Thermal Stability of Polyoxymethylene and Its Blends with Poly(ethylene-methylacrylate) or Poly(styrene-butadiene-styrene)

Qian Wang

Section for Chemical Engineering, Department of Biotechnology, Chemistry and Environmental Engineering, Aalborg University, Niels Bohrs Vej 8, DK-6700 Esbjerg, Denmark

ABSTRACT: Polyoxymethylene (POM) copolymer and its blends with poly(ethylene-methylacrylate) (EMA) or poly(styrene-butadiene-styrene) (SBS) up to 5 wt % were conducted to thermooxidative ageing in oven at 140°C for 111 days. POM showed continued degradation as seen from the gradual decrease in the crystallization temperature from differential scanning calorimetry (DSC) study, while no change in Fourier transform infrared spectra (FTIR) and low weight loss were observed (2.5% after 111 days' ageing). The POM degradation was characterized by the initial increase of crystallinity due to crystal perfection, which then kept nearly unchanged until 35 days' ageing, and lastly increased again to result in embrittlement and decrease in tensile strength. Increase in the tensile stress and strain was observed up to 35 days' ageing. POM blends with SBS or EMA had similar degradation behavior as POM, but addition of SBS accelerated the POM degradation significantly, while POM blend with 1 or 3% EMA just showed slightly lower thermal stability than POM. Degradation in POM and SBS/POM occurred in amorphous phase while EMA/POM degraded in both amorphous and crystal phase. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 376–388, 2011

Key words: polyoxymethylene; blends; elastomers; thermoxidative ageing; crystallization

INTRODUCTION

Polyoxymethylene (POM) is one important engineering thermoplastic due to its high solvent resistance, high mechanical strength, thermal stability, and self-lubrication properties, but has poor impact strength. Like other thermoplastic polymers, POM has also been explored to blend with other plastics and inorganic materials to enhance its performance, for example, PTFE has been blended with POM to increase the friction properties of POM[1,2]; other polymers such as thermoplastic polyurethane, EPDM elastomers, ionomers, and polypropylene have been used to increase the toughness of POM.[3–5] However, because of the poor compatibility of POM with other plastics, POM is seldom applied to polymer blend, only few polymers that contain phenol group such as Novolak resin and polyvinylphenol have been reported to be miscible with POM.[6,7] Compatibilizers that containing alcohol functional group as in ethylene-vinyl alcohol copolymer and acid and metal ions in the ionomer ethylene-methacrylic acid copolymer have been employed to improve the miscibility of POM with polypropylene or methyl methacrylate-*co*-styrene-*co*-butadiene copolymer in the blend.[4,8] Generally, the blends mentioned as above are mainly with high amount of the other part in the POM blends, which in most cases higher than 20%. The study of the mixing and distribution of small amount of adding polymers into POM is seldom.[9]

The high thermal stability of POM has been achieved by acetylation of the end hydroxyl groups or copolymerization with comonomer.[10,11] All these modifications in the structure are found to be able to stop the formation of the major degradation product formaldehyde thus hinder the chain scission. Considering the thermooxidation of POM, it is established that thermal ageing of POM at moderate temperatures under 150°C results essentially from radical chain oxidation which produces hydroperoxides, and decomposition of hydroperoxide leads to one chain scission with one formate formation and either a formaldehyde monomer and a primary alcohol chain end or a primary alkoxy free radical chain end formation. The primary alcohol or primary alkoxy free radical chain end can then initiate further depolymerization. The degradation is accelerated in presence of oxygen.[12] It is also found that under moderate temperature (130 or 140°C) in air, the stabilized POM copolymer has relatively high thermal stability and no significant changes were

Correspondence to: Q. Wang (qwang@bio.aau.dk).

found in molecular weight or tensile strength.[13,14] The degradation occurs initially in the amorphous phase.[15] Since additives disperse normally in the amorphous phase, the presence of additives will influence the thermal stability by either react with oxygen to form active species or interact with the active species generated during the degradation.

The thermoxidative degradation of EMA copolymer occurs via free radical mechanism too. Different from the chain scission in the POM degradation, at low degree of oxidation, PE sequence is subjected to chain scission but poly(methylacrylate) (PMA) sequence is subjected to crosslinking where intermolecular ester group is formed together with intra- and intermolecular hydrogen bond formation. At higher degree of degradation, both PE and PMA should lead to crosslinking product. The presence of PMA in the copolymer leads to a faster degradation conversion than either pure polyethylene (PE) or PMA, and different mechanism takes on action at higher conversion which results in gels that cannot dissolve in the alkali solution after seven days' ageing at 180°C.[16]

The degradation of SBS copolymer is found to occur with a firstly phase separation where the polybutadiene chain undergoes chain scission and leads to a polystyrene rich segment immiscible with the polybutadiene segment. Polybutadiene segment then keeps on degradation to form small chain scission segment as well as crosslinked products to result in a secondary phase separation.[17] Since both SBS and EMA undergo free radical thermooxidative degradation as that of POM, addition of these two polymers will influence the stability of the final POM blends, both in the short or the long period stability at low ageing temperature, as well as short term stability under higher temperatures.

To improve the dispersion of fillers and other additives in POM, the possibility of blending POM with small amount of EMA or SBS copolymers as carrier material up to 5 wt % is investigated in this work. The tensile strength and thermooxidative stability of the blend are studied and compared with the virgin POM. The thermooxidative ageing was carried out in oven at 140°C for 111 days, and the changes were studied by weight loss, tensile test, FTIR, DSC, polarized light microscopy, and TGA analysis.

EXPERIMENTAL

Materials

Polyoxymethylene copolymer (POM, Hostaform C 9021 from Ticona GmbH, Kelsterbach), poly(styrene-butadiene-styrene) triblock copolymer (SBS), and poly(ethylene-*co*-methylacrylate) (EMA, 25% methyl acrylate, tensile strength 14 MPa, Elvaloy from DuPont, Switzerland) were kindly supplied by Controlled Polymers A/S, Denmark. All materials were in granular form.

Polymer blends

POM and POM blends with 1, 3, and 5 wt % of SBS or EMA were made by injection molding (Battenfeld Unilog 4000). The temperatures for Zone 1 to Zone 4 were 230, 225, 220, and 215°C, respectively. The dumbbell-shape bar with dimension of $14.85 \times 1.0 \times 0.3 \text{ cm}^3$ was obtained.

Tensile strength test

The tensile strength and strain of the injection molded bar was tested on Instron LR50K using a 5000 Newton load transducer with the crosshead speed of 30 mm/min.

Differential scanning calorimetry (DSC)

DSC scanning was carried out on Mettle Toledo DSC 822[e] module equipped with sample robot TSO 801RO. The sample was heated from 25 to 200°C, kept at 200°C for 3 min, then cooled down to 25°C and finally heated up to 230°C again. The heating or cooling rate was 10°C/min.

The melting enthalpy of the sample (ΔH_s) from the first heating step was used for calculation of the degree of crystallinity of the sample (X_c) according to eq. (1). The ΔH_s was calculated by the evaluation function in the associated STAR[e] software, that is, the area of the melting peak (ΔH_s) was integrated by assigning the start and end temperature of the baseline and integration limit. For the samples before ageing the baseline and integration limits were at around 100°C and 180°C, and baseline type was spline. For the samples after ageing the limits were at around 135°C and 180°C, and baseline type was line. The melt enthalpy of 100% POM crystals (ΔH_{ref}) is assumed to be 326 J/g.[1]

$$X_c = \frac{\Delta H_s}{\Delta H_{\text{ref}}} \times 100\% \qquad (1)$$

Thermal gravimetrical analysis (TGA)

TGA was done on Mettle Toledo TGA/SDTA 851[e] module. The sample was put into 40 μL aluminum pan and heated from 30 to 400°C at a heating rate of 20°C/min. The analysis was carried out under oxygen flow at a flow rate of 50 mL/min.

