Structure and Thermomechanical Evaluation of Melt Processed Organoclay/ABS/PC Nanocomposites

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Summary: In this work, blends of ABS and PC with various compositions were processed by melt compounding in a twin screw extruder and the obtained samples were studied in terms of structure and thermomechanical properties. The effect of incorporation of organically modified montmorillonite (OMMT) nanoparticles on the above properties was also investigated. The addition of PC improves the thermal degradation resistance and tensile properties of ABS. The incorporation of OMMT into ABS/PC mixtures alters the thermal degradation mechanism for blends containing more than 50% PC and further improves the tensile properties and especially the modulus of elasticity.

Keywords: ABS; blends; nanocomposites; organoclay; polycarbonates

Introduction

The PC/ABS blends are systems with improved mechanical and thermal properties due to the PC matrix, whereas the contribution of ABS focuses on the ease of processing, economy and more reliable impact strength.[1] The desired mechanical properties and thermal stability can be achieved by changing PC/ABS ratio. PC and the Styrene-Acrylonitrile (SAN) phase of ABS can be well dispersed in each other, promoting a strong adhesive bonding between the phases.[2] An alternative way to improve the internal adhesion is the use of nanoparticles, acting as linkages between the two phases by embedding in both of them.[3] Hong et al.[4] studied the morphology of ABS/PC (70/30 wt%)/clay nanocomposites and confirmed the existence of clay in the ABS phase as well as at the interphase of ABS and PC. Wang et al.[5] prepared ABS/PC/clay nanocomposites and discovered that it is mainly the ABS molecules which were intercalated into the clay layers rather than PC molecules. Ibeh et al.[3] studied ABS/PC nanocomposites and found that the presence of nanoclay improves the processability of ABS/PC formulations for concentrations up to 4 phr, as well as that it enhances the flammability resistance and modulus of the polymer matrix.

Experimental Part

ABS was supplied by BASF, under the trade name Terluran® GP-35 and PC by Bayer, under the trade name Makrolon® 2805. Commercial montmorillonite clay, Cloisite® 30B was purchased by Rockwood Clay Additives GmbH.

ABS/PC blends with compositions 70/30, 50/50 and 30/70 w/w were prepared in a co-rotating twin-screw extruder, with L/D = 25 and 16 mm diameter (Haake PTW 16). The rotational speed of the screws was 200 rpm. Nanocomposites of the above blends were prepared at 1, 2 and 3 phr under the same conditions.

The morphology of the above blends was explored by XRD, in a Siemens 5000 diffractometer. Scanning Electron Microscopy (SEM) has also been performed, with a JEOL system and accelerating voltage of

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30 kV. The cryogenically fractured surfaces of ABS/PC blends 70/30 and 50/50 w/w were alkali treated at 100 °C, whereas the 30/70 blend was immersed into chromosulfate solution at 80 °C. TGA measurements were accomplished in a thermal gravimetric analyzer (Mettler Toledo, TGA-DTA) from 25 to 800 °C, at rate of 10 °C/min, in N_2 and DMA was performed in an Anton Paar analyzer, MCR 301, with a frequency of 1 Hz, from −120 to 200 °C, in N_2. DSC measurements were carried out in a Mettler Toledo apparatus, DSC 1, with samples heated from 30 to 250 °C, then cooled to 30 °C and heated again to 250 °C at a rate of 10 °C/min, in N_2. Mechanical testing of the injection molded specimens was run in an Instron tensometer (4466 model), operating at grip separation speed of 50 mm/min.

Results and Discussion

From Figure 1, the characteristic peak (001) of the Cloisite 30B is observed at about $2\theta = 5.05^{\circ}$, corresponding to an inter-layer spacing of 1.75 nm. The XRD patterns of Cloisite 30B/ABS/PC blends (Figure 1) show that the peak corresponding to the (001) plane reflection of clay shifts to lower angles with decreasing intensity. The increase of *d*-spacing of Cloisite 30B/ABS/PC nanocomposites suggests the formation of intercalated structure. It can also be seen that the secondary peak that corresponds to the (002) peak of the nanocomposites emerges at higher angle. The presence of the (002) peak indicates that the intercalated structure of the clay is obtained in the nanocomposites. The higher PC content in ABS/PC blends seems to promote the intercalation process in the prepared nanocomposites, as the 2θ decreases.

