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Mechanical and Thermal Degradation Properties of Isotactic Polypropylene Composites with Cloisite15A and Cloisite20A

In this work, the influence of maleic anhydride grafted polypropylene (PP-g-MA) content on thermal and mechanical properties of polypropylene (PP) composites with two types of clays, differing modifier density in the interlayer space, Cloisite15A and Cloisite20A, was studied. PP/clay composites were melt blended in presence of different content of PP-g-MA from 3, 6, 9, and 12 wt.%. It was found that Cloisite15A with a high density of the modifier promotes the formation of intercalated structures, while Cloisite20A with a low density of the modifier, predominantly exfoliated nanocomposites are formed. In the first case, the structure tends to become intercalated whilst composites with Cloisite20A favor the formation of predominantly exfoliated structures. The formation of the nanocomposite is accompanied by a significant increase in thermal stability (50 % weight loss is observed at temperatures of 360 °C and 430 °C for polypropylene and nanocomposites based on it, respectively). An analysis of the mechanical properties of nanocomposites generally indicates an increase in the elastic modulus by 15–20 %, and this effect is more pronounced for exfoliated structures, the yield strength practically does not change and the elongation at break decreases noticeably.

Keywords: polypropylene, clay, composite, polypropylene grafted maleic anhydride, intercalation, exfoliation, oxidation, montmorillonite.

Introduction

Recent research in polymer science has shown finer dispersed inorganic layered silicates or smectite clays through the organic polymer, increasing its mechanical, thermal, barrier, and fire retardant properties [1–7]. Layered silicates are made up of several hundred thin platelets stacked in orderly particles or tactoids with dimensions of 8–10 µm. Each disk-shaped platelet has a large aspect ratio of approximately 100–1000 and is easily agglomerated due to the interlayer van der Waals forces. Each leaf contains an octahedral layer of alumina or magnesium flanked by two outer tetrahedral layers of silica, so the octahedral layer shares the tetrahedral layer with its oxygen atoms. Accordingly, clay particles should be homogeneously finer dispersed and exfoliated as individual platelets within the polymer matrices to accomplish the ultimate properties. Moreover, the lower clay content is also essential to achieve the large contact surface area between the polymer matrix and the fillers and to obtain good dispersion by alleviating the clay aggregation [8–9, 20].

Due to its hydrophilic properties, clay minerals are incompatible with organic polymers like polyolefins. Researchers employed surfactants aim to make compatible clay with PP. Alkyl amines are widely used surfactants in obtaining PP clay nanocomposites. In particular, exceeding amine modifiers number 12 provides exfoliation and self-assembly of individual silicate layers within the PP matrix [20]. Cloisite 15A and Cloisite 20A are organophilic clay minerals modified with dimethyl, dehydrogenated tallow, quaternary ammonium. Hydrogenated tallow includes 65 % C18, 30 % C16, and 5 % C14. The only difference between these two clays is the surfactant concentration between layers which accounts for 1,25 and 0.95 meq/g in Cloisite 15A and Cloisite 20A, respectively. Accordingly, the interlayer distance of Cloisite15A (3,06 nm) is bigger than Cloisite 20A (2,4 nm) [10].

Tessier et al. [11] used two types of clays: Cloisite 20A and Cloisite 30B (modified with a polar surfactant) to obtain starch-grafted polypropylene organoclay nanocomposites. They used Cloisite 20A due to its affinity to the polypropylene phase of the polymer matrix while Cloisite 30B has an affinity to the starch phase. They interpret that the initial inter-platelet distance of this non-polar modified montmorillonite (Cloisite 20A) is higher than that of its polar modified counterpart (Cloisite 30B). For this reason, on the occasion of Cloisite 20A, the exfoliation mechanism is more mechanically driven (by polypropylene chain insertion) rather than chemically in PP/clay nanocomposites.

Thermal stability of PP/clay composites was considerably increased as soon as obtained exfoliated structure [12–16]. The authors concluded that the improvement in the thermal properties was correlated with lower oxygen permeability resulting from an increased diffusion path for oxygen as well as volatile decomposition products. PP-g-MA was found the most effective compatibilizer for PP/clay composites in many articles [17–20]. There are a lot of publications that investigate the effect of different clay modification techniques [21, 22].

