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Chlorosulfonated polypropylene: preparation and its application as a coupling agent in polypropylene–clay nanocomposites

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Abstract

Polypropylene nanocomposites containing organophilic layered silicate were prepared by melt mixing. In order to increase polypropylene polarity, Cl and SO_2Cl groups were introduced by reaction with sulfuryl chloride under UV irradiation. Chlorosulfonated polypropylene was subsequently melt-compounded with organophilized montmorillonite clay to produce a masterbatch. The masterbatch was then blended with commercial isotactic polypropylene. An organophilized silicate (Cloisite 15A) and three chlorosulfonated polypropylenes with different degrees of functionalization were used in this study. The effect of various processing procedures was examined as well. The morphology of nanocomposites obtained was examined using TEM and X-ray diffraction. It has been shown that the presence of polar groups leads to an increased gallery distance and partial exfoliation. Nevertheless, full exfoliation of clay platelets has not been achieved. The observed morphologies affected the resulting tensile mechanical behaviour: both stiffness and strength significantly increased.

Keywords: Polypropylene; Nanocomposites; Melt-compounding

1. Introduction

Isotactic polypropylene is a versatile thermoplastic material, compatible with many processing techniques and used in many different commercial applications. It has been the fastest growing polymer in the recent decades among all thermoplastics worldwide [1,2]. The reasons are not only properties attractive for various application segments and a favourable price/performance ratio of this material but also the possibility to modify its properties in a very wide range. The development of nanocomposites combining mineral and polymer material characteristics on a very fine structural level is definitely one of the most interesting perspectives for isotactic polypropylene.

Polymer-layered silicate nanocomposites are an alternative to conventional microcomposites, because they exhibit improved stiffness and strength as well as decreased thermal expansion coefficients and enhanced barrier properties. An important fact is that the mentioned improvements are obtained at very low filler loadings (~5 wt%). To take the advantage of nanocomposites, the silicate must be finely and uniformly dispersed, i.e. intercalated and/or exfoliated in the matrix [3–5]. The commonly used clay is natural montmorillonite modified with a quaternary ammonium salt, which makes the hydrophilic silicate surface organophilic. In general, polymer/clay nanocomposites can be prepared by three methods [3]: in situ polymerization, polymer intercalation from solution and direct melt compounding. The main advantage of the last method is that it is compatible with current industrial processes and, at the same time, is environmentally friendly.

The polyolefin nanocomposites with layered silicates are relatively difficult to obtain by melt compounding because polypropylene and polyethylene do not contain any polar groups and layered silicates, even if modified with nonpolar alkyl groups, are polar and thus incompatible. To solve the problem, a modified polymer is introduced as a coupling agent, which overcomes the polarity difference between the layered silicate and polypropylene. Usually maleic-anhydride grafted species are added as compatibilizers. It has been shown that the polar anhydride functionality promotes dipole and/or hydrogen bonding between the filler and the

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polyolefin, leading to improved clay dispersion in the polymer matrix [4–11]. Positive effect of an antioxidant on compatibility between polypropylene and layered silicate modified by octadecylamine has been also reported [12]. However, the authors did not evaluate resulting mechanical properties.

Our objective was to develop another, new method to prepare melt-compounded polypropylene/clay nanocomposites without maleic-anhydride grafted polypropylene. In this article, we report on the effect of the presence of chlorosulfonated polypropylene on clay delamination and resulting mechanical properties of polypropylene nanocomposites.

2. Experimental section

2.1. Materials

A commercial-grade isotactic polypropylene homopolymer (PP) Mosten 58.412 (Chemopetrol, Litvínov, Czech Republic) was used as the matrix. The material is characterized by a melt flow index of 3 g/10 min (230 °C, 21.2 N) and a weight-average molecular weight M_w of ca. 320,000. Three types of chlorosulfonated polypropylenes (CS-PP1, CS-PP2 and CS-PP3) with different degrees of functionalization were used as coupling agents. Their preparation is given below. A commercial type of nanoclay based on natural montmorillonite modified with dialkyldimethylammonium chloride (with alkyls derived from hydrogenated tallow), Closite 15A (Southern Clay Products, Gonzales, Texas, USA) [13], was used as a nanofiller. It is labeled as 15A.