The micrographs obtained by SEM clearly show even distribution of the two polymers, especially for ABS/PC 50/50 w/w blend (Figure 2).

From Table 1 it can be observed that as the PC content in ABS/PC blends increases the thermal characteristics are improved, but this dependence is not consistent with the ''rule of mixtures''. The incorporation of nanofillers increases the residue, mainly in pure ABS due to the formation of char with a multilayered carbonaceous-silicate structure which builds up on the surface

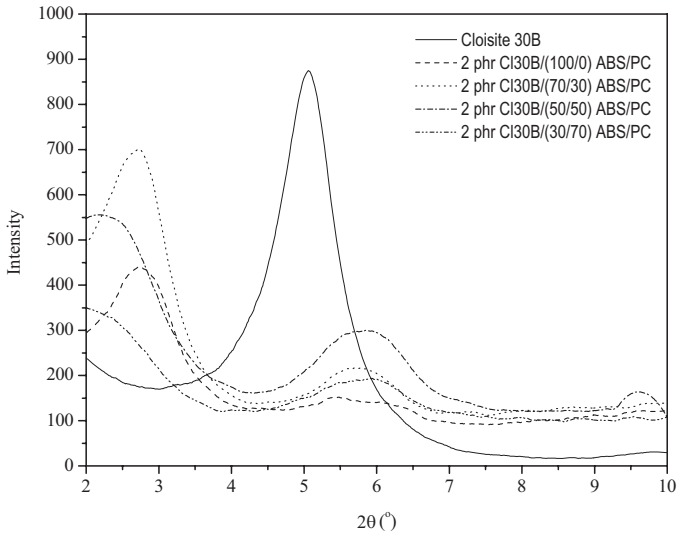

Figure 1.
XRD patterns of Cloisite 30B and 2 phr Cloisite 30B/ABS/PC blend nanocomposites.

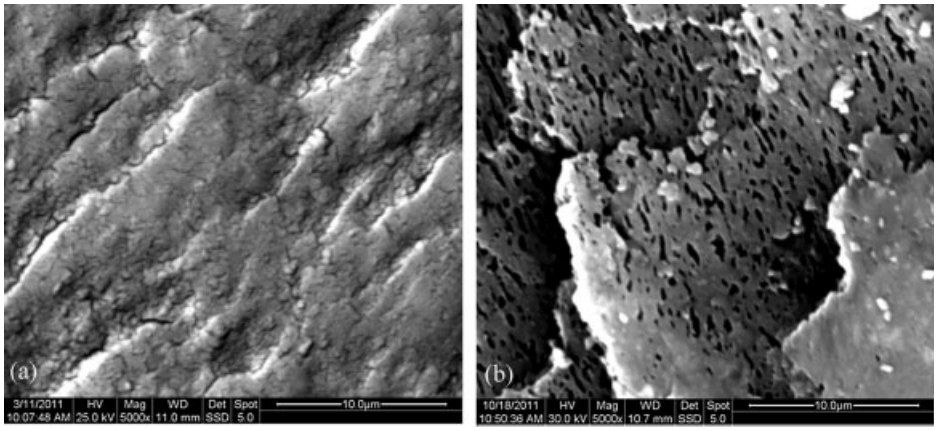

Figure 2.
SEM photos of (a) pure ABS and (b) 50/50 w/w ABS/PC blends.

Table 1.
Onset temperature of thermal degradation (T_{onset}) and residue during TGA of ABS/PC blends and their nanocomposites.

Cloisite 30B (phr)	T_{onset} (°C)				Residue (%)			
	ABS/PC (w/w)							
	100/0	70/30	50/50	30/70	100/0	70/30	50/50	30/70
0	402.23	408.32	410.98	413.43	0.91	6.47	11.34	15.39
1	402.43	408.01	412.86	417.21	3.45	7.42	12.43	16.97
2	402.16	407.08	411.67	414.15	3.89	9.13	14.08	16.78
3	400.73	404.61	409.80	413.69	3.83	10.35	12.96	15.85
PC	503.80				27.59			

during burning, insulating the underlying material.

