Research Article

Development of Mineral-Filled Polymeric Membranes Obtained by Extrusion to Implement In Separation by MEAUS Procedure

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Abstract

Micro-sized calcium carbonate was selected to develop polypropylene-based microporous membranes through MEAUS process (melt extrusion – annealing – uniaxial strain). Different filler percentages were added to polypropylene (1, 5, 10 wt. % calcium carbonate) Parameters such as draw ratio during extrusion, annealing temperature, strain rate, and strain extension were kept as constant in order to analyze the effect of the calcium carbonate, and content of the obtained membranes. The stress applied involved a pre-orientation of the amorphous tie chains prior to crystal chain unfolding, which can be related to the first yield point. A logical pattern of increasing elastic modulus as filler content does is found in calcium carbonate compounds.

Keywords: *Microporous Membranes; Annealing Temperature; Amorphous Tie Chains; Elastic Modulus.*

Introduction

Membranes are increasingly employed for separation processes in many areas such as chemical technology, and they are used in a broad range of applications. The most important property of membranes is their ability to control the rate of permeation of different species the key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane.

Separation of well stream gas from free liquids is the first and most critical stage of field-processing operations is another application of membranes. The composition of the fluid mixture and pressure determine what type and size of the separator are required [1,2] Polymeric membranes are made through various techniques such as phase separation, track etching, leaching, thermal precipitation, and stretching. In phase inversion, the polymeric raw

material is mixed with a solvent as well as a no solvent and during phase separation, a first phase rich in polymer forms the matrix and the second phase poor in polymer creates the pores. In track etching, the polymeric film is irradiated to create tracks followed by acid etching. leaching technique is based on extrusion of the polymeric row material added with the solid particles followed by the extrusion of the solid, leading to pores formation. In thermal precipitation cooling of a mixture of a polymer with a solvent is applied to enable phase separation followed by extrusion of the solvent. Stretching technique is based on the stretching of a polymer film containing a dispersed phase whereupon stretching pores are created due to stress concentration at the interface of these sites, or stretching specific crystalline morphology [1-5]. Phase separation is the most employed technology to produce polymeric membranes. Nevertheless, environmental concerns have to be taken into account, such as solvent contamination and costly solvent recovery is two drawbacks for solution casting, although some improvements have been made in the recent decade.

In the present work, we have employed a technology based on polymer stretching, called MEAUS (melt extrusion – annealing – uniaxial strain). This procedure is applicable to semi-crystalline polymers, based on (1) the stretching of a thin film with a row nucleated lamellar structure (2) annealing of the film to thicken the lamellae, and (3) stretching of the film at a low temperature to create voids and then stretching at high temperature to enlarge the pores. In MEAUS process, the extrusion and production of the precursor films is a delicate process since the samples should be produced under high draw ratio and cooling rates. Obtaining a very uniform film is a major concern since any non-uniformity and thickness variations cause irregularities in the stress distribution. This method is relatively less expensive and there is no solvent contamination. Some drawbacks of the technology and industrial market of this products are the difficulty to have a homogenous distribution of the pore morphology created, and the narrow range of polymers that are able to create the initial row-lamellar structure, being the most employed in the industry polypropylene [6].

The research group of Ajji [7], Caihong **[8]** are the ones performed among several works in the literature by focused mainly on the use of neat polyolefins. However, only a few works dealing with in the filled polyolefin**.** Nakamura and Nago [9,10], created the pores through debonding of calcium carbonate from the polymeric matrix and also evaluated the dependence of properties of the microporous polypropylene sheets on stretching degree. Saffar et al [11], developed polypropylene microporous hydrophilic membranes and also changes in the crystalline structure and membrane performance were investigated in details to optimize annealing and stretching conditions. The use of mineral fillers can provide to the membrane an increase in rigidness, an enhancement of the hydrophilic surface characteristic and also can affect to the final porous morphology of the membranes, as most of the fillers have some nucleate ability in the crystallization processes of polyolefins [8-13].

The largest application, currently under development, is the production of CO_2 from flue gases from gas-fired cogeneration plants and re-use in greenhouses. Captured CO_2 utilized for EOR (Enhanced oil recovery) at mature oil fields in the Gulf Coast region. This CO_2 capture plant consists of pre-treatment, CO_2 absorption, and regeneration, CO_2 compression with dehydration and utility system [14]. Membrane gas absorption based on the novel absorption liquids and porous polyolefin membranes is an efficient technique for the removal of sulfur dioxide from various

burning flare gases. A feasibility implement has demonstrated that the sulfur dioxide can be captured economically from flue gas on a large scale [15].