2.2. Functionalization of polypropylene

Chlorosulfonated polypropylene (CS-PP) was prepared by reaction of polypropylene powder with sulfuryl chloride. The reaction was carried out at elevated temperature under UV irradiation in the presence of a small amount of pyridine as catalyst. In this way, sulfochloride groups SO_2Cl were introduced into polymer chains, together with a certain amount of chlorine atoms Cl, Fig. 1. Polypropylene powder, sulfuryl chloride and pyridine were reacted in tetrachloromethane, unless otherwise specified. The reaction mixture was stirred at 50 °C under UV irradiation. The reaction times and compositions of the starting suspensions are summarized in Table 1. After reaction the suspension was left standing overnight, then it was filtered, washed three times with chloroform, dried in air at room temperature and finally in vacuum at 100 °C.

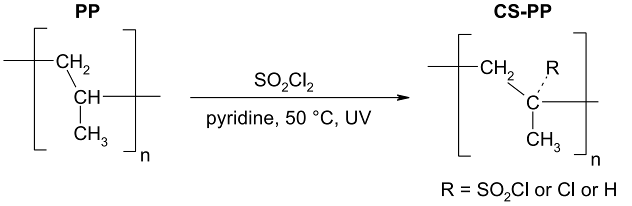


Fig. 1. Schematic grafting of polypropylene.

2.3. Sample preparation

Two different compounding procedures were used: direct melt mixing and a masterbatch mixing process. In the direct mixing process, matrix polypropylene, functionalized polypropylene and a nanofiller (80/15/5) were compounded in one step using a DSM research 5 cm^3 twin-screw microcompounder at 190 °C and 220 rpm for 10 min. Prior to mixing the clay was dried under vacuum in an oven at 70 °C for 12 h. In the masterbatch mixing process, a masterbatch was first prepared by compounding 25 wt% of clay with 75 wt% of chlorosulfonated polypropylene. The masterbatch was then blended with matrix polypropylene. The device and mixing conditions were the same as in the direct mixing process. The masterbatch was also compounded with matrix polypropylene in an internal mixer Brabender Plasticorder at 190 °C and 60 rpm for 10 min to obtain sufficient amounts of the material for mechanical testing.

Sheets with the thickness 1.5 mm were prepared by compression moulding. The material removed from the mixing chamber was immediately compression-moulded between stainless steel plates in three steps: 3 min at 190 °C without any pressure, 3 min at the same temperature at 25 bar and cooling down to the room temperature in a cold press at 25 bar. The PET film was used to avoid adhesion of polymers to the steel plates. The dumbbell specimen for tensile testing (type 5A according to the ISO 527 standard) were die-stamped from the compression-moulded sheets.

2.4. X-ray diffraction (XRD)

XRD studies were carried out in order to evaluate the degree of clay delamination. Wide-angle X-ray diffraction patterns (WAXS) were obtained using a powder diffractometer HZG/4A (Freiberger Präzisionsmechanik GmbH, Germany) and monochromatic Cu K_α radiation. The diffractograms were scanned in the 2Θ range from 1.4 to 10°.

2.5. Microscopy

Ultrathin sections for transmission electron microscopy, ca. 40 nm thick, were cut with a Leica Ultracut UCT ultramicrotome equipped with cryo attachment. Temperatures during cutting were −110 and −50 °C for the sample and knife, respectively. Transmission electron microscopy (TEM) was performed with a microscope JEM 200CX (JEOL, Japan). All TEM micrographs were taken at acceleration voltage 100 kV, recorded on a photographic film and digitized with a PC-controlled digital camera DXM1200 (Nikon, Japan).

Table 1
Reaction compositions and conditions

	PP (g)	SO_2Cl_2 (g)	Pyridine (g)	CCl_4 (ml)	Reaction time (h)
CS-PP1	50	8	2	200	8
CS-PP2	50	100	2	–	5
CS-PP3	250	167	10	750	6

2.6. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was performed in single cantilever mode using a DMA X04T (R.M.I., Czech Republic) device. The temperature sweep mode was used in the interval from −120 to 165 °C at the heating rate 1 °C min^{-1}, with frequency 1 Hz. The specimens were bars cut from compression-moulded sheets. The distance between clamps, width, and thickness were 12, 10 and 1.5 mm, respectively.