Fourier transform infrared spectroscopy (FTIR)

FTIR was done on Perkin–Elmer Spectrum 1000 FTIR (Llantrisant, UK). The attenuated total reflectance
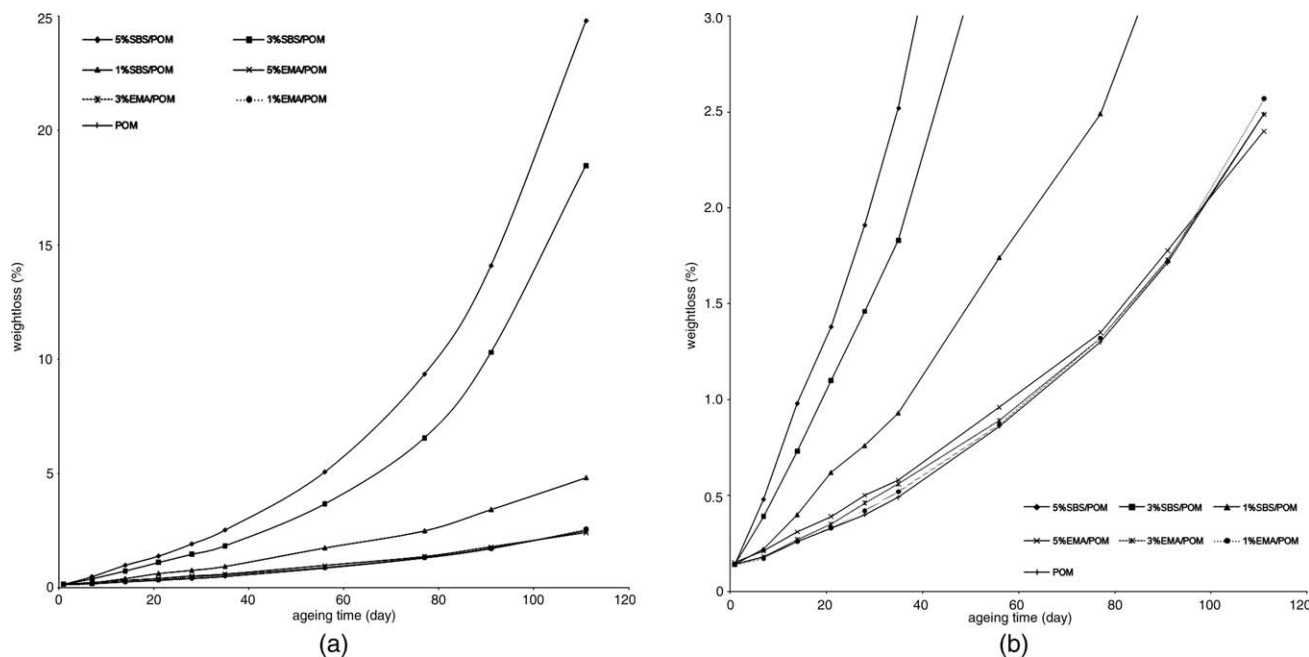
Figure 1 The weight loss of POM and its blends with EMA and SBS during ageing in oven at 140°C.

(ATR) spectrum was taken in the range 4000 to 650 cm^{-1} at a resolution of 4 cm^{-1} with a single reflection ATR accessory (Performer Swap-Top module).

Polarized light optical microscopy

Thin film of virgin POM and its blends with EMA or SBS was prepared according to Ref. 18. 1 wt % of sample was dissolved in N, N-dimethyl foramide at 160°C for 5 min and dropped on the objective glass. After drying at room temperature overnight, the sample was further dried at 105°C for 2 h and at 130°C for 30 min. The sample was then melted at 200°C for 6 min and crystallized at 105°C for 15 min before cooling down for microscope observation. To study the change of spherulites in the thin films, these samples were also put into oven and aged at 140°C for 35 days. The Olympus polarized light microscope U-CMAD-2 with ×40 times' magnification was used.

Thermal oxidative degradation

Thin sample films with 50 μm thickness were cut from the injection bars by the microtome and used for the degradation study. About 0.3 g of the sample was put into an air circulated oven kept at 140°C and taken out after 1, 7, 14, 21, 35, 56, 77, and 111 days of ageing for the FTIR, DSC and TGA characterization. At the same time, the dumbbell-shaped samples were put into the same oven for ageing to measure the change in weight, tensile strength, and strain.

RESULTS AND DISCUSSION

Thermal oxidative degradation

Weight loss

The dumbbell-shaped samples made from POM and its blends were subjected to degradation in oven at 140°C for different time. The weight loss against ageing time is shown in Figure 1(a). It can be seen that POM and its blends with EMA have slight weight loss after 77 days of ageing, which are 1.30, 1.44, 1.32, and 1.35 wt % for virgin POM, 1, 3, and 5% EMA/POM blend, respectively. EMA/POM blends lose weight faster than POM until 35 days' ageing, but then slow down. When more EMA is present in the blend, the slower down in the rate of weight loss is more obvious as can be seen from 5% EMA/POM blend [Fig. 1(b)]. Cracks on the surface of 5% EMA/POM after 111 days ageing are observed. The degradation behavior observed in the present work is different from the former study on the same EMA/POM blends, where a drastic weight loss and powdered degradation product were obtained for the 5% EMA/POM blend.[19] The possible reason is that the cut thin samples aged in the former study have been exposed to solvent vapor such as water or other solvent during the ageing in oven. This result shows that EMA/POM blend is more susceptible to the degradation environment. Unlike EMA blends, SBS/POM blends lose weight much faster during the ageing [Fig. 1(a)]. The more the amount of SBS in the blends, the larger the weight loss is observed. The weight loss for 1, 3 and 5% SBS/POM blends after 77 days ageing is 2.49, 6.55, and 9.34%, respectively.
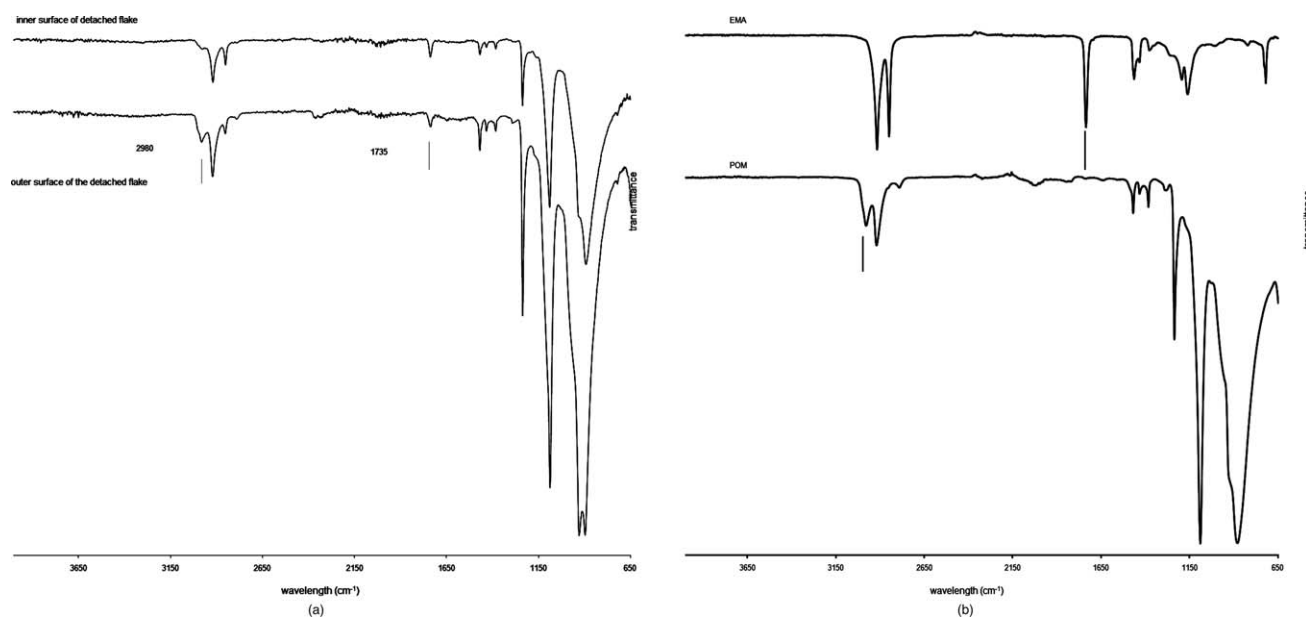
Figure 2 Comparison of the FTIR spectra of the outer surface and the inner surface of the detached flake obtained at the surface of the fracture site after tensile test from 5% EMA/POM dumbbell-shaped sample after 56 days ageing in oven at 140°C.