In this paper, the key point of this work is the combination of an advanced modification of the extrusion process (rapid air cooling) of the extruded exit along with the addition of calcium carbonate of mineral filler. Micro-sized calcium carbonate is added at different concentration to polypropylene, in order to analyze the crystalline orientation, membrane morphology, thermal behavior, membrane permeability and mechanical properties of the precursor films, and evaluation of the influence of the cold and hot strain stages of MEAUS process on the permeability and mechanical properties of the membranes.

Materials

A commercial extrusion grade with tradename PP020 kindly supplied by Repsol S.A. has been selected with the melt flow rate (230 °C, 2.16 kg) was 1.0 dg·min^{-1}, Average number and mass molecular weights were M_n =119 kg·mol^{-1} and M_W = 659 kg·mol^{-1} respectively, showing a monomodal mass molecular weight distribution. As filler micro-sized (4□m average size) ultrafine surface-treated precipitated calcium carbonate (Reverté Calcium Carbonates) was added.

Experimental Procedure

**Figure 1:** Process outline for the compounding of polypropylene/filler blends.
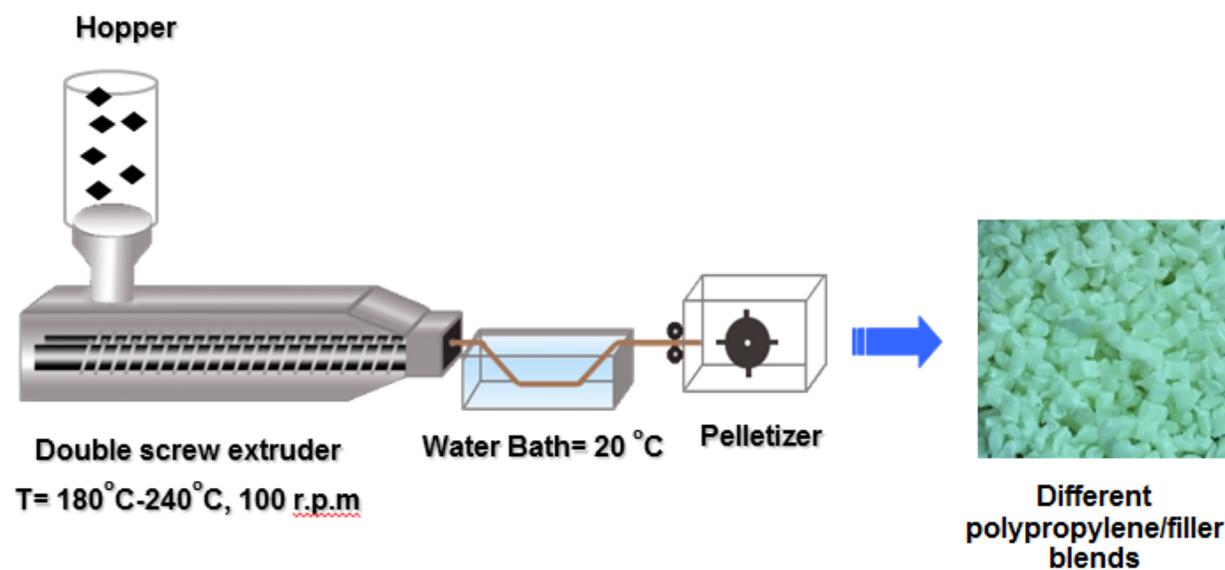
Film extrusion and precursor preparation: Polypropylene/calcium carbonate pellets (1, 5, 10 wt. % calcium carbonate) which are called C1, C5 and C10 were prepared by melt mixing using co-rotating twin-screw extruder (length/diameter = 36, diameter = 25 mm) (Figure 1), With these pellets, polypropylene-calcium carbonate films (1, 5, 10 wt. % calcium carbonate) were prepared at a constant rotating speed of 40 rpm and a die temperature of 240 ° C. At the end of the extruder, a rectangular cross-section die was adapted, with nominal dimensions 122 mm x 1.9 mm. A system of two air knives was mounted close to the die to provide air to the film surface right at the exit of the die and get a fast cooling. After the air knife, a three-calander system pulled the cooled film, providing a nominal draw ratio of 70 (Figure 2). The nominal thickness of the films ranged between 25-35 □m.

All the extruded films were annealed at three different temperatures 90, 115, 140 ℃ for 15 minutes in an oven. The uniaxial strain on these rectangular samples was performed in a universal testing machine *Galdabini Sun 2500*, dotted with a load cell of 1 kN and a climatic chamber.

