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Comparison of the Effect of an Organoclay, Triphenylphosphate, and a Mixture of Both on the Degradation and Combustion Behaviour of PC/ABS Blends

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Summary: Polycarbonate Acrylonitrile-Butadiene-Styrene blends (PC/ABS) with flame retardants Triphenyl Phosphate (TPP), nanoclay and their mixtures were prepared in a twin- screw extruder. The morphological properties were characterized by X-ray diffractometry (XRD) which showed the intercalated structure of nanoclay in the matrix. Thermal stability of the samples was studied using Thermogravimetric Analysis (TGA), and the degradation kinetic parameters were determined using various methods including Kissinger, Flynn-Wall-Ozawa and Coats-Redfern methods. It was found that the sample containing both TPP and nanoclay has the highest activation energy. The activation energy order of PC/ABS blends with different flame retardant packages, obtained by Kissinger method agrees well with that obtained by Coats-Redfern. Cone calorimetry and limited oxygen index (LOI)/underwriters laboratory 94 (UL94) methods were used to investigate the fire behaviour and flammability of materials. The reduced mass loss rate (MLR), peak heat release rate (PHRR) and enhanced LOI of the composite containing mixture system confirmed a synergistic effect of TPP and nanoclay.

Keywords: activation energy; nanocomposite; PC/ABS blend; thermogravimetric analysis; triphenyl phosphate (TPP)

Introduction

PC/ABS alloys are well-known commercial polymers, which are extensively used as engineering thermoplastics.[1] Because of the combustible nature of PC/ABS blend, it is desirable to reduce the burning rate in the initial phase of a fire by using flame retardants.[2] Organophosphorous compounds are good flame retardants for polymeric materials.[3] Nanomaterials are also finding considerable interest as part of non-halogenated flame retardant additive packages.

There are several reports on thermal or thermo-oxidative degradation kinetics of flame-retarded polymeric materials.[4–8] No reports are available on the thermal stability of the PC/ABS/TPP/nanoclay system. In this paper, the effect of TPP, nanoclay and their mixture on thermal stability and degradation kinetics of PC/ABS matrix are investigated by thermogravimetric analysis (TGA). Various methods[1,9] were used to determine the degradation kinetics of the PC/ABS blend and its composites.

Experimental Part

Materials and Methods

PC (Makrolon 2858 of Bayer AG, Germany), and ABS (SD0150, Tabriz Petrochemical Company, Iran) were supplied as

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pellets. Nanolin DK2, a modified organoclay with a cation exchange capacity of 110–120 meq/100 g, was obtained from Zheging Fenghong Clay Chemicals Co. of China. Halogen-free flame retardant Triphenyl Phosphate (TPP), Merck Co., with 9.5% phosphorus content.used.

Sample Preparation

All ingredients (PC, ABS, TPP and nanoclay) in a weight percentage according to Table 1, were first dry blended in a tumbler mixer. The formulations were prepared via melt mixing in a Brabender co-rotating twin screw extruder (L/D = 40) at 300 rpm with temperature profile of 200 to 250 °C from hopper to die. The PC/ABS ratio was kept constant (65/35, wt. %) in all formulations.

Evaluation of the Dispersion of the Nanoclay in PC/ABS Alloy

XRD experiments were performed at room temperature on a Siemens D5000, D/max – rA X-ray diffractometer (30 KV, 10 mA) with Cu ($\lambda = 1.54178$ Å) irradiation scanning at a rate of 2°/min in the range of $2\theta = 1.5$–10°.

Thermal Analysis

Thermogravimetric analysis was performed with a Polymer Laboratory PL102–England. Samples were heated in the temperature range 20–700 °C using heating rates of 5, 10, 15 and 20 °C/min, with a controlled dry nitrogen flow of 50 °C/min.

Cone Calorimetry, LOI & UL 94

The flammability properties were measured with a cone calorimeter manufactured by Fire Testing Technology (FTT) Co. England at incident heat flux of 50 kw/m^2 according to ISO 5660-1 test method. The samples (100 mm × 100 mm × 3 mm) were measured horizontally in a frame. PHRR (Peak Heat Release Rate), Mass Loss Rate (MLR) and ignition time (t_{ign}) data are collected during the test.