FTIR spectra

No significant change is found in the FTIR spectra of the virgin POM and EMA/POM blends during and after 111 days' ageing. However, yellowish appears after 77 days' ageing which indicates the degradation product formation. It is noteworthy that in case of 5% EMA/POM bone sample, after 35 days' ageing and the tensile test, thin flake is peeled away from the sample surface at the fracture site. The FTIR spectra of the outer surface of the flake and its inner surface adjacent to the sample body are compared in Figure 2(a). It is clear that the outer surface of the detached flake resembles the original blend most, but there is more EMA on the inner surface of the flake where peak at 1735 cm^{-1} is stronger and peak at 2980 cm^{-1} is weaker in the spectrum [see Fig. 2(b)]. These indicate a nonhomogeneous distribution of EMA in the sample. The accumulation of EMA close to the surface in 5% EMA/POM bone sample might partially delay its weight loss due to higher thermal stability of EMA than POM [see Fig. 1 and Fig. 9(a) in the TGA study]. None such flake after tensile test is obtained in other samples.

In case of POM blend with SBS, new degradation peak at 1735 cm^{-1} appears after 56 days' and 21 days' ageing for 1% SBS/POM and 5% SBS/POM blends, respectively. This indicates the formation of aldehyde carbonyl group as one of the degradation product from POM. In addition, the styrene band at 698 cm^{-1} remains after long time ageing in the SBS/POM sample (Fig. 3). Yellowish occur in all SBS blends already after one day of ageing, which can be from the oxidation of carbon–carbon double bonds in

the SBS. POM blend with 5% of SBS turns to be brittle after ageing for 21 days, and cracks and bending appear in the bone sample after 35 days' ageing. The cracks and bending occur later when there was less SBS in the blend, which is 56 and 77 days for 3% SBS/POM and 1% SBS/POM, respectively. These results indicate that degradation happen both in SBS and POM.

Changes from DSC study

Dynamic DSC scan were carried out for all the samples before and after ageing. As seen in Figure 4, the onset melting temperature for the virgin POM before ageing is not obvious that starts at around 100°C and the curve decreases smoothly with increasing temperature, which indicates the presence of the nonperfect crystals in the sample. However, when the sample has been aged in oven for one day, the onset of the melting peak moves to higher temperature at around 135°C and the curve turns to decrease sharper. This change in the melting curve shape implies the decrease of the nonperfect crystals in the sample, either due to the degradation or from the crystal perfection during the ageing.[20] Because of the small amount of samples at 0.3 g, the weight loss of all film samples after one day ageing is not detectable (0.14% weight loss after one day ageing for the bone sample). Furthermore, the same smooth decrease at the onset of the melting curve is observed again when the aged sample is reheated after melting and cooling, the first reason that degradation causes the onset sharpening of the melting peak can be excluded. In addition, the melting peak
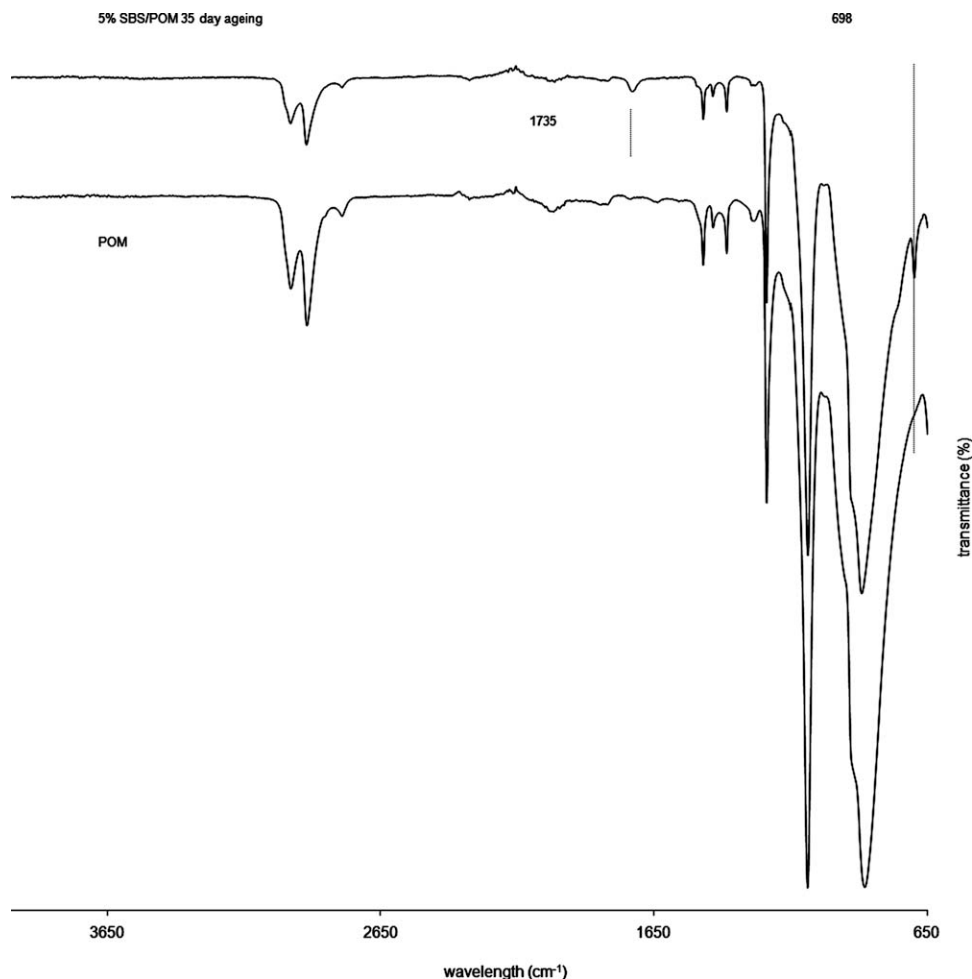
Figure 3 FTIR spectra of POM and 5% SBS/POM aged for 35 days.

temperature increases also after one day ageing, which suggests the increase in the crystal size after crystal perfection. The melting peak shape and melting peak temperatures are similar for the virgin POM and its blends. It is found that all the samples gain the similar sharp onset of the melting peak after one day ageing and keep it until 7 (for 1 and 3% SBS/POM) or 14 (for POM and EMA/POM blend) days' ageing.

The melting peak of POM and its aged samples at different ageing time are compared in Figure 5. Besides the sharp onset of the melting peak after one day's ageing, it is observed that the sharp onset in the melting curve disappears and turns to be smooth again and the melting peak becomes narrower toward higher onset melting temperature with increased ageing time. Same tendency is observed for POM blends with EMA and SBS. A rough comparison of the degree of crystallinity (X_c) between the aged samples in Figure 6(b) indicates that X_c increase in the aged samples, which has also been reported in many investigations on thermal ageing of semicrystalline polymers.[13,21–24] The X_c of