Phase diagram of polymer – clay mixture, proposed by Ginzburg et al., revealed that increased length and density of grafted chains led to improved miscibility of the clay and the polymer, in its turn, proper miscibility contributes to exfoliated structure in the wide range of clay volume ratio. In the case of short surfactant macromolecules, the polymer is not likely to insert space between the clay layers. This causes immiscibility for major values of the Flory – Huggins parameter and the clay volume ratio. There is also a limitation to the strong interaction between grafted chains and polymer macromolecules [23].

For different surfactant lengths, surfactant coverage and surfactant – matrix enthalpic, Balazs et al. studied morphological behavior of polymer clay composites by employing their model named self-consistent field calculation. According to their model, it turned out that a longer organic modifier provides better intercalation of polymer macromolecules to penetrate the space between clay platelets. However, the density of surfactant should be reasonable because dense coverage makes intercalation and/or exfoliation impossible [24].

Accordingly, in this paper isotactic PP, PP-g-MA, and two types of clays were chosen in obtaining composites and the aim of this study is to explore the properties of PP/clay nanocomposites obtained with different modifier densities between interlayer space in the variation of compatibilizer content.

Experimental

Materials

Isotactic PP (J-170T) with MFI = (2.16 kg, 230 °C) 21 g/10 min was kindly provided by JV Uz-Kor Gas Chemical LLC. PP-g-MA with 2.5 wt.% maleic anhydride content and MFI = (2.16 kg, 230 °C) >200 g/min was provided by JV UzAuto CEPLA LLC as a gift. Cloisite15A, (spacing $d_{001} = 3.06$ nm, dimethyl dehydrogenated tallow ammonium conc. 1.25 meq/g), Cloisite20A, (spacing $d_{001} = 2.4$ nm, dimethyl dehydrogenated tallow ammonium conc. 0.95 meq/g) Southern Clay Products, Inc., Gonzales, TX.

Preparation

Components melt blended in Brabender Plastograph (Germany). First PP and PP-g-MA were introduced into plastograph after getting molten mass clay was introduced and kept during 8 min 150 rpm in order to provide better mixing components one another. Next, tensile test samples were prepared by injection-molding machine Mercator 1971 (Poland). Name of samples and their content ratios are given in Table 1.

Table 1

Name of obtained samples and their contents

Name of samples	PP, %	PP-g-MA, %	Cloisite15A, %	Cloisite20A,%
PP	100	–	–	–
PP-g-MA	–	100	–	–
PP/MA10	90	10	–	–
PP/MA20	80	20	–	–
15A3	94	3	3	–
15A6	91	6	3	–
15A9	88	9	3	–
15A12	85	12	3	–
20A3	94	3	–	3
20A6	91	6	–	3
20A9	88	9	–	3
20A12	85	12	–	3

XRD measurements

XRD measurements were conducted with Rigaku Miniflex 600 (Japan) in the condition of 40 kV voltage, 15 mA current and 0.02° step.

DSC and TGA measurements

Thermal properties of the samples studied by DSC and TGA analysis were conducted simultaneously, in the range from room temperature to 600 °C by Linseis thermal analysis PT1610.

Mechanical analysis

Tensile tests were conducted according to ASTM D 638 in Shimadzu AG-X PLUS (Japan). For measuring tensile module (E), 1 mm/min crosshead speed was chosen until 0,3% deformation, after that crosshead speed increased immediately to 20 mm/min for further exploring yield stress (σ) and deformation (ϵ).

MFI measurement

MFI was measured according to ASTM D 1238 using Zwick extrusion plastometer (Germany) at 230 °C/2.16 kg.