Morphology: Scanning electron microscopy was employed (JEOL JSM-5610) for the analysis of the precursor pore structure. The precursors were previously gold-coated to ascertain electrical conductivity. The micrographs were analyzed through the software Buehler Omnimet. Values, pore size, and porous surface area were obtained, for calculation, a circular like porous geometry was employed.

Figure 2: Process of the precursor films production and adjustment of air-knives for obtaining different precursor films.
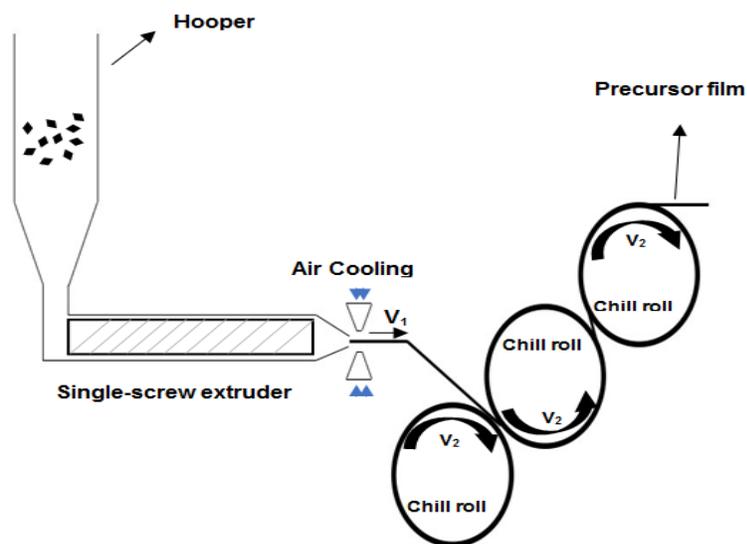
Mechanical Characterization of precursor films: The annealed polypropylene/calcium carbonate precursors (length: 65 mm; width 60 mm) were prepared, and then tensile measurements along extrusion machine direction were evaluated with a universal testing machine Galdabini Sun 2500. when the conditions were as follows: temperature, 23 ℃; and strain rate, 50 mm/min. Three measurements were done for each sample.

Results and Discussion

Precursor films morphology: During stretching, chains part converts to initial connecting bridges. This is similar to the melt of crystalline lamellae under tension followed by the re-crystallization into oriented fibrillar structure [16]. The connecting bridges enlargement process during stretching is proposed by Nilsson et al [17]. Based on the fact that some tie chains did not result from the chain entanglements, but the number of such species was small. The tie chains were concentrated mostly around the vicinity of the entanglement. During annealing, some chains around the initial lamellae are involved in the crystallization process. A typical folded chain lamellar assembly is shown where the frozen entanglement points are confined in the interlamellar amorphous region.

Caihong et al [18] established that, with an increase in annealing temperature, uniform connecting bridges and pore structure are obtained in the stretched microporous membrane. Results of Caihong [18] proved that, during annealing, the lamellar structure is improved due to the occurrence of melting and recrystallization behavior. During cold and hot stretching, the disappearing secondary crystals convert to initial connecting bridges and the improved

lamellar structure supports the scaffold of pore structure. Both cold and hot stretching lead to the best connecting bridge arrangement for the microporous membrane annealed. Annealing induces a difference of lamellar structure. The initial stable lamellae are improved; at the same time, some weak secondary crystals are induced.

With respect to the hot strain stage, Zuo et al. [19], reports that at high temperatures, the enhanced chain mobility can significantly weaken the amorphous entanglement network. As a result, the tensile deformation would lead to chain disentanglement, reducing the constraints for tie chains. These loosened tie chains convert to bridges when stretched. These connecting bridges result in the formation of the pore structure and they also contribute to the stabilization of pore structure compared with that only through stretching under room temperature.

A porous morphology was obtained for the different calcium carbonate-based compounds as a consequence of the final MEAUS stage, giving as result porous-based precursor. This final stage consists of a uniaxial stretching: cold strain (room temperature, 50 mm/min and 35% strain) (Figure 3). In this stage, it is expected that the lamellae of the row-lamellar structure are forced to get separated, and the length of the connecting bridges between lamellae is increased, leading to an increase of the pore size.