virgin POM increases at the initial stage until seven days of ageing, then reaches a plateau until 35 days ageing, and finally increases to 53.3% after 77 days' ageing. This is in consistent with the reported result on the change of crystallinity by WAXS study from POM copolymer degradation in air at 130°C.[13] No weight loss is observed from the film aged for 7 days, and it is reasonable to assume that the degradation of POM makes negligible effect and the initial increase in crystallinity can be allocated to the pure physical crystal perfection and further crystallization of amorphous macromolecules. During 7 to 35 days' ageing, the gradual chain scission keeps on in the amorphous phase but does not make a significant change in the crystallinity. With further ageing and more lower molecular weight chain formed which is then released from the entanglement in the amorphous phase, many new chains can be included in the crystal or form new crystals, a phenomena called "chemi crystallization" to result in a further increase in the degree of crystallinity.[23,25] Furthermore, the smoothing and shifting toward higher temperature at the onset of the melting curve after
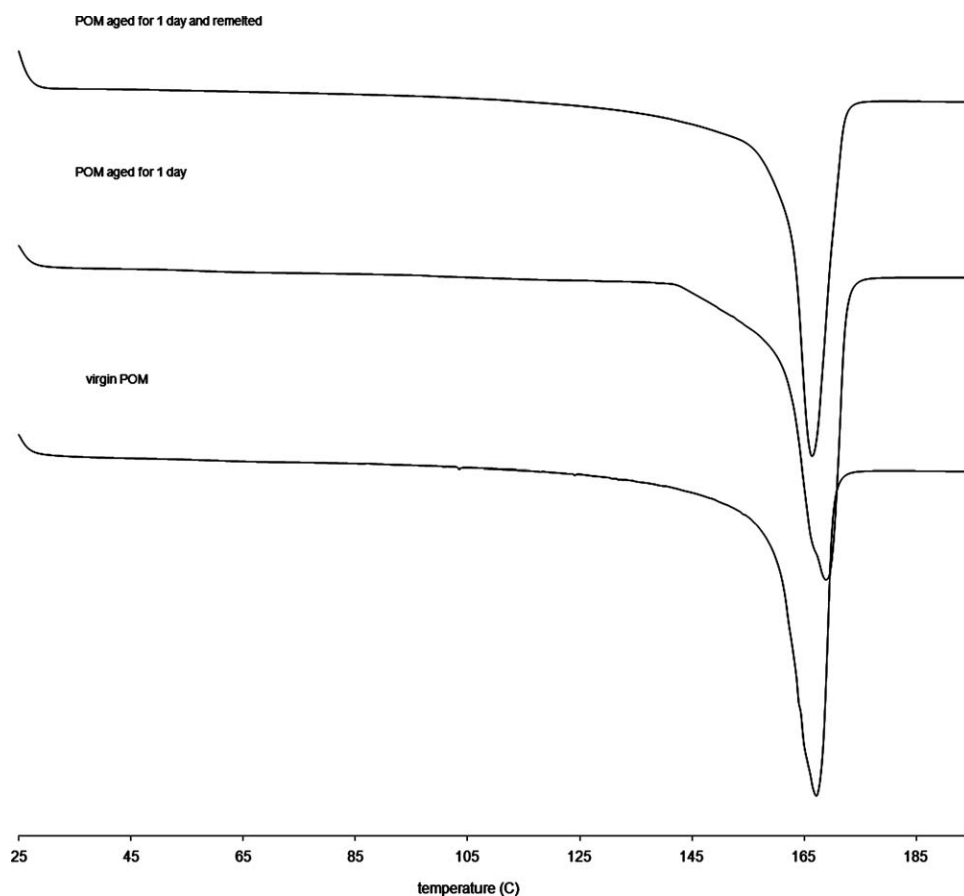
Figure 4 The DSC melting curve for virgin POM (bottom), virgin POM after one day ageing at 140°C (middle) and one day aged virgin POM after remelting (upper). The upper curve was obtained from the one day aged sample, which was heated up to 200°C and kept at that temperature for 3 min (remelt), cooling down to 25°C and heating up again to get the curve.

long time ageing indicate that the original interphase between amorphous and crystalline phase is changed. If it is assumed that only the amorphous phase lose weight during ageing, then the increase in the X_c from 45.8% in the virgin POM to 53.5% after 77 days' ageing would equal to 14% weight loss in the whole sample, which account to 26% of the initial amorphous phase. However, the weight loss of the thin film POM after 77 days' ageing is much lower, which is less than 5%. Therefore, after long ageing the increase in the crystallinity is caused by the integration of released molecular chain from the amorphous into the crystalline phase. This is in agreement in the reported finding that in the POM copolymer the length of amorphous phase decreases from about 6.3 nm to 5.2 nm after 158 days' ageing at 130°C, while the length of the long period l_p that include both the length of crystalline and amorphous phase keeps nearly unchanged at 15.4 nm from SAXS study on the morphology of POM lamellar structure.[13] Although at this stage of degradation we still cannot observe oxidation product formation from FTIR study, the second time increase in X_c indicates significant changes in the sample.

EMA/POM blend have similar change as that of POM, which suggests similar degradation process as in virgin POM. However, the initial increase in X_c is slower in the EMA/POM blend that could be due to the interaction between EMA and POM to retard the rearrangement of POM segments into the crystalline phase. In addition, it is found that after the initial increase in X_c, a decrease in X_c occur followed with an increase in X_c again during the course of the ageing. The more the EMA in the blend, the more obvious and earlier of the phenomena can be seen in Figure 6(b).

In case of SBS/POM blends, a continuous increase in the degree of crystallinity can be seen in Figure 6(b). This implies that the degradation of POM is accelerated in presence of SBS, which is in agreement with the results from weight loss and FTIR study.

Beside the melting peak, the change in the crystallization peak temperature (T_c) in the aged samples was also studied. First, in Figure 7(a), it can be seen that the addition of EMA or SBS in POM decreases its T_c. The more EMA is added, the lower the T_c in the blend; but for SBS blend, 1% SBS has the lowest T_c, adding more SBS increase the T_c a little. If there is weak interaction between EMA and POM, the
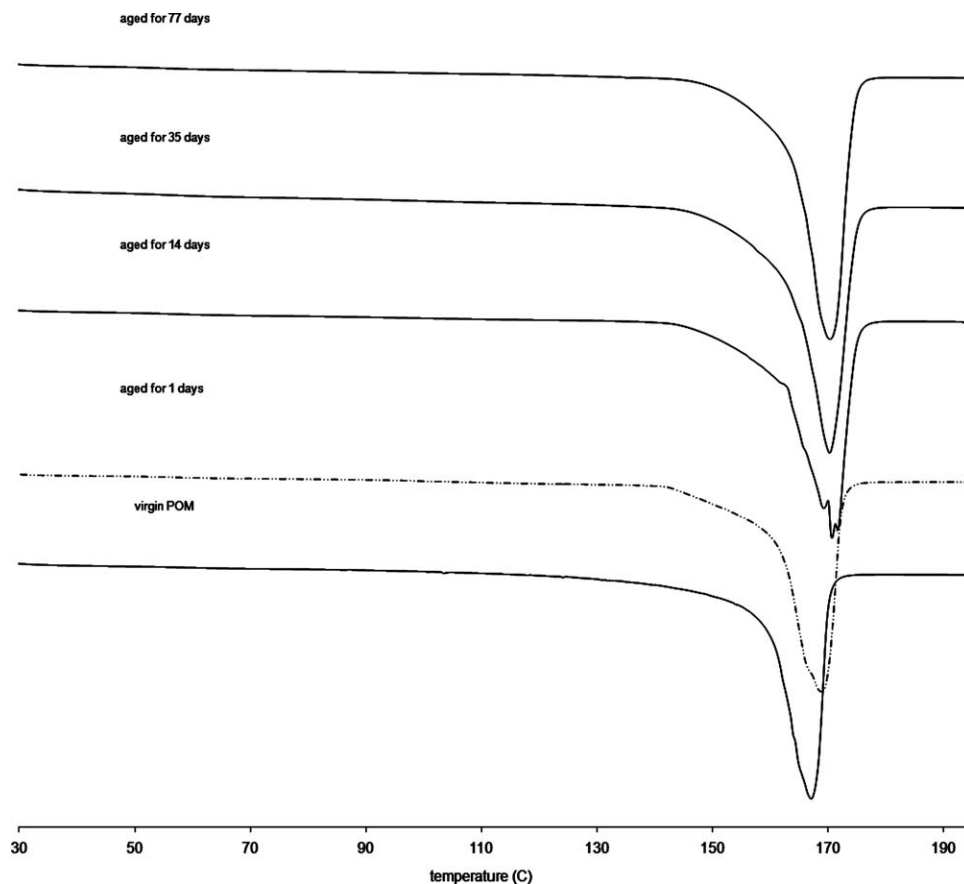
Figure 5 The DSC melting curve for virgin POM after different ageing time at 140°C.