Results and Discussion

Small angle X-ray diffraction

Small angle X-ray (SAXS) diffraction is identical for characterizing clay dispersion in polymer matrix [25–27]. The basal spacing of the silicate layer (d_{001}) was calculated with Bragg's law: $n\lambda = 2d\sin\theta$. Figures 1 and 2 show SAXS pattern of obtained samples. The difference between these two organically modified clays is modifier volume and interlayer distance d (which Cloisite15A has greater than Cloisite20A) [28]. Cloisites have two main peaks, the second peak at $2\theta = 7.2^\circ$ ($d_{001} = 1.2$ nm) corresponding to interlayer distance of pure unmodified montmorillonite (MMT), the first peak occurs at $2\theta = 2.88^\circ$ in Cloisite15A corresponding to intercalation of MMT as a result of modifier penetration during modification while in Cloisite20A, this peak accounts for in $2\theta = 3.68^\circ$. SAXS curves in Figures 1 and 2, compare the effect of PP-g-MA content on the intercalation degree of Cloisite15A and Cloisite20A. There was a considerable difference between the dispersion of clay through the PP matrix. While composites with Cloisite15A show an intercalated structure, Cloisite20A achieves exfoliation except for 20A3. In the case of Cloisite15A first peak in $2\theta = 2.8^\circ$ shifts towards small angles about $2\theta = 2.3^\circ$ corresponding to $d = 38.25$ Å, however, 15A9 has slightly smaller angles than others, indicating all samples' intercalation. The second peak also decreased from $2\theta = 7.2^\circ$ to $2\theta = 4.7^\circ$. With respect to the intensity of the peaks, the smallest intensity was seen in both main peaks in 15A9. This reduction in the peak intensity can be interpreted as the formation particular amount of exfoliated structure as well as intercalated. When it comes to Cloisite20A, except for composite with 20A3 all had a considerable shift in peaks to lower than $2\theta = 2^\circ$ angle, as a result of exfoliation. The reason for exception 20A3 is the lack of compatibilizer to achieve finer dispersion of clay in polymer matrix. Occurrence of exfoliation in the composites with Cloisite20A can be proved shifting of the first peak smaller angle relation to pure Cloisite20A.