2.7. Tensile testing

Tensile testing was performed at room temperature on an Instron 5800 testing machine (Instron, UK) according to the ISO 527 standard. The crosshead speed was 20 mm/min except for the Young modulus determination, which was carried out at a lower crosshead speed of 1 mm/min. The following mechanical characteristics were derived from the stress–strain curves: Young modulus, E, tensile strength, σ_m, and strain at break, ε_b. The reported values are averaged from 10 individual measurements.

3. Results and discussion

3.1. Functionalization of polypropylene

The degree of functionalization of CS-PP prepared using the above-described procedure was determined by elemental analysis. The contents of Cl and SO_2Cl groups are given together with the calculated degrees of functionalization in Table 2.

It can be seen that the contents vary in relatively wide ranges and strongly depend on reaction conditions (temperature, SO_2Cl_2/PP molar ratio, reaction time etc.). We prepared three chlorosulfonated polypropylenes that differ not only in the content of SO_2Cl groups but also in the Cl content. CS-PP1 contains relatively low amounts of both sulfochloride groups (1.9 wt%) and chlorine atoms (1.4 wt%). The medium amount of SO_2Cl groups in CS-PP2 (6.7 wt%) is accompanied by a distinctly higher content of chlorine (11.5 wt%). Finally, CS-PP3 with the highest amount of sulfochloride groups (10.0 wt%), contains only an intermediate amount of chlorine (5.7 wt%).

Table 2
Elemental analysis results and degree of functionalization of prepared chlorosulfonated polypropylenes

	Elemental analysis (wt%)		Calculated content of functional groups (wt%/mol.kg^{-1})	
	Cl	S	SO_2Cl	Cl
CS-PP1	2.1	0.6	1.9/0.19	1.4/0.40
CS-PP2	13.9	2.15	6.7/0.67	11.5/3.20
CS-PP3	9.20	3.12	10.0/1.00	5.7/1.60

3.2. Clay delamination

Clay delamination was studied using XRD and TEM. In XRD patterns the interlayer spacing of clay was determined from the 2Θ position of the peak corresponding to the {001} basal reflection of montmorillonite (referred to as d_{001} peak). The corresponding X-ray diffraction curves of polypropylene/Cloisite 15A microcomposite and the nanocomposites containing chlorosulfonated coupling agent are shown in Fig. 2. A shift of the d_{001} peak to lower angles means that intercalation of polymer chains took place during melt compounding. On the other hand, a reduction in the peak intensity indicates a decrease in the amount of intercalated clay, i.e. it suggests breakdown of platelet agglomerates and/or partial exfoliation.

The original organoclay Cloisite 15A exhibits the gallery distance of 3.15 nm. From Fig. 2 it is clear that melt compounding of the clay with polypropylene does not lead to any significant change in the gallery distance. The d_{001} values of the prepared masterbatches and nanocomposites are summarized in Table 3. The beneficial effect of the presence of Cl and SO_2Cl groups on clay delamination is obvious. Compounding of 25 wt% of clay with 75 wt% of

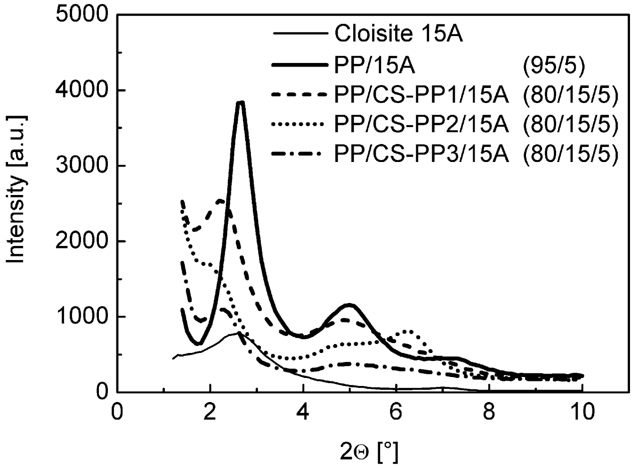


Fig. 2. The effect of coupling agent on X-ray diffraction curves.