addition of EMA in POM could retard the crystallization of POM. It has been found that both alkene and styrene polymers have poor compatibility with POM.[6,7] This implies that SBS disperse in the amorphous phase in the SBS/POM blend, and SBS segments has no interaction with the chain moiety of POM that integrate in the crystalline phase. Therefore, the presence of SBS in POM will function as
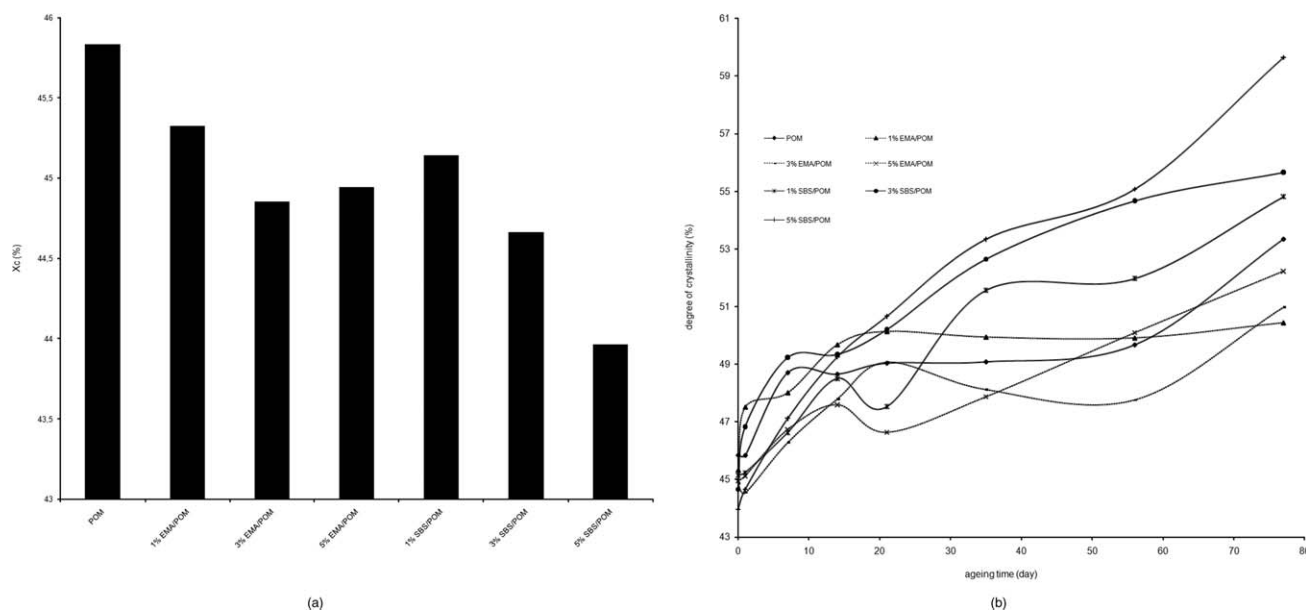

Figure 6 (a) The total degree of crystallinity (X_c) of POM and its blends; (b) The change in the X_c of POM and its blends during ageing in oven at 140°C.
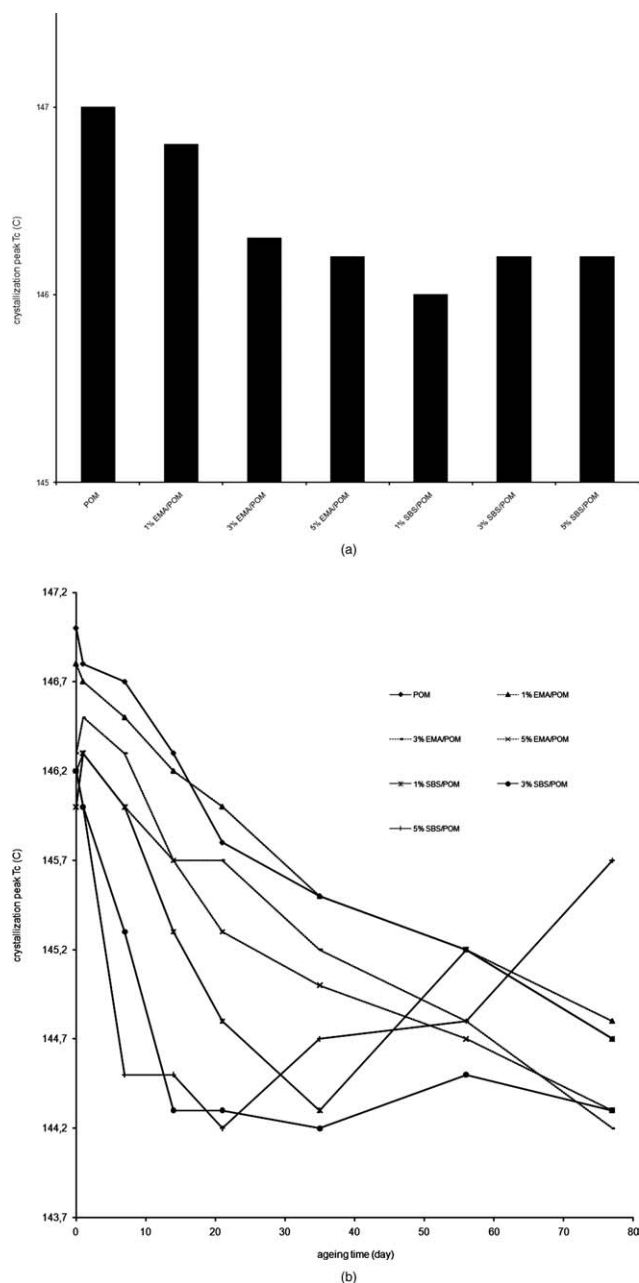
Figure 7 (a) The crystallization peak T_c of POM and its blends; (b) The change of T_c of POM and its blends during ageing in oven at 140°C.

stereo block to retard the POM crystallization. When more SBS is added, SBS will join with each other and be repelled from POM matrix, which makes less effect on retarding crystallization.

Figure 7(b) shows the T_c of the aged film samples after different ageing time. The aged film sample was heated up to 200°C first and kept at this temperature for 3 min for melting, then was cooled down and the crystallization peak was recorded. For the POM and its blends, the gradual decrease of the crystallization peak temperature with increased ageing time is observed. The decrease of crystallization

peak indicates that the molecular weight of POM decrease due to the chain scission caused by the active degradation site accumulated during the long time ageing. POM blend with 1% SBS, 3% EMA, and 5% EMA have increased crystallization peak temperature after one day's ageing. This increase in T_c can be due to the secondary crystallization which will exclude more SBS and EMA from the POM segments, during the DSC remelting and the lack of mixing and melt flow as that in injection molding, EMA and SBS cannot disperse as well as they were in the injection molded bar, and thus make less effect on the retardation of POM crystallization. SBS/POM blends tend to gain increased T_c after long-term ageing, which could be due to the nucleation effect from the degradation product.

The mechanical property of POM and its blends

Addition of EMA and SBS in POM leads to a decreased tensile strength in POM. In comparison with virgin POM, the tensile strength of 5% EMA/POM and 5% SBS/POM decrease 12 and 10%, respectively.[19] This could be due to the low tensile strength of both EMA and SBS, and the decreased total degree of crystallinity in the blends [Fig. 6(a)]. Addition of EMA or SBS does not change the percent strain at maximum load or at break to a large extent.

The change of tensile strength in the samples after different ageing time was also studied. Figure 8 shows that the virgin POM and its blends with EMA have increased tensile strength during ageing up till 35 days ageing. Meanwhile, the percent strain at the maximum load and at break increase also. However, prolonged ageing time to 111 days leads to significant decrease in tensile strength and all the samples turn to be brittle and break at the maximum load (Table I). The first increase in tensile strength and strain (plasticity) during ageing may be caused by the perfection of crystals, and the new crystals formed in the amorphous phase would function as extra crosslinking sites between crystals to enhance the tensile strength and strain. At 35 days' ageing the weight loss for POM, its blends with EMA and 1% SBS/POM are lower than 1%. The same tendency in the change of the mechanical properties of POM and its blends with EMA and SBS indicates that the change in the crystallinity of POM and the degradation degree of POM molecular chain during ageing play the major role in the mechanical property of POM and its blends. An increase in the tensile strength after annealing has also been reported by other workers, for example, for POM, propylene and polylactide.[13,21,22]

