PP composites decreased with increasing filler content. This result indicated that the increasing filler content caused less ductility or more brittle because the addition of filler led to the higher stiffness.

In consideration of the effect of filler types in Figure 5.5-5.8, it can be seen that the spent catalyst/PP composites exhibited higher Young's modulus and greater area under stress-strain curves than fresh catalyst/PP composites. This result indicated that spent catalyst/PP composites exhibited higher stiffness than fresh catalyst/PP composites. This may be due to difference in a polarity miss match of fillers and polymer matrix. Therefore, fresh catalyst has higher surface area than that of spent catalyst. This may induce agglomeration and poor adhesion between fresh catalyst and polymer matrix and decreased the stiffness.

Moreover, it can be seen that tensile strength and elongation at break of spent catalyst/PP composites and fresh catalyst/PP composites were not different.

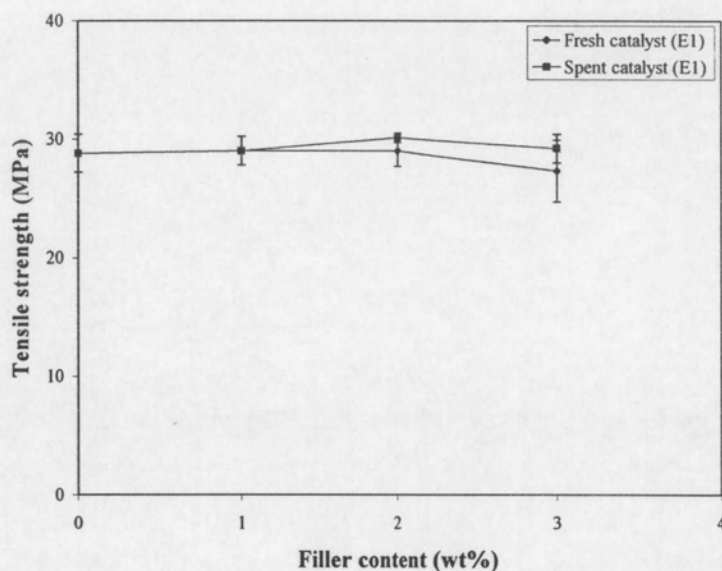


Figure 5.5 Tensile strengths of the fresh catalyst/PP composites and spent catalyst/PP composites at various filler contents and filler types.

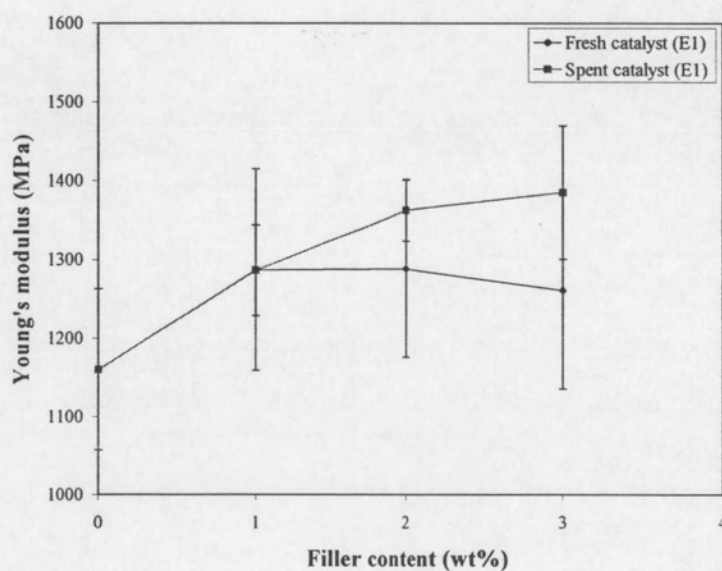


Figure 5.6 Young's modulus of the fresh catalyst/PP composites and spent catalyst/PP composites at various filler contents and filler types.

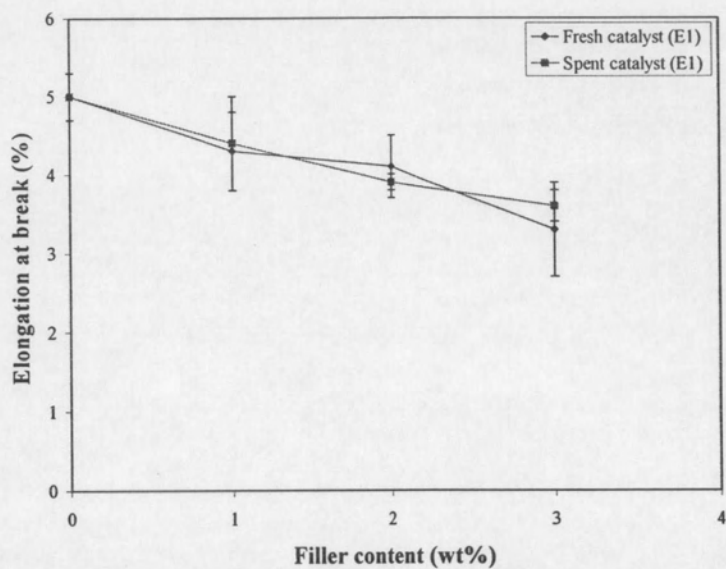


Figure 5.7 Elongation at break of the fresh catalyst/PP composites and spent catalyst/PP composites at various filler contents and filler types.

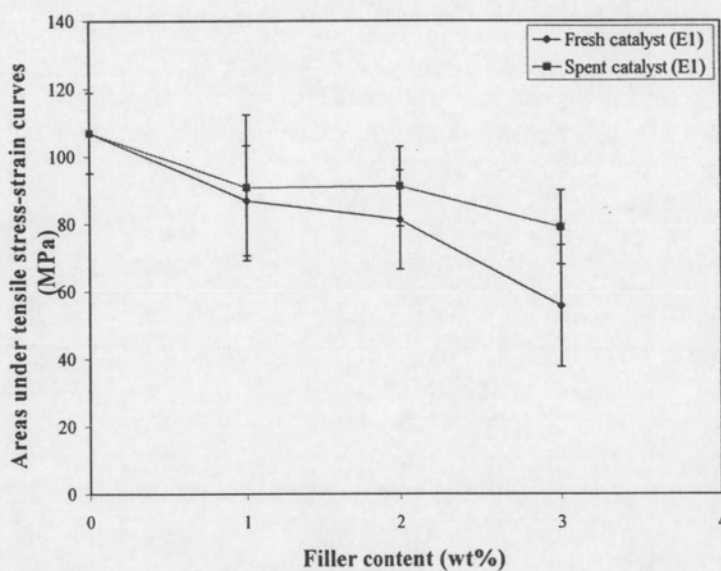


Figure 5.8 Areas under tensile stress-stain curves of the fresh catalyst/PP composites and spent catalyst/PP composites at various filler contents and filler types.