Table 3
Interlayer distances of studied nanocomposites prepared by different compounding processes

	Interlayer distance d_{001} (nm)				
	Cloisite 15A, 0/0/100	Masterbatch, 0/75/25	NC 1, 80/15/5	NC 2, 80/15/5	NC 3, 80/15/5
PP/CS-PP1/15A	3.15	3.79	3.68	3.65	3.92
PP/CS-PP2/15A	3.15	4.20	4.01	4.20	4.40
PP/CS-PP3/15A	3.15	3.68	3.92	4.01	3.84

Compounding: masterbatch, DSM microcompounder; NC 1, DSM microcompounder, one step direct melt mixing; NC 2, DSM microcompounder, mixing of the masterbatch with neat PP; NC 3, Brabender, mixing of the masterbatch with neat PP.

chlorosulfonated polypropylene in order to obtain the masterbatch led to a marked increase in interlayer spacing. The highest degree of intercalation was observed for systems with CS-PP2, i.e. with the polypropylene containing a medium amount of SO_2Cl groups, but a distinctly higher amount of Cl. It seems that chlorine is more efficient in organoclay delamination. Its positive effect on polymer intercalation into montmorillonite gaps is reported [14,15]. On the other hand, the difference between CS-PP1 with the lowest degree of functionalization and CS-PP3 with the highest degree is hardly noticeable.

When all the three components are directly compounded in a DSM microcompounder (column NC 1 in Table 3), final nanocomposites exhibit the degree of intercalation comparable with the masterbatches. Compounding of the masterbatches with neat polypropylene does not markedly change the interlayer spacing. There is only a small increase in the d_{001} value, but in some cases the interlayer spacing slightly decreases. This can be a result of degradation of the ammonium compound or diffusion of excess intercalant out of the gaps. No significant difference between compounding in the DSM microcompounder and Brabender mixer has been observed. Therefore, the following reported data are obtained on nanocomposites prepared using the Brabender mixer (column NC3 in Table 3).

In addition to the X-ray diffraction, TEM observation was performed in order to describe the degree of delamination of the clay. In Fig. 3 are evident micrometer-sized clay agglomerates in the PP/15A system without any coupling agent. The original clay agglomerates are broken down due to external forces from the polymer melt during compounding. Nevertheless, the diffusion of polypropylene macromolecules into the gaps is limited as a result of weak interactions between clay surface and polypropylene. Neither an exfoliated, nor an intercalated structure was obtained. It has been demonstrated by XRD that the interlayer distance of PP/15A microcomposite is virtually identical with that of pristine Cloisite 15A, see Fig. 2. On the other hand, TEM confirmed the coexistence of both intercalated and exfoliated structures in nanocomposites containing the coupling agent, Fig. 4(a) and (b). Typically, the layers with larger lateral dimensions retain a parallel registry and form intercalated structures, whereas smaller layers disperse throughout the matrix. It can bee seen that such a structure and clay dispersion are qualitatively the same for all the nanocomposites prepared.

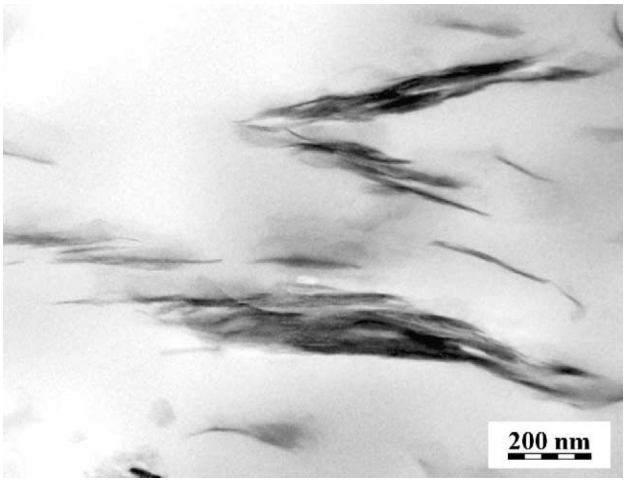


Fig. 3. TEM micrograph of PP/15A microcomposite.

3.3. Mechanical behaviour

Fig. 5(a) shows the temperature dependence of storage modulus, E', of neat polypropylene and its nanocomposites with Cloisite 15A. It can be seen that the nanocomposites show systematically higher moduli than the neat polypropylene. The corresponding dependences of loss modulus, E'', are depicted in Fig. 5(b).

The neat polypropylene exhibits its two characteristic features: a glass transition relaxation peak around 0 °C and a high-temperature shoulder associated with chain relaxation in the crystalline phase. There is no significant change in the position of the T_g maximum for all the nanocomposites prepared within this study. In the case of nanocomposites a pronounced peak around 50 °C appears. The exact nature of these peaks remains unclear, but we assume that they are associated with the relaxation of polymer chains constrained between individual silicate layers. There are several reasons for this suggestion: First, the overall crystallinity of nanocomposites, which ranges between 46 and 50% is lower to the corresponding value of neat polypropylene (55%). Second, the peak becomes larger with increasing clay content as demonstrated in Fig. 6 by the dependence for the masterbatch.