SBS/POM blends undergo faster degradation than POM, and the time that embrittlement occurs follow the order 5% > 3% > 1% SBS/POM blend.
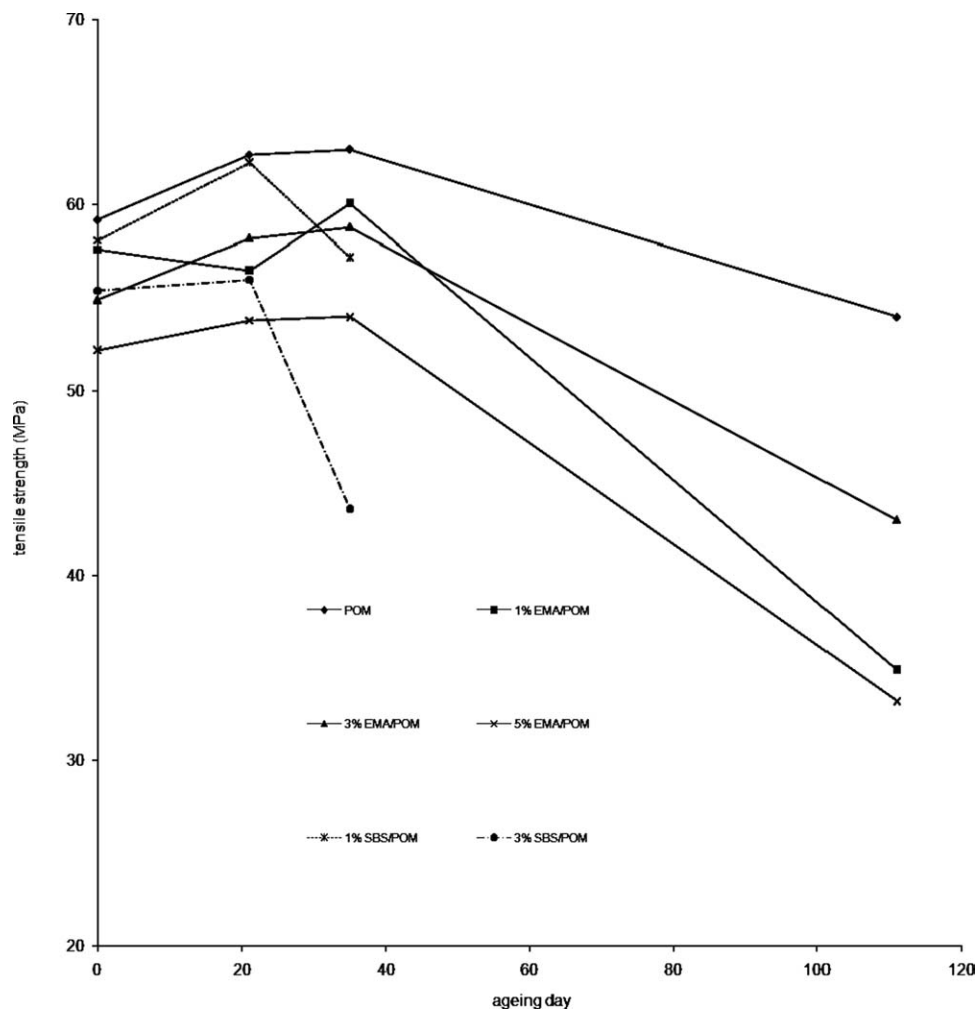
Figure 8 The change of tensile strength of POM and its blends with EMA and SBS during ageing in oven at 140°C.

Conversely, the influence of EMA on accelerating the POM degradation is not very obvious. Nevertheless, POM is more thermooxidative stable than its EMA and SBS blends, addition of EMA up to 3% does not make a big effect in reducing POM's mechanical property and thermostabilty.

The thermal stability of the samples from TGA study

First, the influence on the dynamic thermal stability of POM by addition of EMA and SBS was studied. Figure 9(a) and Table II show that the onset of thermal degradation of POM ($T_{3\%}$ at 3 wt % weight loss) is lower than EMA, and POM lose its weight much faster at lower temperature than that of EMA due to the autocatalytic chain scission. By the addition of EMA or SBS in POM, the $T_{3\%}$ decreases with increased amount of EMA or SBS in the blend, which indicate that some voids or weak sites are generated during the injection molding. This suggestion is supported by the following two observations.

First, when the POM and its blends undergo TGA analysis under nitrogen flow,[19] an increase of 15°C in 1% SBS and 13°C in 1% EMA blend in $T_{3\%}$ as compared with the virgin POM (299.2°C at 3% weight loss) are observed. The increase of EMA amount up to 5% leads to no further increase in $T_{3\%}$, but increase SBS to 5% leads to 30°C higher under nitrogen flow. Second, after the POM and its blend with EMA and SBS have been aged at 140°C for one day, the $T_{3\%}$ of POM blends under oxygen flow increase a little while that of virgin POM decreases (see Table II). The increase of $T_{3\%}$ is possibly due to the secondary crystallization, removing of trace amount of volatile component and relocation of EMA or SBS in the blend after ageing to decrease weak sites. From Figure 9(b), it can also be seen that EMA and SBS in the POM blend lead to slowing-down of thermal degradation at high temperature. Since free radicals are the major active species involved in the thermal degradation, the carbon–carbon double bond will be more reactive to receive the free radical species to hinder the formation of

TABLE I
The Tensile Stress and Percentage Strain of POM and Its Blends During the Ageing

Sample	Ageing day	Tensile strength (MPa)	Tensile strain (%)	Breaking stress (MPa)	Breaking strain (%)
POM	0	59.2	13.1	43.9	38.2
	21	62.7	34.5	58.4	65.6
	35	63	34.0	61.9	46.7
	111	54	9.2	54.0	9.2
1% EMA/POM	0	57.6	12.5	49.3	34.9
	21	56.5	33.9	57.8	63.7
	35	60.1	33.7	59.1	47.9
	111	34.9	3.9	34.9	3.9
3% EMA/POM	0	54.9	12.8	44.4	34.6
	21	58.2	32.8	55.5	59.6
	35	58.8	35.9	57.3	45.4
	111	43	9.5	43	9.5
5% EMA/POM	0	52.2	11.4	43.6	37.7
	21	53.8	32.7	50.2	53.5
	35	54.0	32.4	51.5	49.1
	111	33.2	4.4	33.2	4.4
1% SBS/POM	0	58.1	12.2	50.0	37.1
	21	62.3	17.6	61.4	46.1
	35	57.2	32.7	57.2	32.7
3% SBS/POM	0	55.4	15.7	48.0	40.8
	21	56.0	13.4	56.0	13.4
	35	43.6	4.7	43.6	4.7
5% SBS/POM	0	53.2	13.3	39.3	39.8

formaldehyde as chain scission product, and the benzene group in SBS can lead to high stability at high temperature. The presence of EMA may also help the acceptance of the free radicals to form crosslinked product, therefore, the weight loss rate in the blend decrease at high temperature.

The change of thermal stability of POM and its blends after ageing at 140°C for different time was also studied by TGA. Table II shows that after 77 days of ageing $T_{3\%}$ of virgin POM decrease with 7.4°C, and 5% SBS/POM blend decrease with 8.3°C, which is comparable, while the weight loss for 5% SBS/POM bone sample aged at 140°C is at least five times larger than POM. This indicates that the degradation in 5% SBS/POM occurs mainly in the amorphous phase. On the other hand, the decrease in $T_{3\%}$ for 5% EMA/POM after 77 days' ageing is much lower (2°C), which suggests the retardation of POM degradation in presence of EMA.

The change in spherulites observed from polarized light optical microscopy

The spherulites pictures of virgin POM and its blend with 5% EMA or 5% SBS are shown in Figure 10. No big difference in the spherulite size and their distribution can be seen when comparing POM with its blends. This is due to the film preparation process where a crystallization step at 105°C was applied to all the samples to allow slow crystal