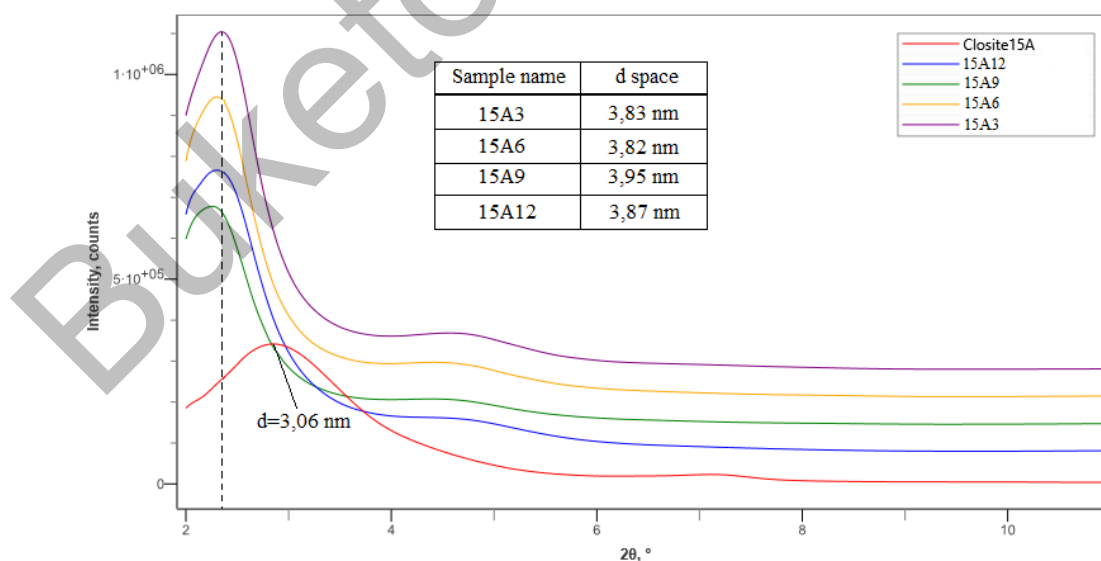


Figure 1. PP and Cloisite15A composites small angle X-ray curves

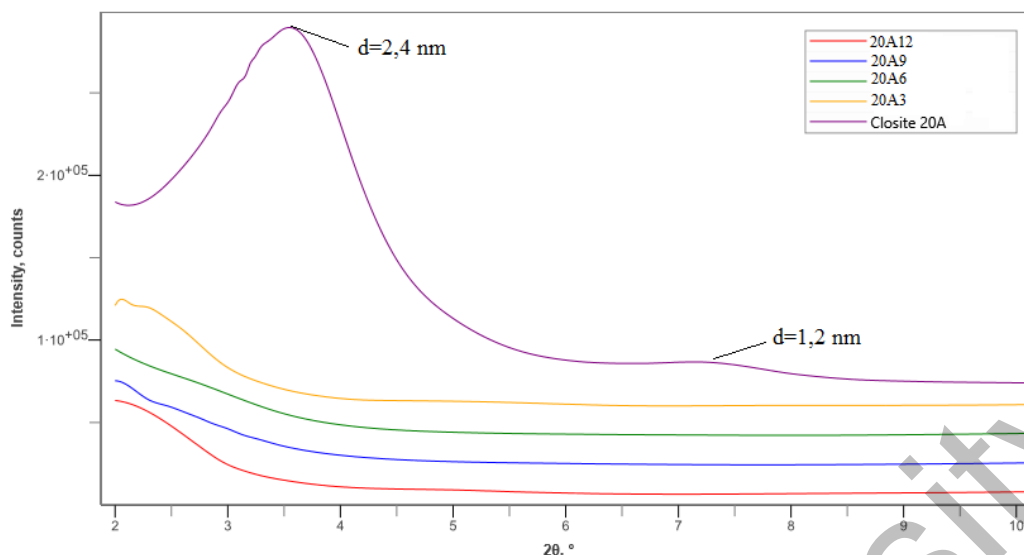


Figure 2. PP and Cloisite20A composites small angle X-ray curves.

MFI

Figure 3 compares MFIs of PP and PP-g-MA blends. PP-g-MA shows more than 200 g/10 min MFI while PP has 21 g/10 min. Presence of 10 wt.% PP-g-MA in PP/PP-g-MA blends MFI accounts for 56 g/10 min and further addition of PP-g-MA increases MFI to 94 g/10 min. This is due to the low molecular weight of PP-g-MA and, as shown in a number of works [14, 15, 23, 24], it is oligomeric functionalized PP that provides favorable conditions for intercalation in the interlayer space and subsequent exfoliation of MMT particles. For PP and clay systems, MFI decreases as soon as the formation of exfoliated and intercalated structures. Our compounds also exhibited these properties (Figure 4). For composites with Cloisite15A, when the ratio of compatibilizer/filler was 1, MFI is 58.6 g/10 min and as compatibilizer content increases MFI decreases to 17.5 g/10 min in the 15A9, however, subsequent addition of PP-g-MA causes slight growth in the 15A12. The initial reduction in MFI is related to the extension of clay particles dimensions as a result of intercalation. When PP-g-MA content reaches saturation point, that is 9 wt.%, additional PP-g-MA causes to increase MFI. With regard to composites with Cloisite20A, an optimal amount of compatibilizer is 6 wt.% and extra compatibilizer just leads to the increase in the melt flow without participating in intercalation or exfoliation. Intercalated centers in the form of physical knots (similar to crosslinking), as PP-g-MA rises, leads to the increase of the compounds' viscosity. An extremal dependence of viscosity is observed for exfoliated structures (uniform distribution of nanoparticles) with a minimum at a PP-g-MA content of 6 wt.%. For these structures, the contribution of low-viscosity PP-g-MA above 6 wt.% becomes noticeable.