The presence of Cloisite 30B does not essentially affect the temperature of maximum degradation rate of ABS/PC blends. The addition of clay in 50/50 w/w ABS/PC blend causes significant changes to the thermal degradation mechanism, that takes place in two stages, whereas the degradation of non reinforced blend proceeds in one stage (Figure 3).

The incorporation of Cloisite 30B in the 30/70 w/w ABS/PC blend enhances the resistance to thermal degradation in the second stage of the process (Figure 4).

Cloisite 30B seems to inhibit thermal degradation of the PC phase, which might be due to the formation of a protective layer of nanoclay at the ABS/PC interface or to the creation of new paths of the degradation reaction. The improvement of thermal characteristics of ABS/PC blends 50/50 and 30/70 w/w is attributed to better intercalation of montmorillonite silicate layers in these mixtures in comparison with 70/30 blend.

Using DSC analysis the thermal transitions of AB/PC blends and their nanocomposites were evaluated and the results are presented in Table 2. The first transition is slightly higher than the T_g of pure ABS, probably due to PC dissolution in it and shifts to slightly higher temperatures as the PC content in the blend increases. The second transition is lower than the T_g of pure PC, due to ABS dissolution in it and further decreases as the ABS content in the blend increases. The shift of T_g is much more obvious for PC, maybe due to a plasticizing action of ABS to the PC phase,

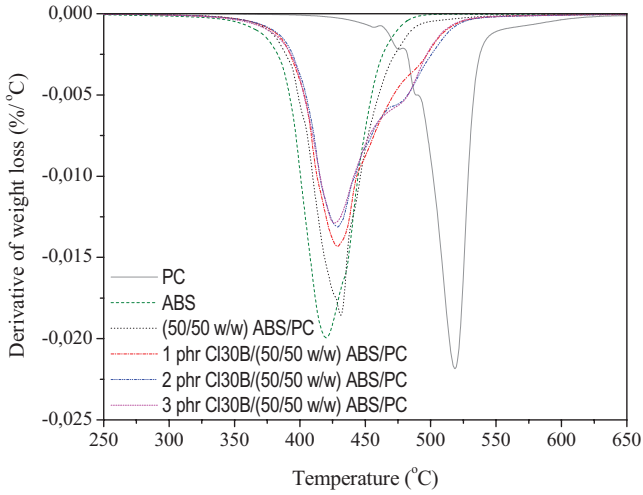

Figure 3.
DTG curves for ABS/PC 50/50 w/w.

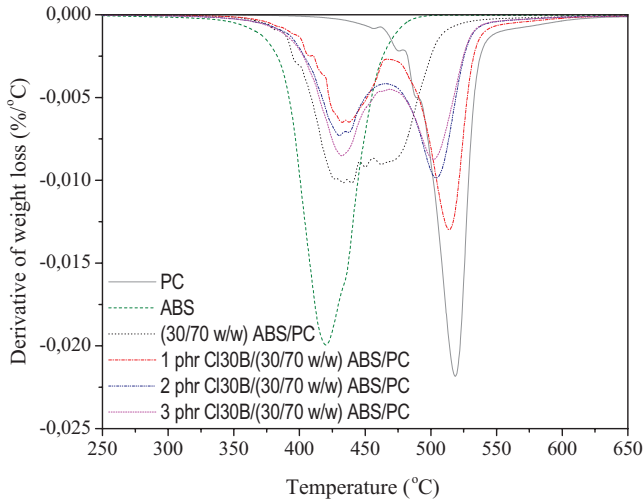

Figure 4.
DTG curves for ABS/PC 30/70 w/w.

which is likely to happen due to the polybutadiene (PB) phase present in ABS.