5.2.3 Effects of filler contents and filler types on morphological properties of polypropylene composites

Figure 5.9 shows the SEM micrographs of the tensile fracture surfaces of spent catalyst filled PP composites compared to pure PP at various filler contents. It exhibits the fibrils and the plastic deformation of the matrix polymer. There is a greater amount of plastic deformation of the matrix polymer in the spent catalyst/PP composites than in the pure PP. This appearance reveals the good adhesion between PP matrix and catalyst. Moreover, it could be expected that the composite had higher stiffness than pure matrix. However, this result from the tensile test presented the higher stiffness of the composite because of the properties of the spent catalyst.

Figure 5.10 shows that SEM micrographs of the tensile fracture surfaces of fresh catalyst filled PP composites compared to pure PP at various filler content. SEM micrographs show that the dispersion of the fresh catalyst on the polymer surface was non-uniform. This non-uniform dispersion led to local agglomeration of fresh catalyst within the polymer. Fresh catalyst/PP composites and pure PP present similar fracture features is surface roughness. It can be seen that, there was good adhesion between the fresh catalyst/PP composites. These observations support the results of the tensile tests where the fresh catalyst/PP composites displayed higher stiffness than the pure PP.

Figure 5.11 shows that SEM micrographs of the tensile fracture surfaces of spent catalyst filled PP composites compared to fresh catalyst filled PP composites at various filler content. It can be seen that spent catalyst filled PP composites had higher plastic deformation of polymer than fresh catalyst filled PP composites. These observations support the results of the tensile tests where the spent catalyst/PP composites displayed higher stiffness than the fresh catalyst/PP composites.

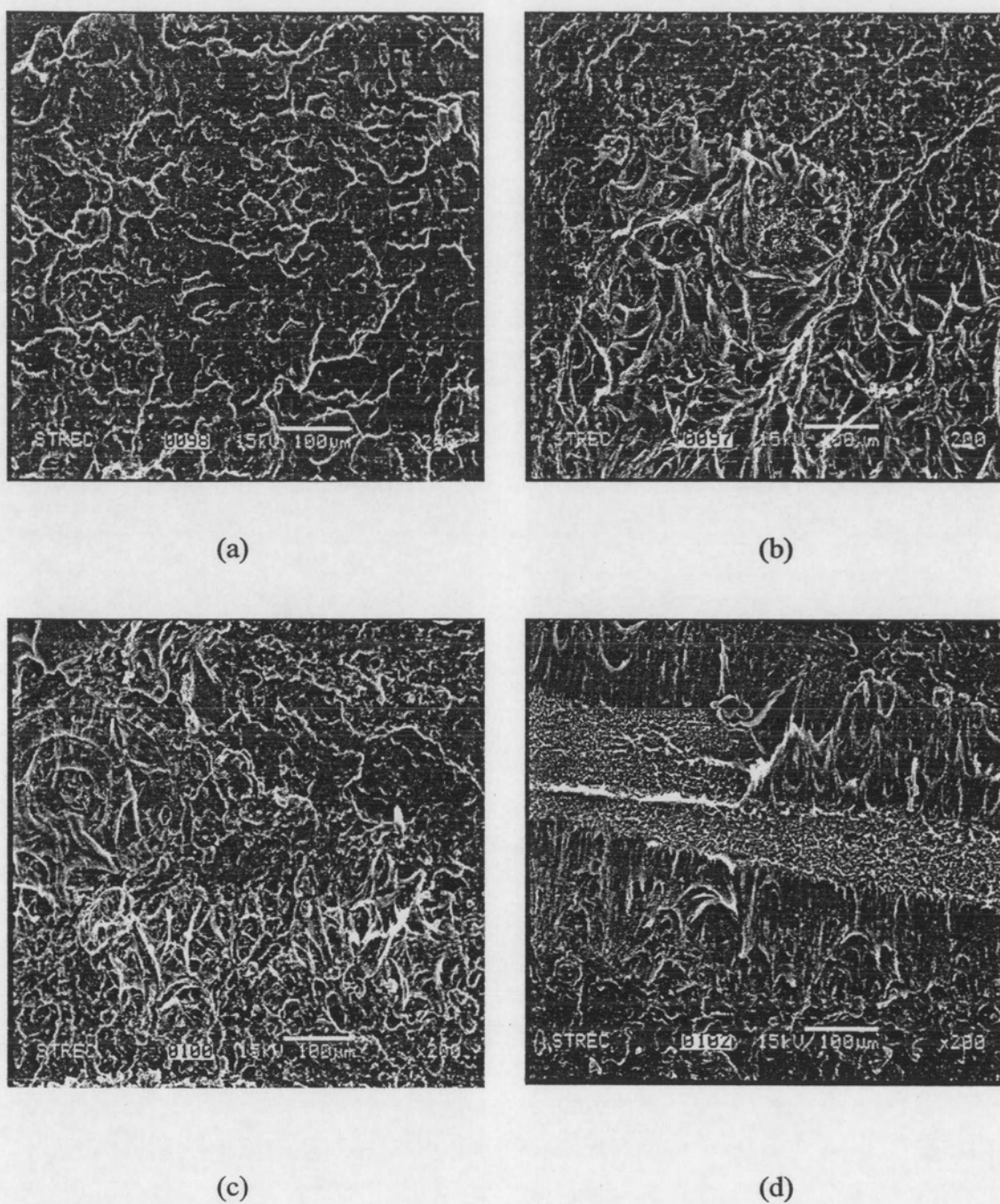


Figure 5.9 SEM micrographs of the tensile fracture surface of (a) Neat PP (b) 1 wt% spent catalyst/PP composite (c) 2 wt% spent catalyst/PP composite and (d) 3 wt% spent catalyst/PP composite.