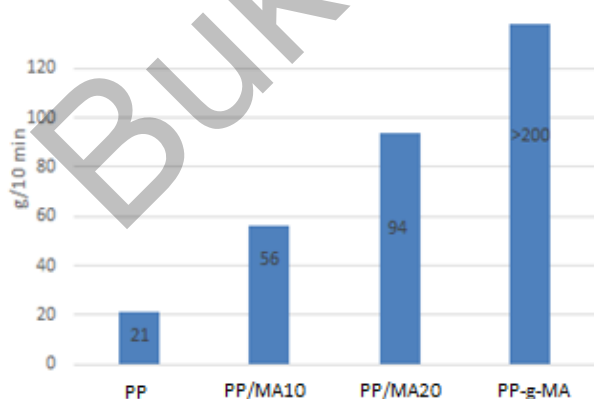


Figure 3. MFI of PP and PP-g-MA blends

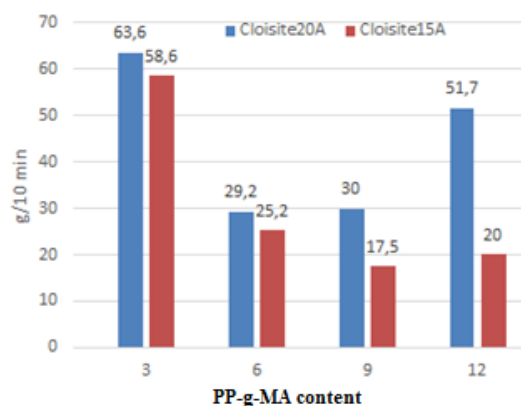


Figure 4. MFI of composites based on Cloisite15A and Cloisite20A

DSC and TGA measurements

DSC curves for PP and PP-g-MA blends show different oxidation behavior while the melting temperature of the samples is almost the same. Showing a melting point of 158.5°C, PP stands stable until 220 °C, and subsequent heating causes intensive oxidation. PP-g-MA with a melting point of 160.6 °C is immediately engaged in oxidation after melting. Their blends indicate thermal behavior corresponding to individual components. As PP-g-MA content increases in the blend, oxidation occurs in relatively lower temperatures (Figure 5). Figure 6 compares DSC curves of composites with Cloisite15A, reflecting differences only in oxidation behavior. In composites with 9 and 12 wt.%, although PP-g-MA leads to oxidation due to intercalation, engaging in oxidation is reduced. DSC curves of composites with Cloisite20A show distinction in both melting point and oxidation (Figure 7). 20A3, intercalated composite, has a melting point of 159.1 °C and gets involved in oxidation intensively after melting. However, when PP-g-MA content is increased by 6 wt.% the composite is stable to oxidation until 188 °C. Due to the penetration of PP-g-MA molecules into the interlayer space of filler, this exfoliated composite has a lower melting point temperature, which is 157.9 °C, in this case. Even though there is exfoliation, the subsequent addition of PP-g-MA again causes more sensitive oxidation behavior and increased melting points, in the compositions with 9 and 12 wt.% of Cloisite20A.