Organoclay concentrations up to 3 phr in ABS/PC blends do not produce any obvious effect on the T_g of ABS. The addition of organoclay to 70/30 ABS/PC blends, reveals the transition of PC phase during the DSC runs. It can also be observed a slight increase of T_g of the PC phase in the 50/50 ABS/PC blends, which suggests that organoclay restricts the free volume and chain mobility under these conditions in that phase.

By means of dynamic mechanical analysis the T_g of the polybutadiene (PB) phase in the blend became apparent and the calculated values are presented in Table 3. It is clear that this transition is not

Table 2.
Glass transition temperature (T_g) of SAN and PC in ABS/PC blends and their nanocomposites using DSC analysis.

Cloisite 30B (phr)	Glass transition temperature, T_g (°C)						
	ABS/PC						
	100/0 w/w	70/30 w/w		50/50 w/w		30/70 w/w	
	$T_{g,SAN}$	$T_{g,SAN}$	$T_{g,PC}$	$T_{g,SAN}$	$T_{g,PC}$	$T_{g,SAN}$	$T_{g,PC}$
0	105.03	105.30	–	106.35	124.35	108.31	134.19
1	105.74	105.68	124.37	106.52	129.26	107.81	135.74
2	105.01	105.33	124.31	106.16	127.59	107.80	134.47
3	106.61	104.93	125.59	105.80	125.98	107.77	135.93

T_g pure PC 142.77 °C.

Table 3.
Glass transition temperature (T_g) of PB in ABS/PC blends and their nanocomposites using DMA.

Cloisite 30B (phr)	Glass transition temperature, $T_{g,PB}$ (°C)			
	ABS/PC			
	100/0 w/w	70/30 w/w	50/50 w/w	30/70 w/w
0	−81.49	−83.40	−82.67	−80.75
2	−81.98	−83.57	−83.65	−77.04

Table 4.
Tensile strength and Young's modulus of of ABS/PC blends and their nanocomposites.

Cloisite 30B (phr)	Tensile strength (MPa)				Young's modulus (MPa)			
	ABS/PC (w/w)							
	100/0	70/30	50/50	30/70	100/0	70/30	50/50	30/70
0	46.77	51.96	57.00	58.87	2105.42	2181.15	2358.99	2113.00
1	47.22	53.45	57.73	59.82	2230.01	2108.78	2378.53	2115.76
2	47.19	54.37	57.80	60.91	2366.98	2409.35	2458.35	2399.69
3	48.39	50.90	58.23	62.08	2513.62	2693.86	2669.73	2237.99
PC	64.72				1933.32			

significantly affected by the presence of PC and the participation of Cloisite 30B into the mixture.

Regarding the mechanical properties, the tensile strength increases in the presence of PC and obeys the rule of mixture as it can be seen in Table 4.

As far as the Young's modulus, a synergic action between ABS and PC was observed. The highest improvement of Young's modulus was recorded for the composition 50/50 w/w. A significant enhancement of modulus is clear, since the contribution of PC leads to an increase of the rigidity of ABS and limits the plasticizing effect of the rubber phase. The incorporation of Cloisite 30B in ABS and its blends with PC seems to cause a slight increase in tensile strength. On the other hand, the addition of nanofiller significantly improves the Young's modulus of the examined blends.

Conclusion

The incorporation of PC improves the resistance to thermal degradation of ABS/PC blends, with respect to pure ABS. The addition of OMMT affects the degradation mechanism and properties of 50/50 and 30/70 w/w ABS/PC blends, where

a shift of PC phase degradation to higher temperatures becomes obvious, in comparison with the respective unreinforced blends.

The incorporation of PC in ABS results in a slight increase of the T_g of SAN phase and decrease of the T_g of PC. The addition of OMMT in ABS/PC blends does not affect the T_g's of SAN, whereas an increase of the T_g of PC in 50/50 w/w ABS/PC blends was observed.

Regarding the mechanical performance, the incorporation of PC in ABS improves the tensile strength of ABS/PC blends according to the law of mixtures and the addition of nanofiller further improves this property. A synergistic effect was observed for modulus of elasticity upon the addition of PC in ABS, especially in 50/50 w/w ABS/PC blends.

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