growth for perfect spherulites' formation. And in addition, this result shows that allowing enough long crystallization time at high temperature in the absence of mechanical strength, either EMA or SBS make significant effect in POM crystal growth. Further observation is that the spherulites of POM and EMA/POM blend are clear with high contrast, but those of SBS/POM blend are weak with low contrast. Since SBS and POM are immiscible, SBS may separate from POM and form an upper layer that cover the POM during the preparation of thin film sample on the objective glass. The low contrast could be due to the difference in the refractive index
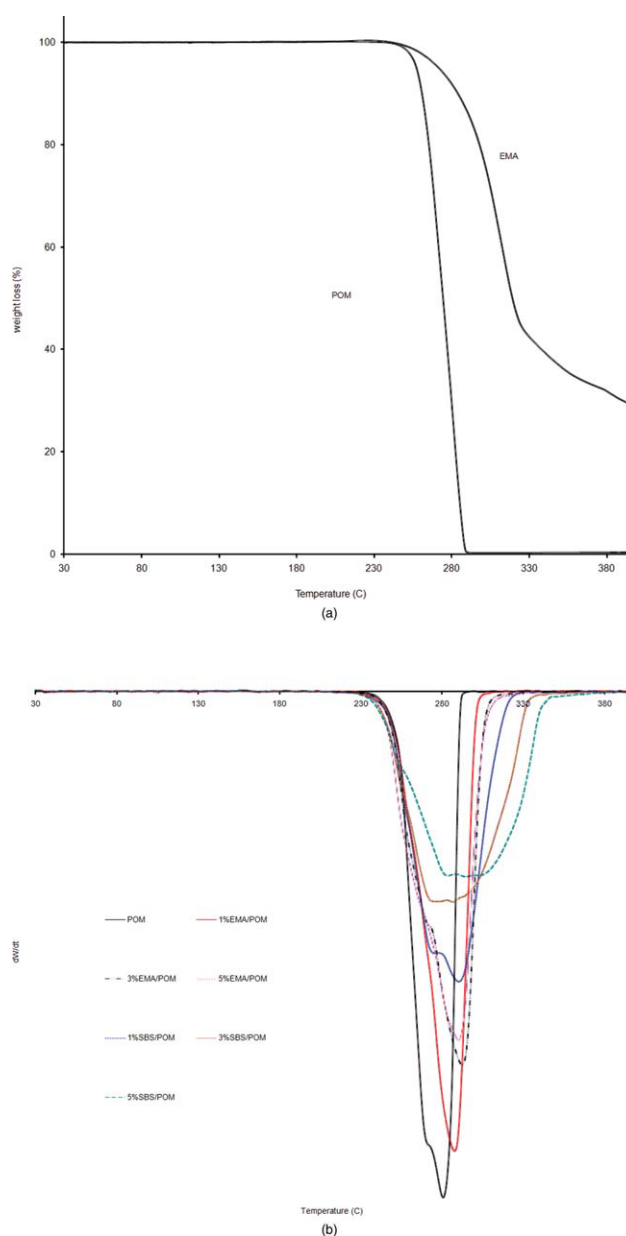

Figure 9 (a) The TGA curve of POM and EMA; (b) The DTG curve of POM and its blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sample	$T_{3\%}$[a] (°C)	$T_{50\%}$[b] (°C)	$W^c_{400°C}$ (%)
POM	254.7	274.7	0.30
aged for 1 day	251.7	273.3	0.47
aged for 77 days	247.3	272.7	0.41
1% EMA/POM	253.7	280.7	0.44
aged for 1 day	254.3	280.3	0.44
3% EMA/POM	253.0	283.0	0.55
aged for 1 day	253.7	281.3	0.84
5% EMA/POM	249.7	280.7	0.63
aged for 1 day	251.0	282.3	0.52
aged for 77 days	247.7	280.0	0.75
1% SBS/POM	253.0	283.7	0.71
aged for 1 day	254.3	285.7	0.78
3% SBS/POM	250.7	274.7	1.11
aged for 1 day	254.7	325.0	0.75
5% SBS/POM	249.3	294.7	0.28
aged for 1 day	251.3	302.7	1.68
aged for 77 days	241.0	275.7	1.83
EMA	264.3	319.3	28.8

[a] The temperature at 3% weight loss.
[b] The temperature at 50% weight loss.
[c] The residual weight percentage at 400°C.

between POM and SBS (n_D 1.48 for POM and 1.53 for SB copolymer[26]). By monitoring the change in the spherulite during the ageing at 140°C, it is clear that POM have the highest stability, where no change is observed after 21 days' ageing. After 35 days' ageing, whitening of the film can be viewed by eye and a blurring of the crystal boundary is seen from the micrographs, but the shape and size of the spherulites keep the same. Since the thermo-oxidation depends on the oxygen amount and pressure, the sample thickness and the temperature, the degradation of thin films of POM and its blends as observed are faster than the dumbbell-shaped bars.

Similar to the results that obtained from weight loss, FTIR and DSC study, the degradation of thin EMA/POM and SBS/POM film are faster than that of the virgin POM film. Both blends undergo no change until seven days' ageing, but after 21 days, film whitening and crystal blurring are obvious from the micrographs, where the degradation of EMA/POM blend is much severe than the SBS/POM blend. After 35 days' ageing, the fast degradation of EMA/POM blend lead to dramatic destroy of the spherulites, while in SBS/POM blend the main spherulites structure still exists.

Characteristics of thermooxidation of POM and its blends

Thermooxidation of virgin POM copolymer

Two characteristics accompanied with virgin POM copolymer thermooxidative degradation at 140°C found in this study are firstly the change in the degree of crystallinity and secondly the reduction in
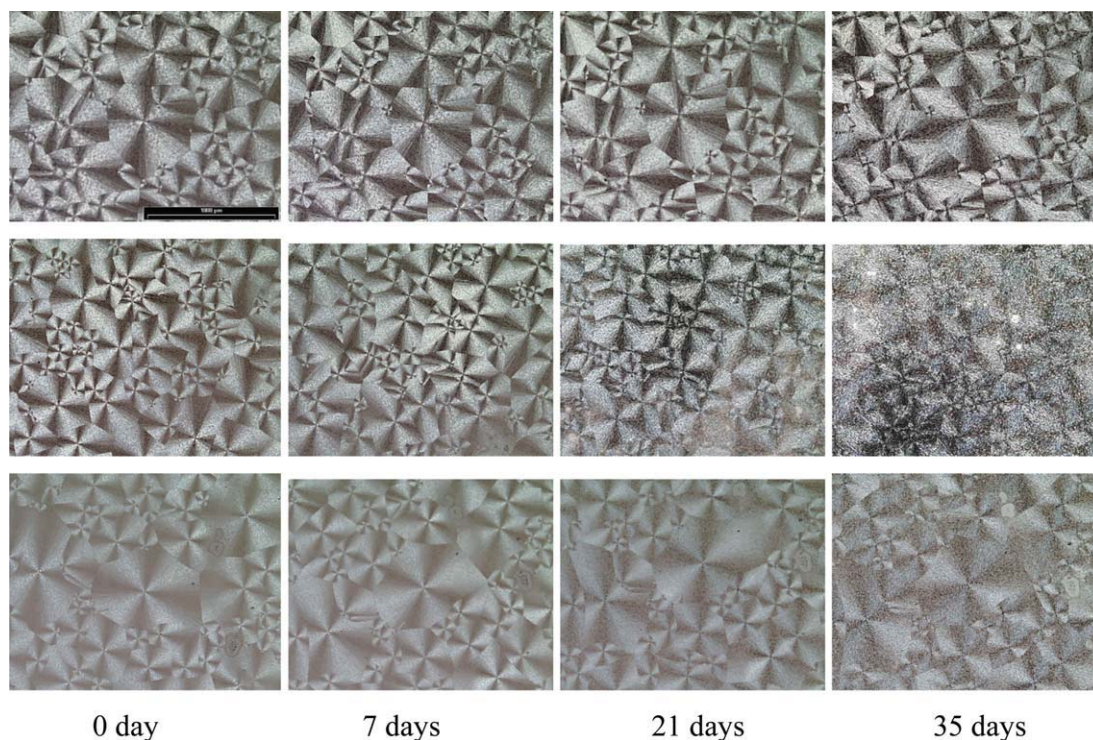

| 0 day | 7 days | 21 days | 35 days |

Figure 10 The polarized optical microgarphs of the POM and its blends aged at 140°C for different times. The upper row (virgin POM), the middle row (5% EMA/POM), and the bottom row (5% SBS/POM), the scale bar is 1000 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

molecular weight observed indirectly by the continuous decrease in the crystallization temperature.

The degree of crystallinity of virgin POM increases at the first seven days' of ageing, then keeps nearly unchanged up to 35 days' ageing and increases again thereafter with prolonged ageing time at 140°C. The degradation until 35 days' ageing happens primarily in the amorphous phase due to the fact that the main spherulite structure is kept nearly unchanged on the POM thin film within the same aging period, as well as that the weight loss is lower than 0.4%. When the crystallinity starts to increase again, more and more chain scission occur, the constrained amorphous phase degrade and the crystal boundary is destroyed continuously, until the amorphous phase of POM can not bear more mechanical load and tend to break at the maximum load, at which point no plastic behavior remain and the sample change to be brittle.

It is noticeable that although no obvious changes or degradation can be seen from FTIR spectra, weight loss, color, and mechanical properties at the initial stage of thermooxidative ageing, a continuous decrease in the peak crystallization temperature is observed in the POM sample during ageing, which indicate the accumulation of degradation chain scission sites and gradual decrease in the molecular weight, which has not been reported before.

Thermooxidation of EMA/POM blend

EMA/POM blends show similar thermooxidative stability as that of POM although some differences still exist. Generally, at the initial stage of ageing, the degradation of EMA/POM is slightly faster than the virgin POM due to the fact that the total degree of crystallinity of the blend decreased. The increased amorphous phase in the blend causes more degradation than the virgin POM.