Finally, this peak is not a manifestation of the presence of chlorosulfonated polypropylene, since no such maximum

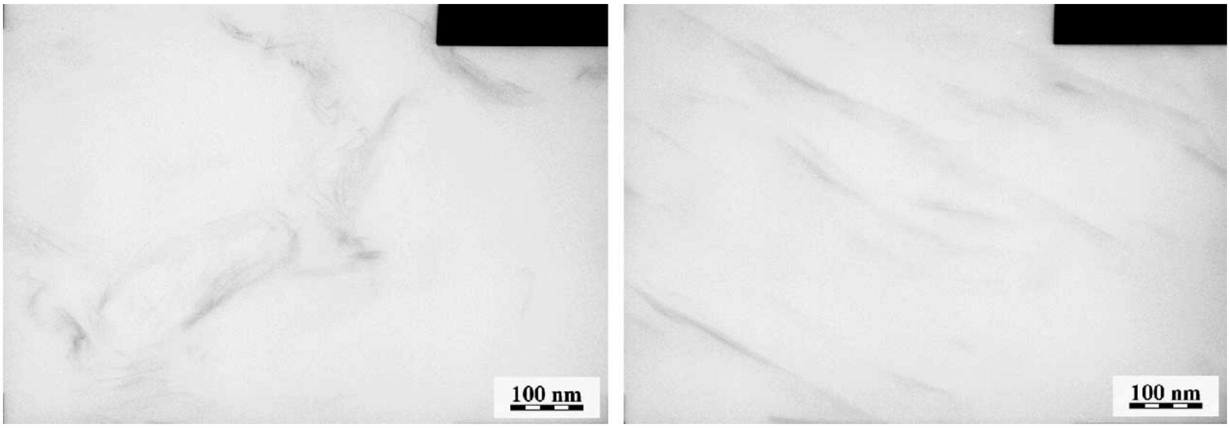
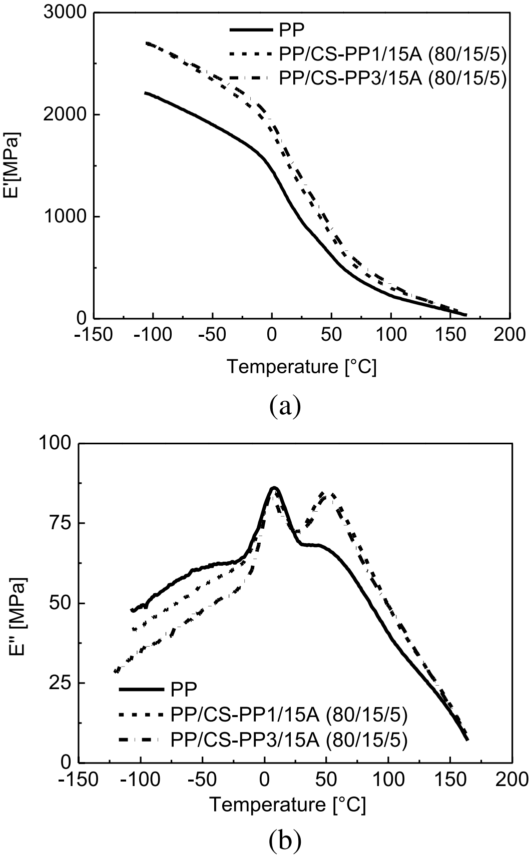


Fig. 4. (a,b) TEM micrographs of PP/CS-PP1/15A (left) and PP/CS-PP2/15A (right) nanocomposites.

appears on the temperature dependence of loss modulus of the functionalized polypropylene. The T_g of chlorosulfonated polypropylene is shifted to higher temperature (~16 °C) as a result of the presence of the SO_2Cl groups and Cl in polypropylene chains. Obviously, they restrict the vibrational ability and thus shift the glass transition to higher temperature. Furthermore, the shoulder around 50 °C associated with the chain relaxation in the crystalline phase disappears as a result of low crystallinity of functionalized polypropylene. The crystallinity of neat polypropylene is about 55%, while that of CS-PP3 is only 34%.