The LOI was determined using an LOI instrument on 100 × 6.5 × 3 mm samples sheets according to the ASTM D2863 test method. The test is based on the lowest oxygen gas concentration that still sustains combustion of the sample. The UL 94 classification test was carried out on 3mm thick sheets according to ASTM D3801 standard test method. This test provides qualitative classification of the samples by measuring the ease of burning of a polymer sample.

Table 1.
Compositions of formulations.

Compounds	PC	ABS	TPP	Nanoclay
	(wt.%)			
PC/ABS	65	35	–	–
PC/ABS/2% nano	63.7	34.3	–	2
PC/ABS/10%TPP	58.5	31.5	10	–
PC/ABS/(10%TPP + 2%nano)	58.5	31.5	8	2

Results and Discussion

Thermal Stability

The TGA thermograms of PC/ABS, PC/ABS/2%nano, PC/ABS/10%TPP and PC/ABS/(10% TPP + 2%nano) at heating rates of 5, 10, 15, 20 °C/min are shown in Figure 1. As is seen, the TGA curves are shifted to higher temperature by incorporation of flame retardants.

The isothermal weight loss of PC/ABS in the composite with TPP and nanoclay at all heating rates is greater than in the other three samples which can be ascribed to the effect of nanoclay particles on formation of a reinforcing network structure. The active and acidic sites on layered silicates formed by the decomposition of organoclay can catalyze dehydrogenation, crosslinking and charring of the nanocomposite. The protective coat-like char and physical-chemical crosslinking should be responsible for the delay in weight loss.[10]

TPP stabilizes polycarbonate and delays the degradation of polycarbonate and some of the phosphate undergoes alcoholysis with alcohol products that are evolved during thermal degradation. Some phosphate undergoing alcoholysis can form

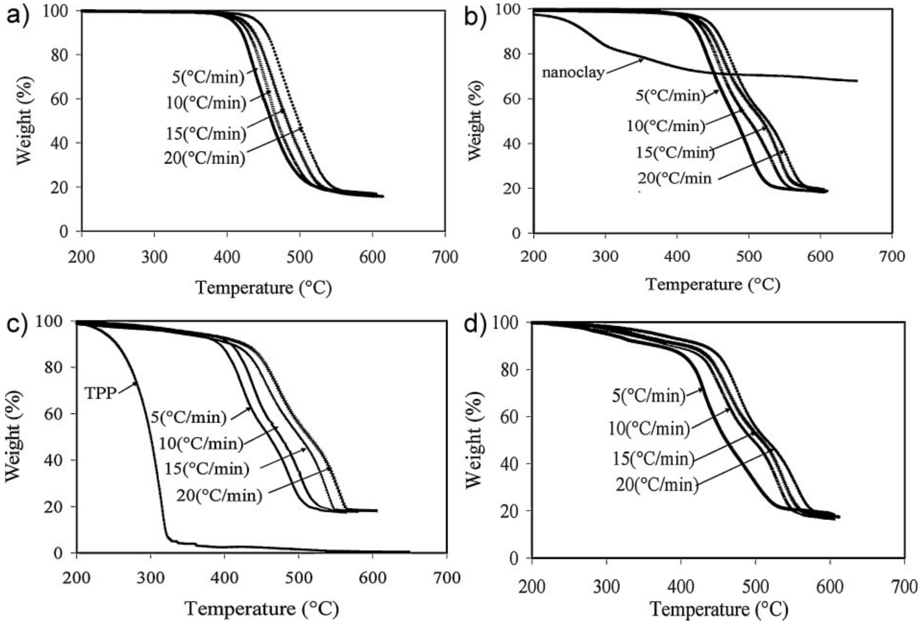


Figure 1.
TGA curves of samples at different heating rates under N_2: (a) PC/ABS, (b) PC/ABS/2% nano, (c) PC/ABS/10% TPP and (d) PC/ABS/(10%TPP + 2%nano).