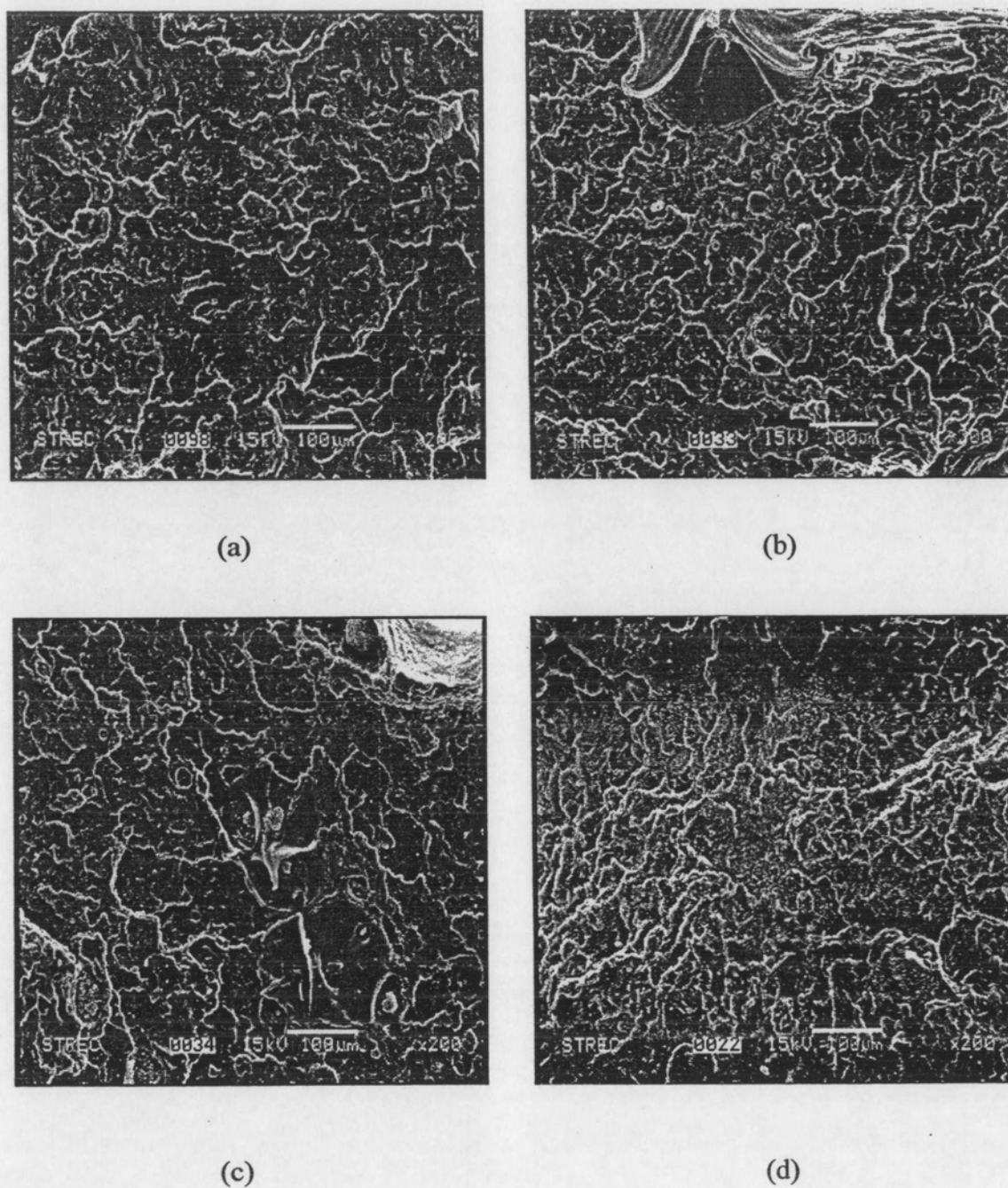


Figure 5.10 SEM micrographs of the tensile fracture surface of (a) Neat PP (b) 1 wt% fresh catalyst/PP composite (c) 2 wt% fresh catalyst/PP composite and (d) 3 wt% fresh catalyst/PP composite.