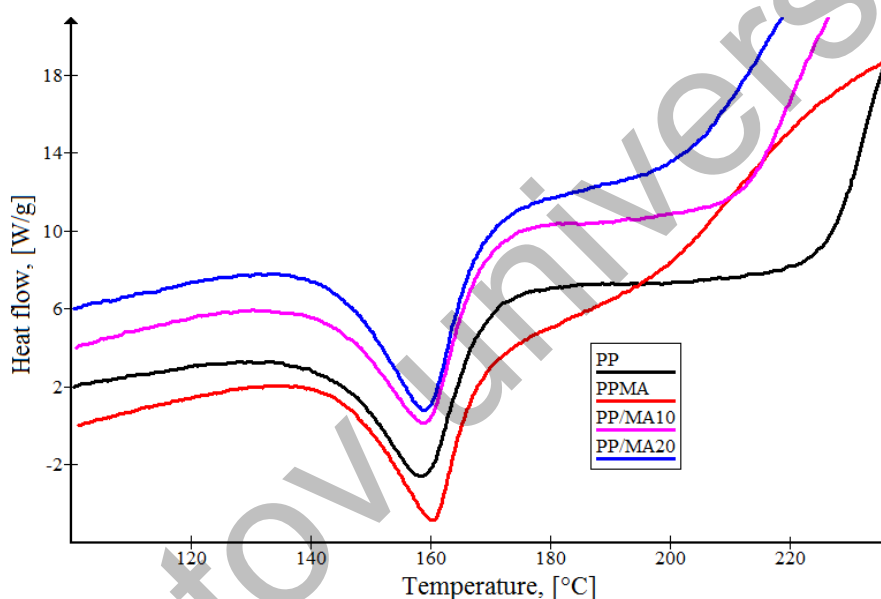


Figure 5. DSC curves of PP and PP-g-MA blends

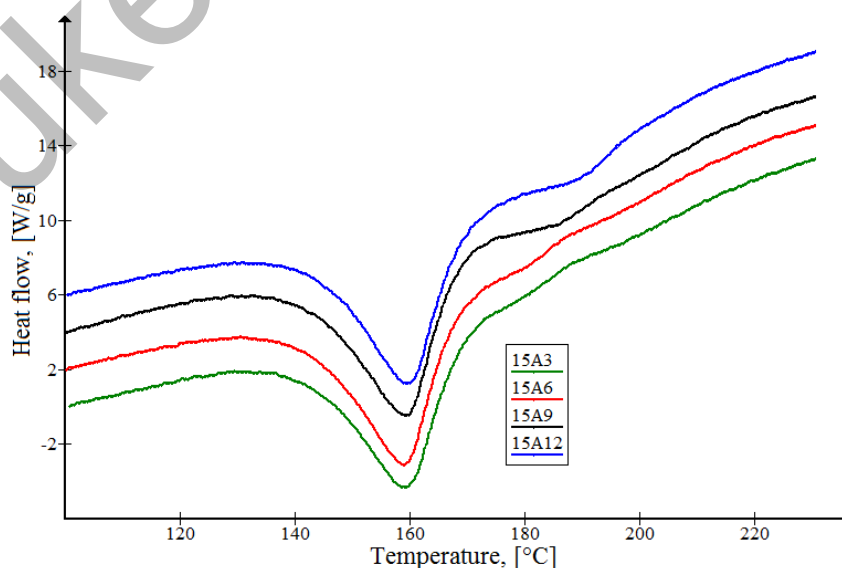


Figure 6. DSC curves of composites with Cloisite15A

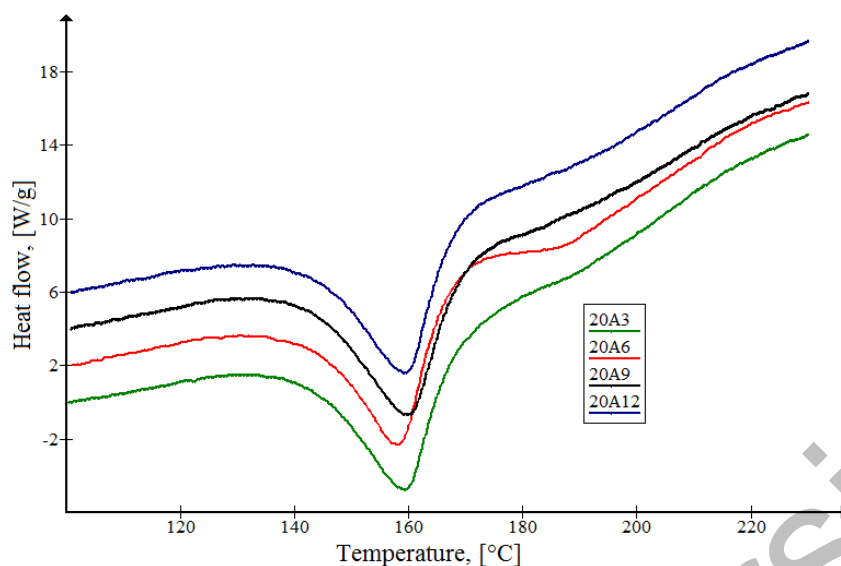


Figure 7. DSC curves of composites with Cloisite20A

Except for DSC, TGA analyses of obtained samples also were conducted. In Figure 8, PP starts mass loss at 237 °C (onset temperature of degradation) while in the case of PP-g-MA accounts for 256 °C. Furthermore, after starting degradation, PP engages in degradation more intensively than PP-g-MA. PP and PP-g-MA blends show different degradation mechanisms, as increases PP-g-MA content in the blends degradation curve of the blend tends to become similar to PP-g-MA. However, PP/MA10 and PP/MA20 blends start degradation in lower temperatures relative to PP. Actually, the onset temperature of degradation must have been between degradation temperatures of PP and PP-g-MA according to the rule of polymer additiveness. The reason for this is that PP-g-MA makes PP sensitive toward oxidation, due to its individual thermal behavior, during melt processing components, according to the DSC curves in Figure 5. PP-g-MA uptakes oxygen during melt processing and then this absorbed oxygen leads to degradation by generating free radical which causes PP/MA10 and PP/MA20 blends mass loss in relatively earlier temperatures [9]. With regard to TGA analysis of composites obtained with Cloisite15A and Cloisite20A, though PP shows superior thermal stability to oxidation among samples in DSC analysis, thermal degradation properties — mass loss — of PP are inferior to that of PP/clay nanocomposites (Figure 9). In PP/clay nanocomposites, clay acts as an excellent insulating barrier that slows the release of gas from decomposition, so the degradation temperature increases. In general, the presence of clay in the PP tends to the increased thermal stability of the polymer [29].