branched structures and act as a thermal barrier.[11]

In accordance with Figure 1, decomposition of PC/ABS is a single step process (Figure 1-a). The decomposition of the flame-retarded PC/ABS having nanoclay is a two-step process (Figure 1-b); the first step is in the range of 400–500 °C (1st) and the second step is in the range of 500–600 °C (2st). The two step decomposition in TGA may be attributed to the interaction between nanoclay and polymer matrix. This interaction can lead to a change in thermal stability of ABS resin and emerge two-step process in degradation process. For the samples containing TPP and both TPP and nanoclay, three steps in the decomposition curve were observed in TGA (Figures 1-c and 1-d). It means that, the first step is in the range of 300–400 °C (1st) and the second step is in the range of 400–500 °C (2st) and the third step is in the range of 500-600 °C (3st). It is believed that the thermal degradation mechanism of PC/ABS blends consists of several complex processes such as hydrolysis and thermal degradation; each becomes predominant during different stages of the overall process.[12] The activation energy of each step is determined by the Kissinger method via plotting ln(β/T_p^2) versus $1/T_p^2$ and fitting to a straight line.[1] The calculated activation energies (E_a) for each sample are given in Table 2. (β = heating rate, T_p = temperatemperature corresponding to the inflection point of TGA curves).

In the TGA curve of PC/ABS/2%nano, the initial weight loss occurring at 200 °C is related to the thermal decomposition of alkyl ammonium salt on nanoclay. This pre-step weight loss can hardly be detected on the thermogram; however, it has also been reported by other researchers.[13] The decomposition of alkyl ammonium salt causes a delay in the thermal decomposition of the nanocomposite at higher temperature[10] and by doing so increases the activation energy of the decomposition of the matrix in the subsequent steps (1st and 2st) (Figure 1-b). TGA curves of PC/

Table 2.
Activation energies of PC/ABS blends using the Kissinger method.

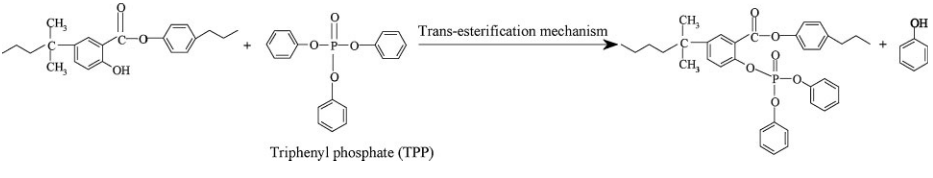
Compounds	Heating rate β (°C/min)	T_{pR1} [a)] (°C)	T_{pR2} (°C)	E_{aR1} (kJ/mol)	E_{aR2} (kJ/mol)	Correlation coefficient (R)
PC/ABS	5	407	–	126	–	$R_1 = 0.9899$
	10	409	–			
	15	413	–			
	20	437	–			
PC/ABS/2%nano	5	412	492	158	166	$R_1 = 0.9956$
	10	419	518			$R_2 = 0.9896$
	15	436	523			
	20	441	530			
PC/ABS/10%TPP	5	407	487	165	182	$R_1 = 0.9756$
	10	426	503			$R_2 = 0.9975$
	15	429	515			
	20	442	523			
PC/ABS/(10%TPP + 2%nano)	5	438	517	171	215	$R_1 = 0.9978$
	10	456	531			$R_2 = 0.9832$
	15	465	541			
	20	471	549			

[a)] T_p = The peak temperature in DTG (Differential Thermogravimetry), R = Stage of reaction.

ABS/10%TPP and PC/ABS/(10%TPP + 2%nano), show a three-step decomposition process, as mentioned earlier. The first step occurring at temperatures between 300–400 °C (1st). This is may be attributed to the presence of weak P-O-C linkages in TPP which are very susceptible to chain scission during thermal degradation and react with the decomposing PC. Upon Fries rearrangement, PC generates phenolic groups, which react with TPP by trans-esterification (Scheme 1).[14] As TPP has several reactive P–O–C bonds, it might be expected to react with another PC chain to produce crosslinking.