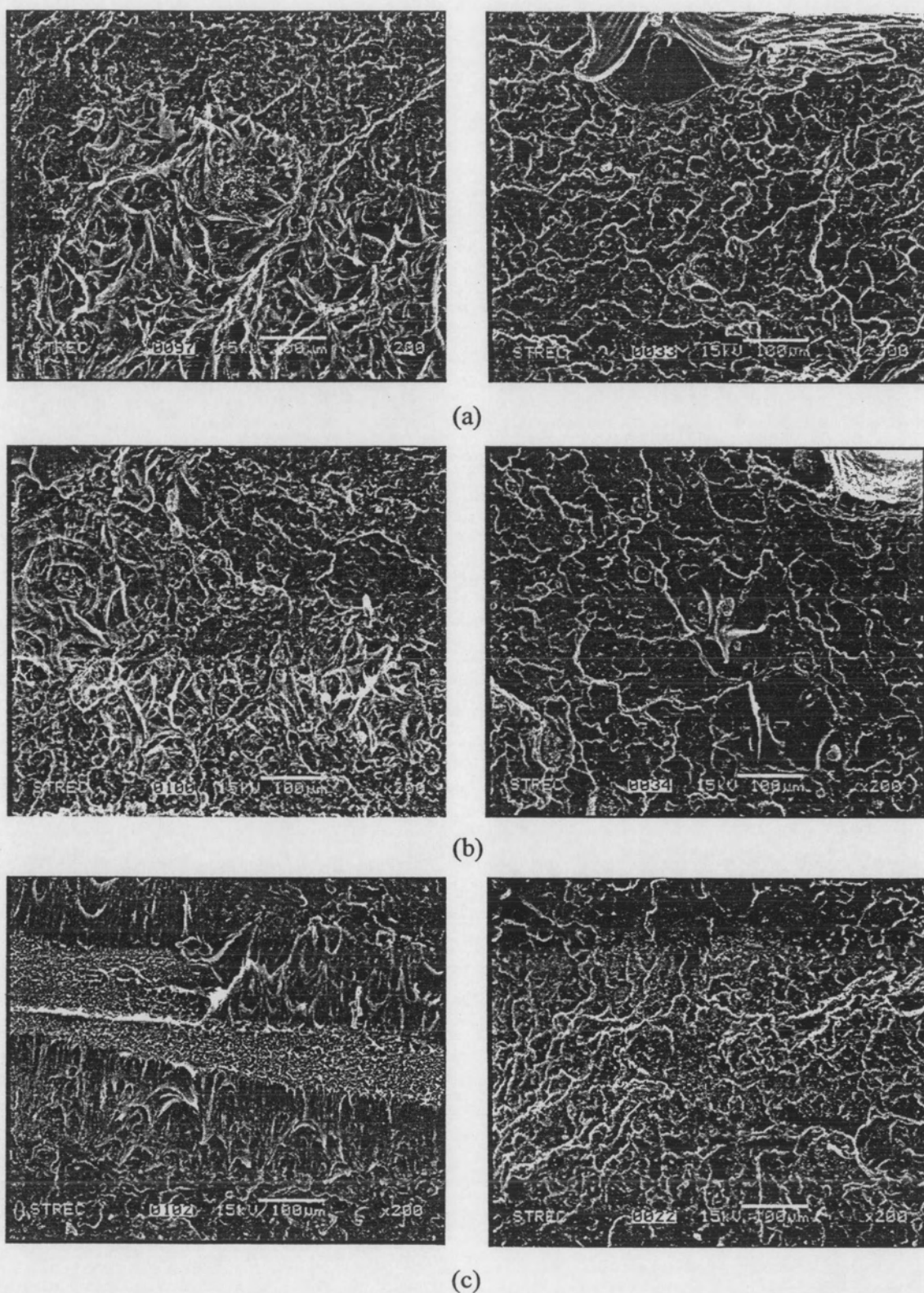


Figure 5.11 Compared to SEM micrographs of the tensile fracture surface between spent catalyst/PP composites and fresh catalyst/PP composites at (a) 1 wt% (b) 2 wt% and (c) 3 wt%.

5.3 Characterization of polypropylene composites at various extrusion cycles

5.3.1 Effect of extrusion cycles on thermal properties of polypropylene composites

The extrusion cycle may have the strong effects on the distribution of the filler in the matrix which will result in improving the properties. However, the polymer might have poor properties because of the degradation and chain scission during the extrusion. The optimum time of the cycles will have to balance both aspects.

The effects of filler contents on the degradation temperature of all composites at various extrusion cycles are shown in Figure 5.12. It can be seen that the degradation temperature decreased with increasing filler contents and extrusion cycles. The decrease in degradation temperature might result from the increase in the melting time in process that usually increases when the cycles of the extrusion increase. The reason for the degradation might come from the chain scissions during the melting process [Gonzalez et al., 1998; Camacho et al., 2002]. It was shown that the thermal stability of pure PP was better than spent catalyst/PP composites and fresh catalyst/PP composites at various extrusion cycles.

Table 5.5 shows glass transition temperature and melting temperature of pure PP and composites at various extrusion cycles. The obtained results show that the effect of the various extrusion cycles on the melting temperature, no significant differences were observed.

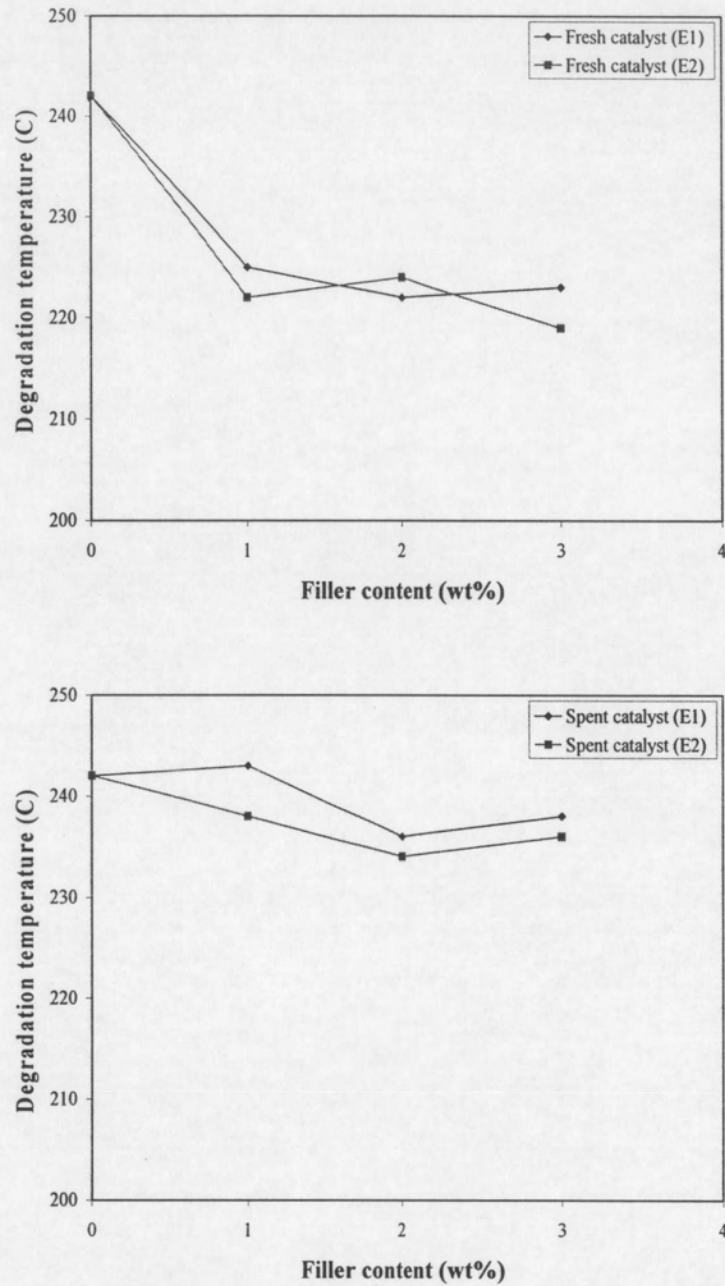


Figure 5.12 Degradation temperatures of the fresh catalyst/PP composites and spent catalyst/PP composites at various extrusion cycles.