EMA have relatively higher thermooxidative stability than POM as can be seen from the TGA study. Therefore, ageing of EMA/POM blend is just slightly faster than POM. Furthermore, after 35 days' ageing, the weight loss slows down as observed from the dumbbell-shaped sample. However, the drastic change in the spherulits in the thin film of 5% EMA/POM blend after 35 days ageing as seen in Figure 10 suggest destroy of POM crystalline phase occur much earlier than the virgin POM and SBS/POM blends. This could be the reason that as observed in Figure 6 after the initial increase in the crystallinity, instead of reaching a plateau as that of POM, the degree of crystallinity of EMA/POM decreases first. Since EMA contain ester bonds that can have weak interaction with POM chain, some EMA chain may stay in the constrained amorphous phase. The earlier degradation in the crystalline phase of EMA/POM blend could be due to the interaction between EMA and POM as well as the degradation product from EMA. However, since oxygen diffusion in the constrained amorphous phase as well as in the crystalline phase is much slower than in the amorphous phase, and the movement of chain segment is also limited, the degradation rate in these phases should be slower than the degradation that going on in the amorphous phase, and in the amorphous phase the EMA degradation is slower than POM, as a result the total weight loss rate slows down after 35 days' ageing. In addition, the EMA rich area beneath the surface of the dumbbell-shaped sample could also retard the POM degradation in the EMA/POM blend. Although the slowing down of weight loss happens during the long period ageing, the degradation in both the amorphous and crystalline phase make a significant destroy in the matrix and the mechanical property, where for 5% EMA/POM sample cracks on the surface and the largest decrease in tensile strength are observed after 111 days ageing.

Thermooxidation of SBS/POM blend

The ageing of the dumbbell-shaped SBS/POM show significant and faster degradation than those of POM and EMA/POM samples, where large weight loss, early decrease in tensile strength and strain, aldehyde degradation product formation from FTIR study, continuous and large increase in the degree of crystallinity are observed. Obviously, the fast degradation is caused by the presence of SBS in the blend. It is reported that SBS could undergo thermooxidative degradation even at 130°C.[17] Because of the large surface area of the thin film on the objective glass, its degradation rate is expected to be faster than the oven aged dumbbell-shaped sample. However, the 5% SBS/POM thin film degradation on the objective glass observed by polarized optical microscopy shows that the spherulites structure is blurred after 35 days' ageing but most of the spherulites keep their original shape, while in 5% EMA/POM sample the spherulites are destroyed to a much larger extent. SBS might separate from POM and form an upper layer that cover the POM during the preparation of thin film sample on the objective glass, which could be the reason that a slow change in the spherulites is observed. Nevertheless, this result shows that the degradation in the SBS/POM blends happen majorly in the amorphous phase. Accordingly,[17] the degradation of SBS happens firstly by chain scission in polybutadiene moiety close to the polybutadiene-polystyrene linkage to result in phase separation between polystyrene rich and polybutadiene rich moiety, further phase separation occurs when polybutadiene crosslink in the

second stage and nonsoluble gels form. The phase separations and crosslinking gels resulted from SBS degradation would lead to changes in the POM chain entanglement in the amorphous phase, fasten and enrich the hydroperoxide formation on the POM chain to result in fast weight loss by formaldehyde formation. The weight loss as well as the formation of crosslinking polybutadiene gels could result in cavities in the sample, where both surface cracks and bending (deformation) of sample are observed at about 2.5% weight loss in the samples. When serious degradation occurs in the amorphous phase of SBS/POM blend, the crystalline phase remains less attacked, which may explain the onset degradation temperature of aged 5% SBS/POM sample from TGA study decreases by nearly the same extent as that of the aged POM.

CONCLUSIONS

The POM copolymer undergoes continuous degradation during thermooxidative ageing at 140°C as seen from the gradual decrease in the crystallization temperature in the degraded sample. With up to seven days' ageing, initial increase in the crystallinity due to secondary crystallization is observed. The increase in tensile stress and strain and the degree of crystallinity keep stable until 35 days' ageing. The ageing then follows with a second time increase in the degree of crystallinity by chemi crystallization due to the chain scission degradation to make the entangled large molecular weight chain segments released into low molecular weight segments in the amorphous phase and the attaching of the released chain segments to the growth faces of pre-existing crystals nearby, or due to the formation of new crystals from the released chain segments. In addition, embrittlement and significant decrease in mechanical properties occur when the chain scission reaches a certain degree, although the total weight loss is just less than 2.5% after 111 days' ageing.

The POM blends with EMA and SBS have similar degradation behavior where the chain scission of POM chain plays the important role. However, the presence of SBS accelerates the POM degradation in a high degree, which means this blends cannot be used at POM's ceiling temperature. Addition of EMA in POM leads to a slightly faster degradation of POM due to the increased amorphous phase in the blend, but generally, blends with 1 and 3% EMA show similar high thermooxidative stability as that of POM.

The degradation of POM and its SBS blends occur mainly in the amorphous phase, but in EMA/POM blends, both amorphous and crystalline phase degrade.

References

1. Kumar, G.; Neelakantan, N. R.; Subramanian, N. J Mater Sci 1995, 30, 1480.
2. Hu, X. G. Polym Plast Tech Eng 2000, 39, 137.
3. Chiang, W. Y.; Huang, C. Y. J Appl Polym Sci 1993, 47, 105.
4. Huang, J. M.; Cheng, H. J.; Wu, J. S.; Chang, F. C. J Appl Polym Sci 2003, 89, 1471.
5. Horrion, J.; Cartasegna, S.; Agarwal, P. K. Polym Eng Sci 1996, 36, 206.
6. Wang, X.; Li, H.; Jin, R. J Mater Sci Tech 2000, 16, 427.
7. French, R. N.; Machado, J. M.; Lin-Wien, D. Polymer 1992, 33, 755.
8. Wang, X. D.; Cui, X. G. Euro Polym J 2005, 41, 871.
9. Ren, X. C.; Chen, L.; Zhao, H. J.; Dan, Y.; Cai, X. F. J Macro Sci Part B Phys 2007, 46, 411.
10. Grassie, N.; Roche, R. S. Die Makromolekulare Chemie 1968, 112, 16.
11. Masamoto, J.; Matsuzaki, K.; Iwaisako, T.; Yoshida, K.; Kagawa, K.; Nagahara, H. J Appl Polym Sci 1993, 50, 1317.
12. Fayolle, B.; Verdu, J.; Bastard, M.; Piccoz, D. J Appl Polym Sci 2008, 107, 1783.
13. Fayolle, B.; Verdu, J.; Piccoz, D.; Dahoun, A.; Hiver, J. M.; G'sell, C. J Appl Polym Sci 2009, 111, 469.
14. Archodoulaki, V. M.; Lüftl, S.; Seidler, S. J Appl Polym Sci 2007, 105, 3679.
15. Mucha, M. Colloid Polym Sci 1984, 262, 841.
16. Dole, P.; Chauchard, J. Polym Deg Stab 1996, 53, 63.
17. Fan, S. B.; Kyu, T. Macromolecules 2000, 33, 9568.
18. Xu, W. B.; He, P. S. Polym Eng Sci 2001, 41, 1903.
19. Wang, Q.; Storm, B. K. Proceeding 8th International Symposium on Polymers for Advanced Technologies, European Polymer Federation, Budapest, 2005, p 3.
20. Wunderlich, B. Macromolecular Physics; New York: Academic Press, 1976; Vol.2.
21. Mathur, A. B.; Mathur, G. N. Polymer 1982, 23, 54.
22. Perego, G.; Cella, G. D.; Bastioli, C. J Appl Polym Sci 1996, 59, 37.
23. Viebke, J.; Elble, E.; Ifwarson, M.; Gedde, U. W. Polym Eng Sci 1994, 34, 1354.
24. Siegmann, A.; Kenig, S. J Mater Sci Lett 1986, 5, 1213.
25. Craig, I. H.; White, J. R.; Kin, P. C. Polymer 2004, 46, 505.
26. Furuta, I.; Kimura, S.-I.; Iwama, M. In V. Physical Constants of Some Important Polymers, Polymer Handbook, 4th ed.; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley: New York, 1999; p V/3, V/106.