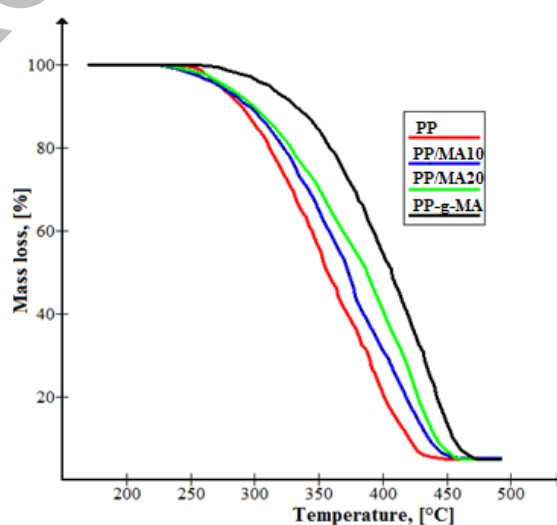


Figure 8. TGA of PP and PP-g-MA blends

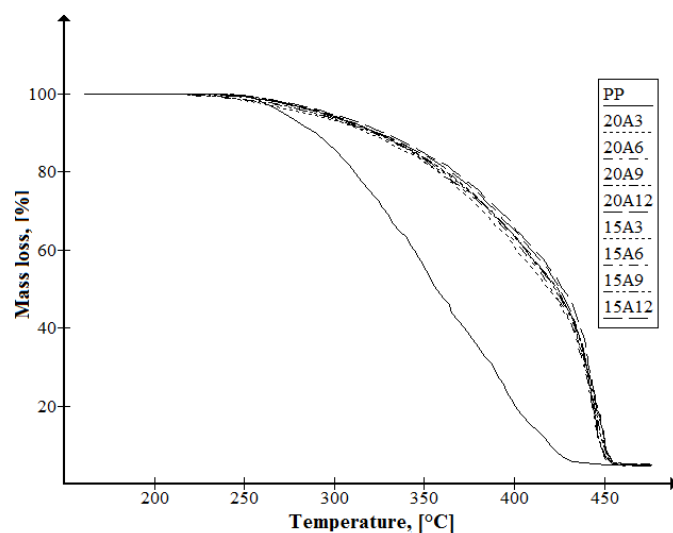


Figure 9. TGA of PP and PP/clay composites

Mechanical measurements

Tensile properties such as tensile module (E), yield stress (σ), and elongation at break (ϵ) have been studied. The results are given in Table 2. The neat PP possesses superior mechanical properties with the best E and σ , while PP-g-MA has good ϵ which is approximately five times more than neat PP. The addition of PP-g-MA to PP makes PP tougher that ϵ increases and reduces E and σ PP tends to become more brittle. In the compositions with Cloisite15A, as PP-g-MA increases, unlike PP/PP-g-MA blend, E and σ also increase; actually, filler content is constant. These phenomena occur due to the development of nano-dispersed clay particles through the matrix as can be seen from SAXS, shifting the peak in d_{001} to small angles. In the case of composites with Cloisite20A, a saturation of composite with PP-g-MA occurs when PP-g-MA content is 6 wt.% and further addition of compatibilizer leads mechanical properties to diminish by causing oxidation of composite in high temperature.

Table 2

Mechanical properties of obtained PP/clay composites

Sample names	E , [MPa]	σ , [MPa]	ϵ , [%]
PP	922±68	36.2±1.2	845±90
PP/MA10	918±54	36.5±1.2	738±93
PP/MA20	770±7	29.9±0.7	984±150
PP-g-MA	713±61	26.2±1.6	697±52
15A3	946±61	32.8±0.6	18.5±2
15A6	960±52	34.5±1.2	17.8±3.8
15A9	968±49	35.2±0.8	127±18
15A12	1008±41	35.3±1.1	102±29
20A3	1000±51	35.4±0.8	12.7±2
20A6	1087±19	37.6±0.3	52±7
20A9	1002±52	35.9±0.5	17.3±5
20A12	932±51	35.4±0.4	16.8±3

Conclusions

Studies have been carried out on the formation of nanocomposites of isotactic polypropylene with modified MMT (Cloisite15A, Cloisite20A), differing modifier densities in the interlayer space. To ensure the diffusion of PP into clays, PP-g-MA (2.5 wt.%) was employed as a compatibilizer, the amount of which a mixture with PP-g-MA varied within 3, 6, 9, and 12 wt.%. It was found that MMT with a high density of the modifier (Cloisite15A) promotes the formation of intercalated structures, while MMT with a low density of the modifier (Cloisite20A), predominantly exfoliated nanocomposites are formed. In the first case, an in-