Table 5.5 The variation of T_g and T_m of pure PP and composites at various extrusion cycles.

Material	One time of extrusion		Two time of extrusion	
	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
Pure PP	-8.8	160.0	-8.8	160.0
PP-Spent catalyst 1%	-8.1	161.4	-9.0	161.4
PP-Spent catalyst 2%	-8.1	161.3	-10.2	160.7
PP-Spent catalyst 3%	-8.0	161.4	-9.5	161.3
PP-Fresh catalyst 1%	-10.8	155.3	-9.0	157.2
PP-Fresh catalyst 2%	-10.2	156.6	-9.0	157.2
PP-Fresh catalyst 3%	-8.9	157.9	-8.2	149.2

5.3.2 Effect of extrusion cycles on mechanical properties of polypropylene composites

The effect of extrusion cycles on tensile strength, Young's modulus, elongation at break and area under tensile stress-strain curve of spent catalyst/PP composites and fresh catalyst/PP composites at various filler contents are shown in Figure 5.13-5.16. It can be seen that the tensile strength and elongation at break of spent catalyst/PP composites and fresh catalyst/PP composites were not different with increasing extrusion cycles. Young's modulus decreased with increasing extrusion cycles both spent catalyst/PP composite and fresh catalyst/PP composites. Area under tensile stress-strain curve at 1 and 3 wt% of spent catalyst/PP composite slightly increased with increasing extrusion cycles whereas area under tensile stress-strain curve of all fresh catalyst/PP composites increased with increasing extrusion cycles. The decrease in Young's modulus and the increase area under tensile stress-strain curve at the second extrusion cycles may be due to an extensive chain scission during the high shear that is applied in the extrusion [Choudhury et al., 2005] and the well distribution of the filler in the matrix might be responsible.

From the results, it could be said that the cycles of extrusion has less affected to the mechanical properties of the PP composites.

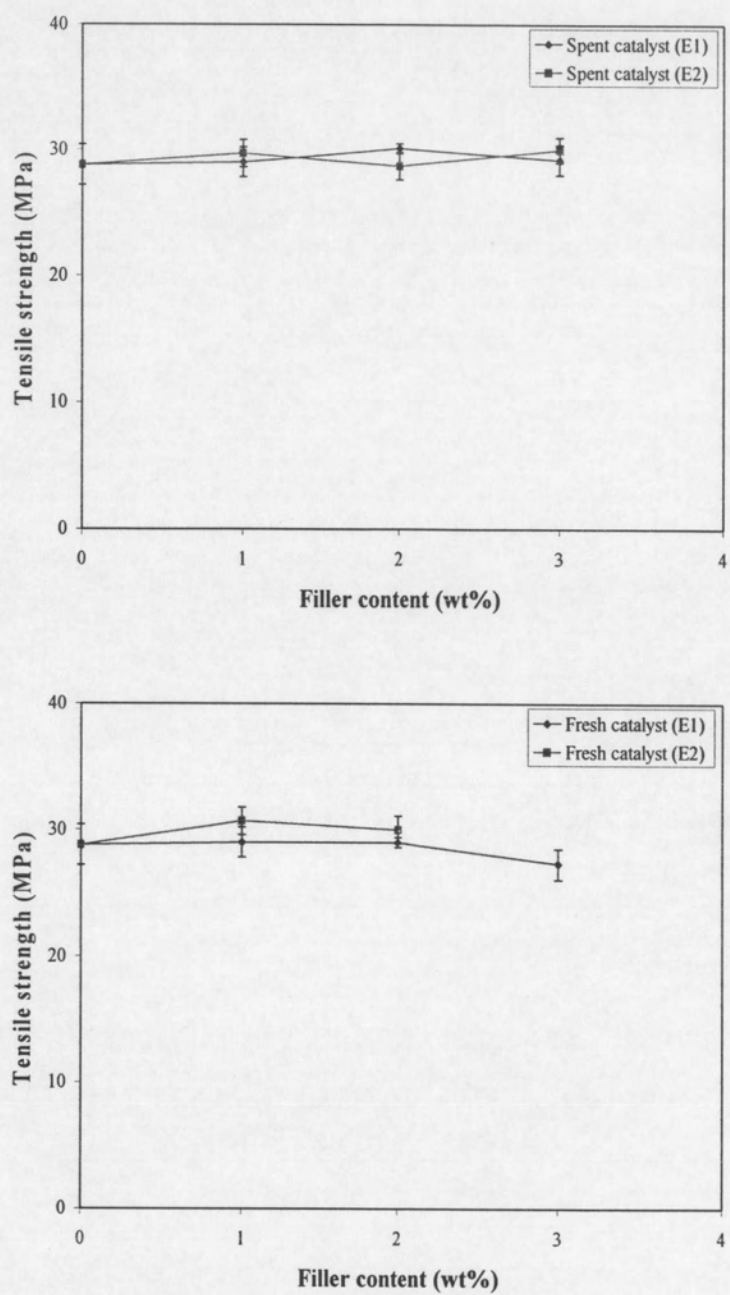


Figure 5.13 Tensile strengths of the fresh catalyst/PP composites and spent catalyst/PP composites at various extrusion cycles.