The presence of the nanoclay and coupling agent strongly affect the tensile mechanical behaviour. While neat polypropylene exhibits cold drawing after reaching the yield point and its strain-at-break value is ca. 280%, clay agglomerates contribute to flaws during tensile stretching and significantly influence the failure. Only nanocomposites containing the coupling agent CS-PP1 with the lowest degree of functionalization exhibit post-yield elongation. However, the original strain-at-break value of neat polypropylene is markedly decreased to 120% for the PP/CS-PP1/15A nanocomposite. The nanocomposites prepared using other chlorosulfonated polypropylenes with higher degrees of functionalization fail without yielding at strain-at-break not exceeding 11%. On the other hand, the presence of clay enhances both tensile modulus and tensile strength, Fig. 7. It seems that the values of tensile modulus are in good agreement with the degree of clay dispersion. Indeed, the PP/CS-PP2/15A nanocomposite with the highest interlayer spacing exhibits the highest stiffness. Its tensile modulus is almost 1.5 times higher than that of neat polypropylene. The highest value of tensile strength exhibits PP/CS-PP1/15A nanocomposite. The strength of other



(a)

(b)

Fig. 5. (a,b) Temperature dependences of storage (E') and loss (E'') moduli of polypropylene and its nanocomposites.

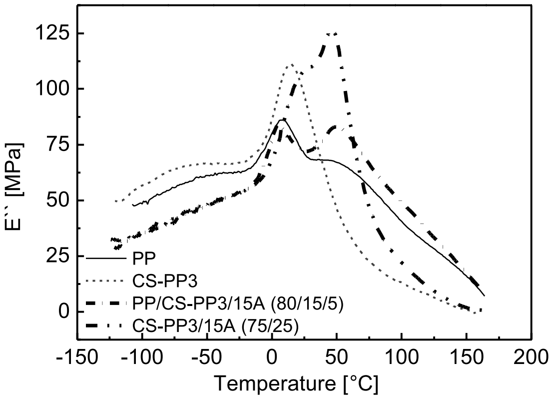


Fig. 6. Temperature dependences of loss (E'') moduli of neat and chlorosulfonated polypropylene and its nanocomposites.

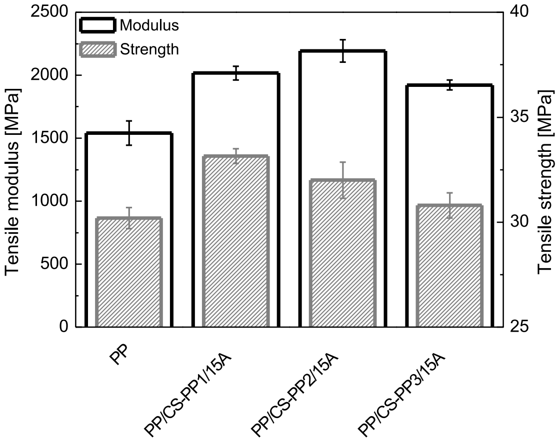


Fig. 7. Tensile properties of polypropylene/Cloisite 15A nanocomposites.

nacomposites decreases with increasing degree of functionalization of the used coupling agent. This is a result of premature failure of these materials. Nevertheless, their tensile strengths still exceed the yield-stress value of matrix polypropylene.

4. Conclusions

In this work, chlorosulfonated polypropylene (CS-PP) was prepared by the reaction of polypropylene powder with sulfuryl chloride under UV irradiation. In this way, sulfochloride groups SO_2Cl were introduced into polymer chains, together with a certain amount of chlorine atoms. We have shown that the presence of such a chlorosulfonated polypropylene in polypropylene/organoclay nanocomposites effectively promotes the clay dispersion in the matrix. The amount of present hydrophilic SO_2Cl groups and Cl atoms and their ratio play a decisive role in clay delamination. The presence of dispersed clay improves the stiffness and tensile strength of the nanocomposites but markedly reduces their strain at break. The most balanced ultimate tensile properties were observed for the polypropylene nanocomposite with Cloisite 15A and chlorosulfonated polypropylene containing 11.5 and 6.7 wt% Cl and SO_2Cl groups, respectively. Its tensile modulus was almost 1.5 times higher than that of neat polypropylene, and, at the same time, the tensile strength was 1.3 times higher than the yield stress of neat polypropylene.

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