crease in the content of PP-g-MA leads to an expansion of the interlayer space (from 30.6 to 39.5 Å). In composites with Cloisite20A, only 3 wt.% content of PP-g-MA shows the formation of mixed intercalated and exfoliated structures, while subsequent increasing compatibilizer content favors the formation of predominantly exfoliated structures. The observed structures are reflected in the viscosity parameter. Nanocomposites intercalated with an increase in less viscous PP-g-MA due to limitations associated with the intercalation of macromolecules in the interlayer space and the presence of a specific interaction with the modifier. The clay surface increases markedly (from 65 to 20 g/min), whereas the exfoliation of the structure passes through a minimum in the region between 6 and 9 % by weight of PP-g-MA. The formation of the nanocomposite is accompanied by a significant increase in thermal stability (50 % weight loss is observed at temperatures of 360 °C and 430 °C for polypropylene and nanocomposites based on it, respectively). An analysis of the mechanical properties of nanocomposites generally indicates an increase in the elastic modulus by 15–20 % (considering the presence of low-modulus PP-g-MA), and this effect is more pronounced for exfoliated structures, the yield strength practically does not change, and the elongation at break decreases very noticeably. Heat-resistance properties of intercalated and exfoliated nanocomposites (with a content of 9–12 wt.% and 6 wt.% PP-g-MA, respectively) with enhanced characteristics according to the tensile module and moderate deformability (more than 100 %) generate diverse practical and technological interest.

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Cloisite15A және Cloisite20A изотактикалық полипропилен композиттерінің механикалық және жылулық қасиеттері

Мақалада малеин ангидридімен (PP-g-MA) егілген полипропилен құрамының Cloisite15A және Cloisite20A қабатаралық кеңістіктегі модификатордың тығыздығымен ерекшеленетін саздың екі түрі бар полипропилен (ПП) композицияларының термиялық және механикалық қасиеттеріне әсері зерттелген. ПП/саз композиттері 3, 6, 9 және 12 массалық % әртүрлі PP-g-MA құрамының қатысуымен балкытылып, араластырылған. Модификатордың жоғары тығыздығы бар Cloisite15A интеркалирленген құрылымдардың түзілуіне ықпал ететіні, ал модификатордың төмен тығыздығы бар Cloisite20A негізінен қабыршақтанған нанокөздіктерді түзетіні анықталды. Бірінші жағдайда құрылым интеркаляциялануға бейім, сол уақытта Cloisite20A композиттері негізінен қабыршақтанған құрылымдардың пайда болуына ықпал етеді. Нанокөздіктің қалыптасуы термиялық

турақтылықтың едәуір артуымен қатар жүреді (50 % салмақ жоғалту полипропилен және оның негізіндегі нанокөміршітер үшін сәйкесінше 360 °C және 430 °C температурада байқалады). Нанокөміршітердің механикалық қасиеттерін талдау, әдетте, серпімділік модулінің 15–20 %-ға артқанын көрсетеді (төмен модульді PP-g-MA болуын ескере отырып) және бұл әсер қабыршақтанған құрылымдар үшін айқынырақ, ақыштық шегінде кернеу іс жүзінде өзгермейді, ал сыну кезінде салыстырмалы ұзару айтарлықтай төмендейді.

Кілт сөздер: полипропилен, саз, композит, малеин ангидридті егілген полипропилен, интеркаляция, қабыршақтану, тотығу, монтмориллонит.

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Механические и термические свойства изотактических полипропиленовых композитов с Cloisite15A и Cloisite20A

В статье изучено влияние содержания полипропилена, привитого малеиновым ангидридом (PP-g-MA), на термические и механические свойства композиций полипропилена (ПП) с двумя типами глин, различающихся плотностью модификатора в межслоевом пространстве, Cloisite15A и Cloisite20A. Композиты ПП/глина смешивались в расплаве в присутствии различного содержания PP-g-MA от 3, 6, 9 и 12 мас.%. Выявлено, что Cloisite15A с высокой плотностью модификатора способствует образованию интеркалированных структур, тогда как Cloisite20A с низкой плотностью модификатора формируют преимущественно эксфолированные нанокөміршітер. В первом случае структура имеет тенденцию к интеркаливанию, в то время как композиты с Cloisite20A способствуют образованию преимущественно эксфолированных структур. Формирование нанокөміршітера сопровождается значительным усилением термостабильности (50 % потеря веса наблюдается при температурах 360 °C и 430 °C для полипропилена и нанокөміршітеров на его основе, соответственно). Анализ механических свойств нанокөміршітеров свидетельствует, в целом, об увеличении модуля упругости на 15–20 % (с учетом присутствия низкомолекулярного ППМА), причем этот эффект более выражен для эксфолированных структур, напряжение при пределе текучести практически не претерпевает изменений, а относительное удлинение при разрушении весьма заметно уменьшается.

Ключевые слова: полипропилен, глина, композит, полипропилен с привитым малеиновым ангидридом, интеркаляция, эксфолиация, окисление, монтмориллонит.

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