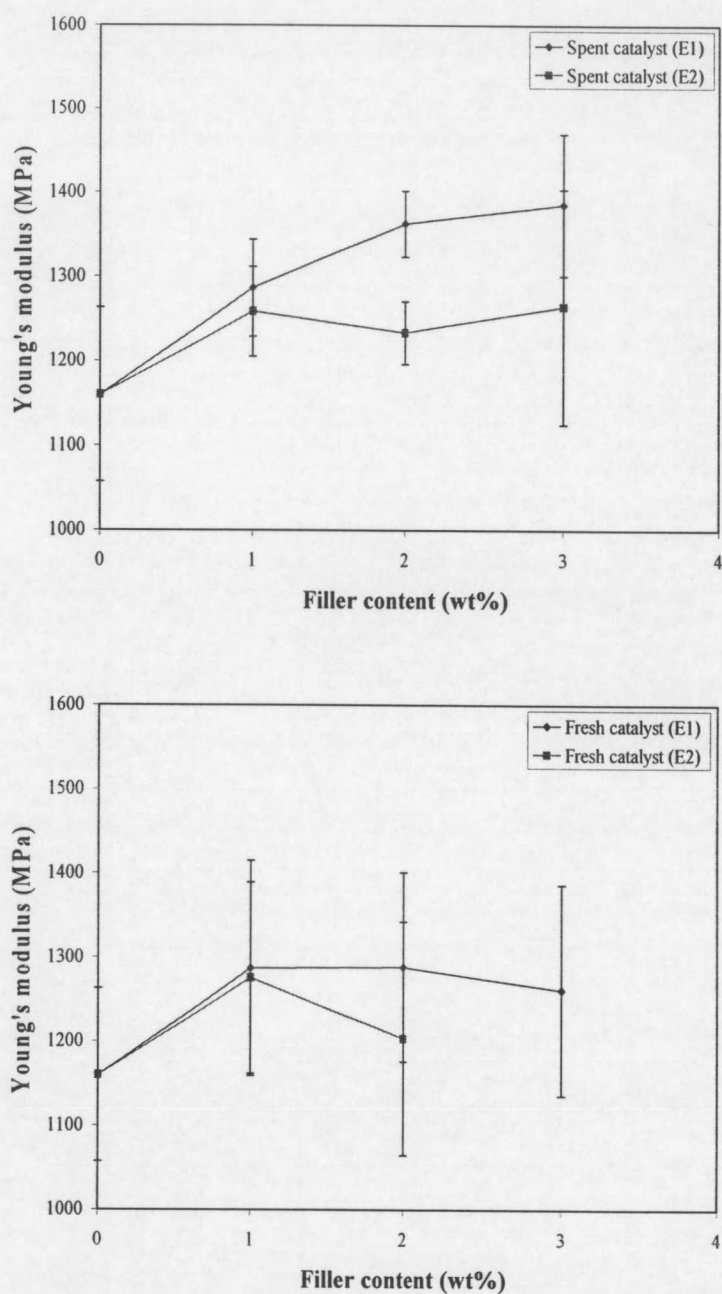


Figure 5.14 Young's modulus of the fresh catalyst/PP composites and spent catalyst/PP composites at various extrusion cycles.

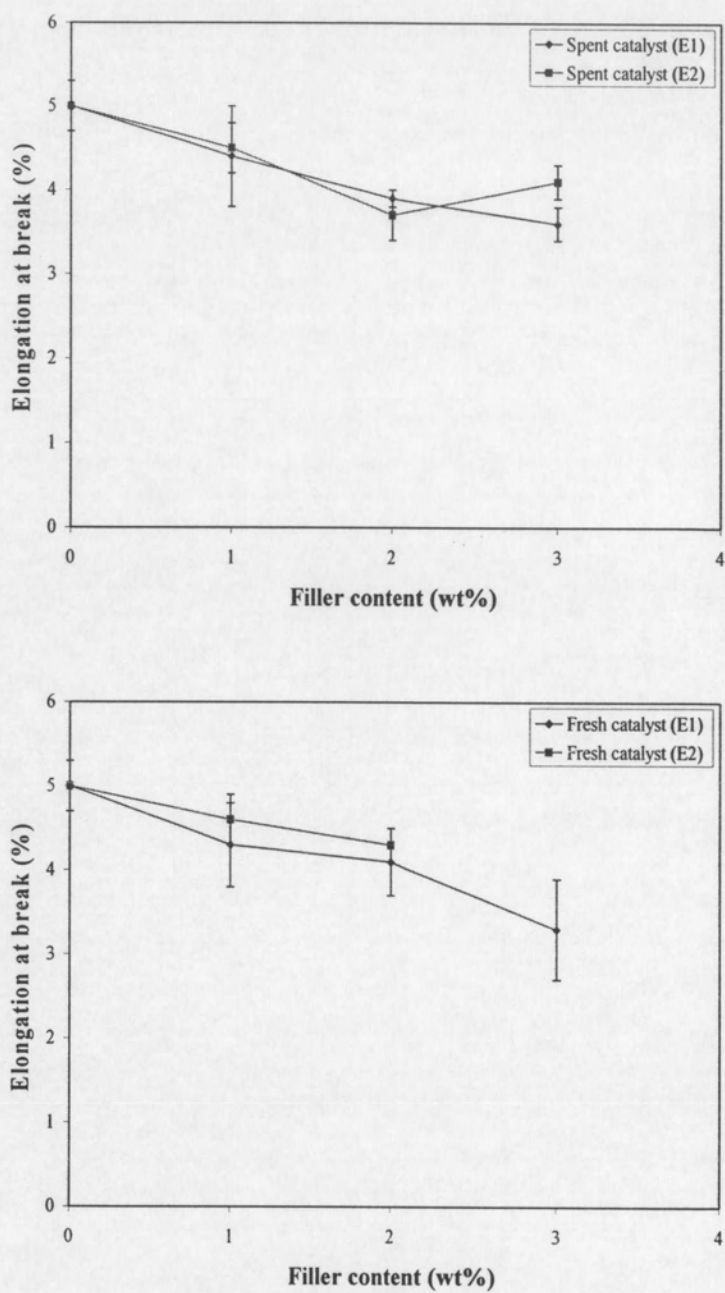


Figure 5.15 Elongation at break of the fresh catalyst/PP composites and spent catalyst/PP composites at various extrusion cycles.