The weight loss rates for the two subsequent steps (2st and 3st) are decreased by the incorporation of phosphorous; hence the activation energies are increased, compared with PC/ABS. It is believed that during thermal decomposition process, phosphorous-rich residues are produced which protect the polymer from heat, thus make the materials more stable at higher temperatures.[15] This plays a critical role in phosphorus-based flame-retarded polymeric materials through condensed-phase as well as gas-phase mechanism. The activation energy of the TPP/organoclay blend is about 215 kJ/mol, which is the highest among the other blends (Table 2). The synergistic effect between TPP and nanoclay can lead to an improved thermal stability, by ease of intercalation of nanoclay and its hindering effect on the evaporation of TPP.[16]

The Coats-Redfern method deals with the main degradation region of the TG curve of the material and requires the TG data at just one heating rate to calculate the reaction order, *n*, and activation energy, E_a,.[17] The kinetic parameters calculated by



Scheme 1.

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Table 3.
The kinetic parameters of PC/ABS composites at the optimum correlation coefficient obtained using Coats-Redfern method at 10 °C/min of heating rate.

Compounds	n (Reaction order)	E_a (kJ/mol)	Correlation coefficient (R)
PC/ABS	$n_1 = 2$	$E_{a1} = 98$	$R_1 = 0.9908$
PC/ABS/2%nano	$n_1 = 1$	$E_{a1} = 149$	$R_1 = 0.9661$
	$n_2 = 3$	$E_{a2} = 160$	$R_2 = 0.9849$
PC/ABS/10%TPP	$n_1 = 2$	$E_{a1} = 127$	$R_1 = 0.9999$
	$n_2 = 3$	$E_{a2} = 227$	$R_2 = 0.9986$
PC/ABS/(10%TPP + 2%nano)	$n_1 = 4$	$E_{a1} = 143$	$R_1 = 0.9527$
	$n_2 = 6$	$E_{a2} = 248$	$R_2 = 0.9794$

Coats-Redfern method are included in Table 3.

The results obtained in this section are similar to those from the Kissinger method. On the other hand the values of the second activation energy that related to third step of decomposition are higher than the first activation energy that related to the second step of decomposition in two methods. The enhanced thermal stability of PC/ABS/(10%TPP + 2%nano) evaluated by Coats-Redfern method confirms the previous finding of the synergistic effect of TPP and nanoclay mixture in improving the thermal resistance of PC/ABS resins.

Cone Calorimetry Analysis

The combustion properties of the samples were characterized by means of cone calorimetry. The data for the PC/ABS blends are shown in Table 4. It can be seen that the MLR and the PHRR of the PC/ABS/TPP, PC/ABS/nano and PC/ABS/(TPP + nano) composites are decreased by increasing of TPP or nanoclay content.

This suggests that the flammability of these composites is due to the difference in condensed-phase and gas-phase decomposition processes.[18] The PHRR value of PC/ABS/2%nano is 600 kW/m^2 (Table 4). It means a 432 kW/m^2 improvement in the PHRR of PC/ABS neat resin (1032 kW/m^2). Using TPP in PC/ABS/10%TPP sample leads to an improvement of 212 kW/m^2 with PHRR of 820 kW/m^2. The PC/ABS/(10%TPP + 2%nano) sample showed improved flammability properties with PHRR of 320 kW/m^2. This is roughly 5% better than the value of 338 kW/m^2 estimated according to the mixing rule; it is too small to prove a synergetic effect of TPP+ Nanoclay in flame retardation of PC/ABS composites.

The same effect is observed for the MLR value of samples. The combustion rate of PC/ABS/2%nano with MLR of 4.45 g/m^{2}s is 0.42 g/m^2 s lower than that of neat PC/ABS. The MLR of PC/ABS/10%TPP (4.14 g/m^2 s) is 0.73 g/m^2 s lower than the value of PC/ABS neat resin (4.87 g/m^2 s). The PC/ABS/(10%TPP + 2%nano) sample showed a decreased combustion rate with MLR of 3.62 g/m^2 s. This is a little lower than the expected rate of 3.72 g/m^2 s.