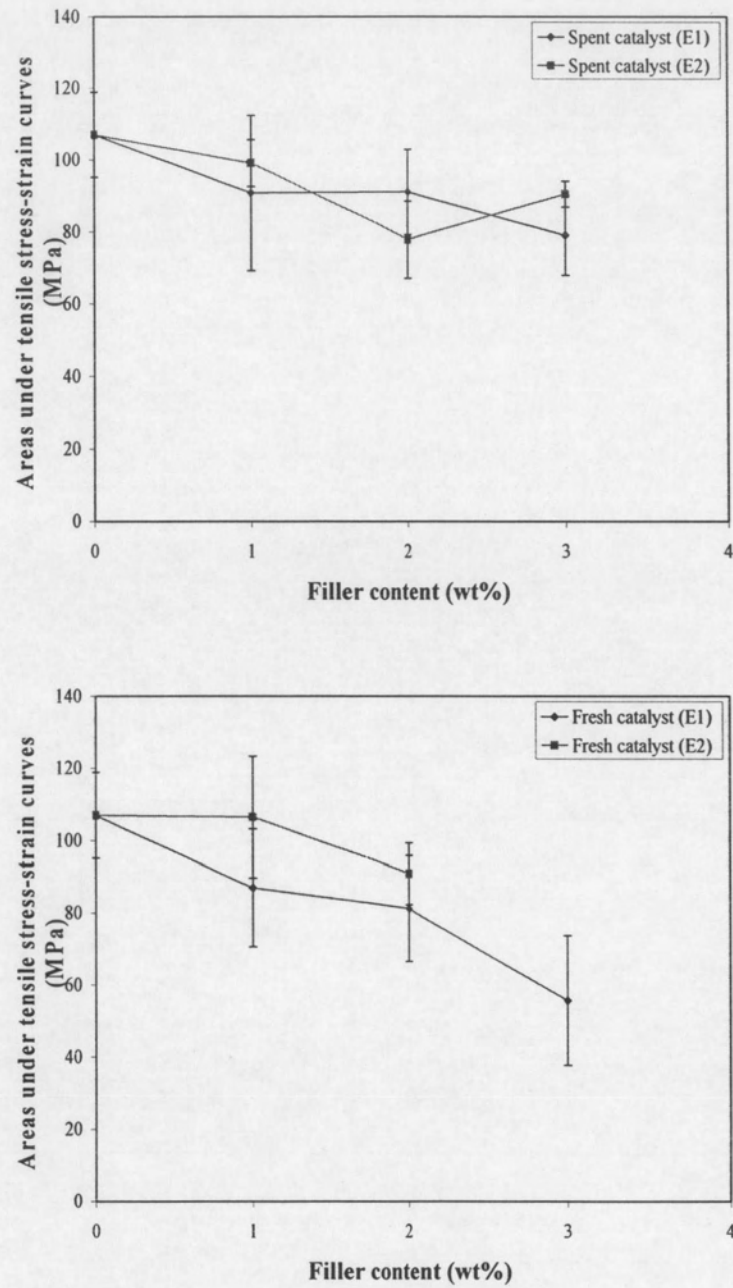


Figure 5.16 Toughness of the fresh catalyst/PP composites and spent catalyst/PP composites at various time extrusion.

5.2.3 Effect of extrusion cycles on morphological properties of polypropylene composites

The tensile fracture surfaces of spent catalyst/PP composites and fresh catalyst/PP composites at various extrusion cycles are shown in Figure 5.17 and 5.18. From SEM, it can be seen that surface of spent catalyst/PP composites and fresh catalyst/PP composites were smoother with increasing extrusion cycles due to well distribution of the filler in the polymer matrix. On the other hand, it also increased in the agglomeration of spent catalyst particle. Therefore, it could be expected that the stiffness of spent catalyst/PP composites decreased with increasing extrusion cycles. These observations support the results of the tensile tests where the spent catalyst/PP composites and fresh catalyst/PP composites at one extrusion cycle displayed higher stiffness than the spent catalyst/PP composites at and fresh catalyst/PP composites one extrusion cycle.

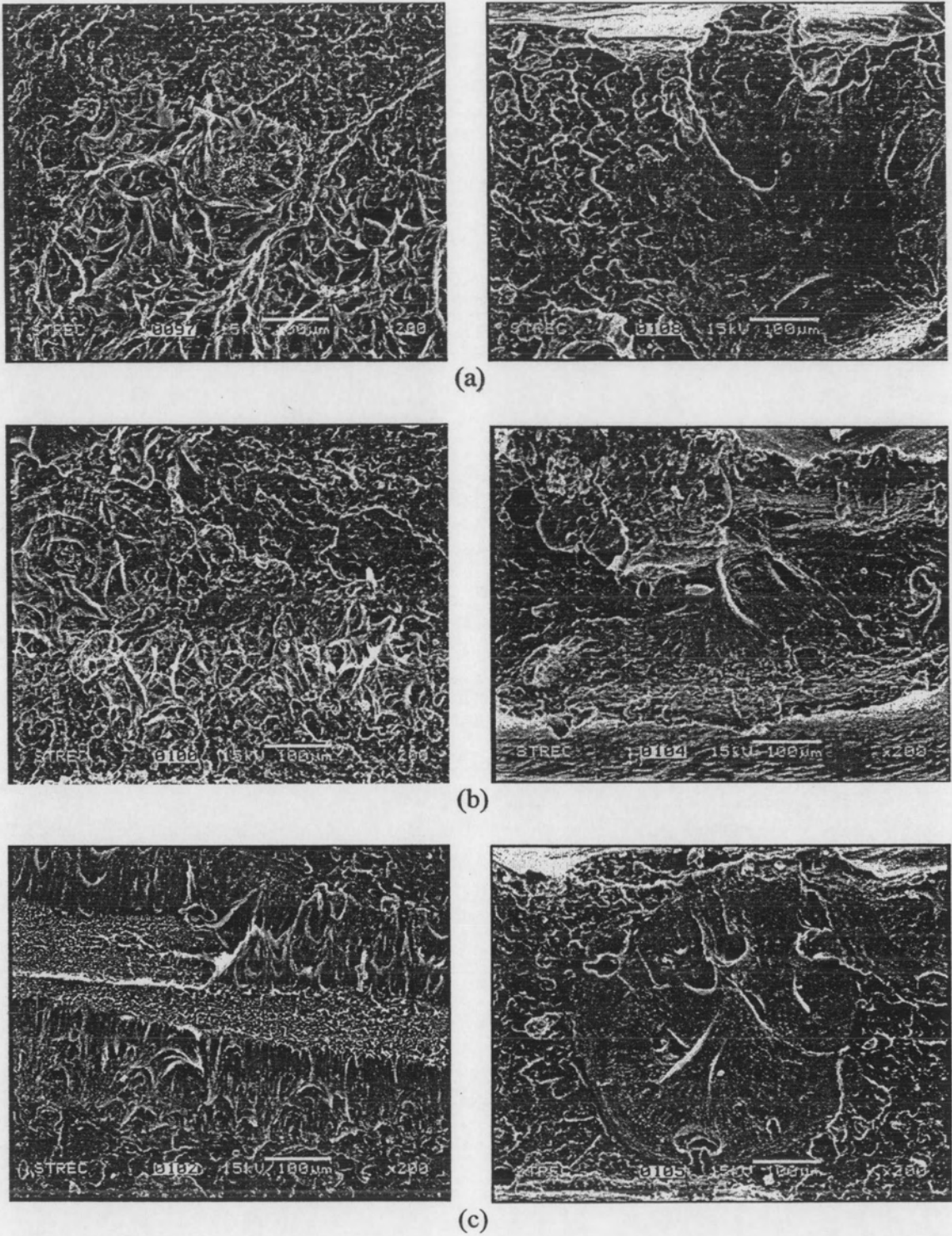


Figure 5.17 SEM micrographs of the tensile fracture of (a) 1 wt% spent catalyst/PP composite (b) 2 wt% spent catalyst/PP composite and (d) 3 wt% spent catalyst/PP composite at various extrusion cycles (left-one extrusion cycle, right-two extrusion cycles).

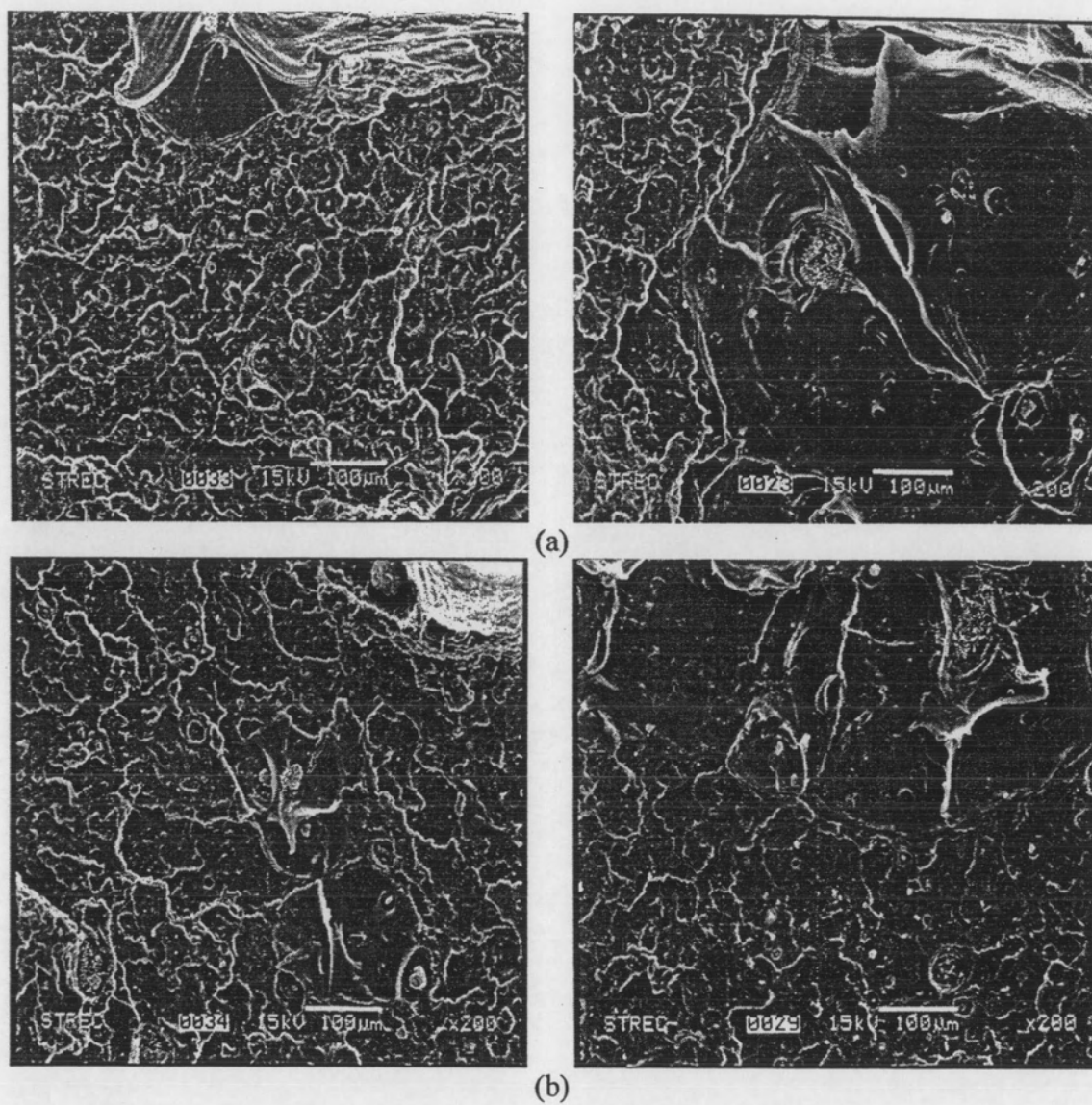


Figure 5.18 SEM micrographs of the tensile fracture surface of (a) 1 wt% fresh catalyst/PP composite and (b) 2 wt% fresh catalyst/PP composite at various extrusion cycles (left-one extrusion cycle, right-two extrusion cycles).

Note

Unobtainable tensile data of the fresh catalyst in the second cycle of the extrusion results from the degradation of the polypropylene which happened in the case of 3%wt fresh catalyst/PP composite.