The heat release rate (HRR) plots for PC/ABS blend and PC/ABS composites are shown in Figure 2.

This Figure has three regimes that include a) the initiation burning zone (0–50 °C), b) the peak section (50–100 °C) and

Table 4.
Cone calorimetric data of PC/ABS blends at 50 kW/m^2

Compounds	Ignition time (s)	Peak HRR (kW/m^2)	MLR (g/m^2 s)
PC/ABS	35	1032	4.87
PC/ABS/2%nano	30	600	4.45
PC/ABS/10%TPP	40	820	4.142
PC/ABS/(10%TPP + 2%nano)	44	320	3.62

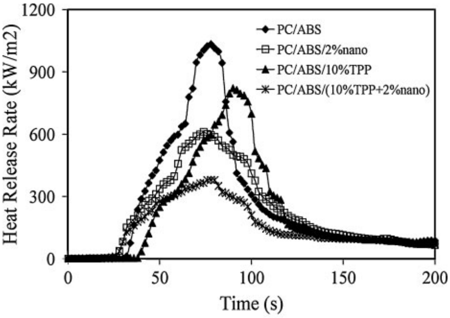

Figure 2.
HRR plots for PC/ABS neat resin and PC/ABS blends.

c) the terminal zone (100–150 °C). The PC/ABS/nano system has a lower peak HRR than PC/ABS in the (b) zone, but a little longer burn time in the (c) zone which suggests a dominant condensed-phase (char forming) mechanism of flame retardancy. The decrease of PHRR of the PC/ABS/nano is mainly due to the delay in the thermal-oxidative decomposition process. It is also observed that the initial decomposition of PC/ABS/nanocomposites in the (a) zone is earlier than that of neat PC/ABS resin, and shortens the ignition time in the (c) zone. On the contrary, the acidic active sites $LS^{-}H^{+}$ can catalyze the formation of a protective char layer on the nanocomposites, as mentioned above in TGA analysis section. Therefore the MLR and PHRR are decreased, and the thermal-oxidative stability of samples increased. It can be seen in Table 4 that, the MLR value of PC/ABS neat resin is higher than that of the PC/ABS/nanocomposite. This trend in MLR changes in cone calorimetry is similar to the variation of the slope of weight loss curves in TGA.

In Figure 2, the PC/ABS/TPP blend has a more delayed t_{ign} value in the (a) zone than the PC/ABS neat resin. TPP, and generally all phosphate flame retardants can protect the polymer, simultaneously by gas-phase and condensed-phase (char forming) mechanism. The combination of these two mechanisms may be responsible for the delayed t_{ign}.[20] The changes of MLR in PC/ABS/TPP formulations are the same as the PC/ABS/nano composites and are in agreement with TGA results.

The HRR plot of PC/ABS/(10%TPP + 2%nano) composite is shown in Figure 2. The hindrance effect of nanoclay in PC/ABS/(10%TPP + 2%nano) composite decreases the release rate of the volatilization of TPP and improves flame retardancy. The minimum PHRR data in the (b) zone is observed for this system.

LOI & UL94 Tests

The LOI and UL 94 test results are summarized in Table 5. PC/ABS/nano composite showed a slight decrease in LOI data from 23% for PC/ABS neat resin to 22.2% for PC/ABS/2%nano which can be because of promoted burning of alkylammonium as nanoclay treatment. Meanwhile an opposite trend in LOI test results was observed for PC/ABS/TPP composite. The LOI of PC/ABS/10%TPP (26.1%) is higher than for PC/ABS (23%). PC/ABS/(10%TPP + 2% nano) composite showed an obvious synergy with a LOI of 33.4%. The improved flame retardancy of TPP + nano can be attributed to enhanced barrier properties of their mixture and also improved char formation due to increased viscosity.[19] The considerable improvement in LOI of PC/ABS/(10%TPP + 2%nano) with respect to PC/ABS TPP and PC/ABS nano so far is he best indication of a synergistic effect.

The PC/ABS, PC/ABS/nano and PC/ABS/TPP failed in vertical UL 94 test and burned completely. In the horizontal test, they self-extinguishing before the mark at 25mm in the sample was reached. The

Table 5.
Fire behaviour of PC/ABS blends

Compounds	LOI (%)	UL 94 (3 mm)
PC/ABS	23	HB
PC/ABS/2%nano	22	HB
PC/ABS/10%TPP	26	HB
PC/ABS/(10%TPP + 2%nano)	33	V-0

failure of samples in the vertical UL 94 burning test can be due to porosity of char, yield during the burning of TPP or nanoclay. The durability of porous char is not sufficient to prevent fuel release and inhibit flame propagation, which leads to HB rating in this test. PC/ABS/(TPP + nano) composites showed immediate self-extinguishing after removing the burner and the V-0 classification was achieved. The maximum flaming time per specimen per flame application was 10 sec and the maximum afterglow time was 30 sec, sufficient to obtain the classification of V-0.

Generally, the discussions made so far, suggest that using the mixture of nanoclay and TPP enhances the thermal stability of composites at elevated temperature as is seen in TGA test results. The cone calorimetry analysis revealed that, the simultaneous using of TPP and nanoclay in the formulations promote the formation of a more thermally stable char and as a physical protective barrier leads to decrease of HRR and MLR as evaluated by cone calorimetry.

Dispersion of Nanoclay in PC/ABS Blend

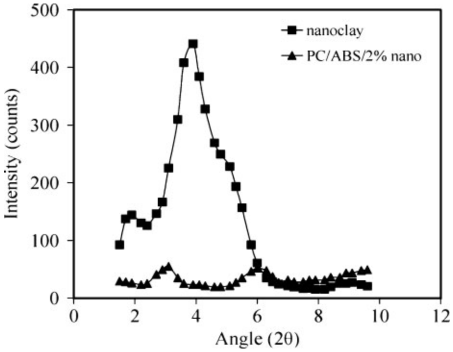

Figure 3.
XRD patterns for patterns for nanoclay and nanoclay-contained formulation.

Figure 3 shows the XRD patterns of nanoclay and PC/ABS/2%nano composite. The peak corresponds to the reflections angle of d_{001} plane of the clay is appeared at $2\theta = 3.8$, for the nanoclay. This peak is shifted to 3.1 in PC/ABS/2%nano composites which is the evidence for intercalation.[20] The average basal spacing of the silicate layers has increased from 2.29 in organoclay to 2.82 nm in the PC/ABS/2%nano composite.

The small reflection observed at XRD Pattern of the PC/ABS/2%nano composite at higher diffraction (ca. $2\theta = 6$) can be due to the degradation of the surface treating agent at high processing temperature which has also been reported by other researchers.[21]

Conclusion

The thermal stability and combustion behaviour of PC/ABS blend and its composites with TPP, nanoclay and their mixture have been studied in this work. The kinetic parameters and flammability properties show the effects of TPP, and nanoclay and their mixture on the thermal degradation and combustion behaviour of PC/ABS resin. It can be concluded that:

1- By using TPP, nanoclay and their mixture in PC/ABS resin, the TGA curves are shifted to higher temperatures. The weight loss of the PC/ABS sample and flame-retarded with nanoclay occurred at one and two steps separately, while for the samples with TPP and hybrid system it was a three-step process, each step was separately evaluated in kinetic study.
2- The enhanced thermal stability of the composite PC/ABS/(10%TPP + 2%nano) did not confirm a synergistic effect of TPP and nanoclay in improving the thermal resistance of PC/ABS resins.
3- The MLR, PHRR and LOI results for the composite containing nanoclay and TPP are supporting a synergistic effect of nanoclay and TPP. This formulation showed immediate self-extinguishing with V-0 classification.

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