Figure 3: SEM micrographs of neat PP and PP/calcium carbonate precursor.
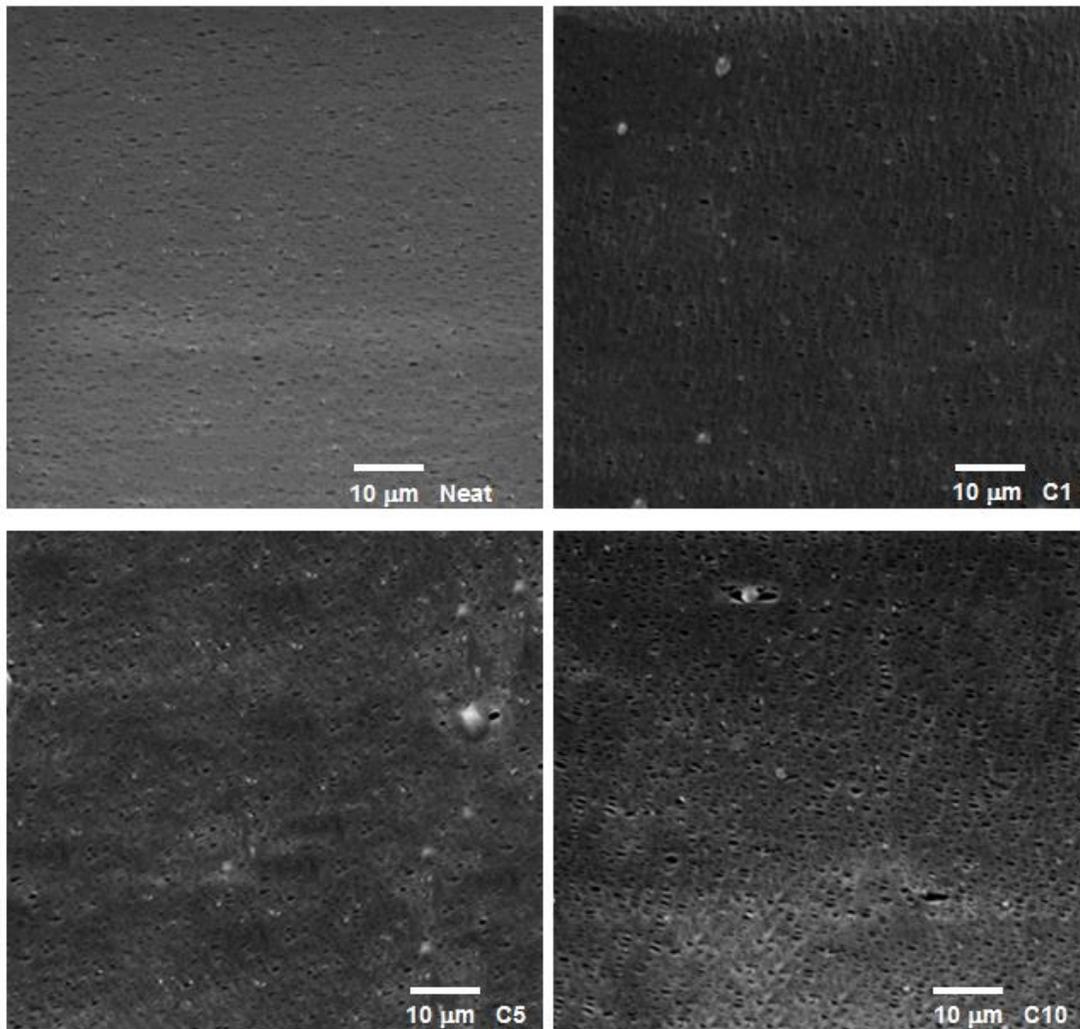
Tensile behavior: For all the samples, during the stretching of the film, a stress-withering phenomenon was observed [20], but no necking was observed, which is a typical behavior of a row nucleated structure two significant points were noticed (Figure 4), known as "first yield point" and "second yield point" [21]. At first yield point, fine chain slip is combined with a transformation a rearrangement within the lamellae being oriented in the stretching direction without breaking. Second yield point might be related to the deformation of the secondary crystalline lamellae. After yielding, the tensile curves presented an increase in the nominal stress with the beginning of the strain hardening.

The stress applied involved a pre-orientation of the amorphous tie chains prior to crystal chain unfolding, which can be related to the first yield point [22]. On the other hand, the strain hardening of the second yield point has been related to the deformation of the secondary crystalline lamellae (formed during the annealing process). Translating these terms into pore morphology, according to Samuels [23], the first and second yield points correspond to the beginning of macropore formation in the amorphous region and disruption of the lamellar structure, respectively, and the lamellae are stretched apart along the tensile direction between these two yield points [24]. It has also been reported the importance of the slope between the first yield point and second yield point. An increasing of this slope has been related [25] to more lamellar separation instead of interlamellar slippage during the stretching process.

Figure 4: Representative stress-strain curve showing 1st yield and 2nd yield point.
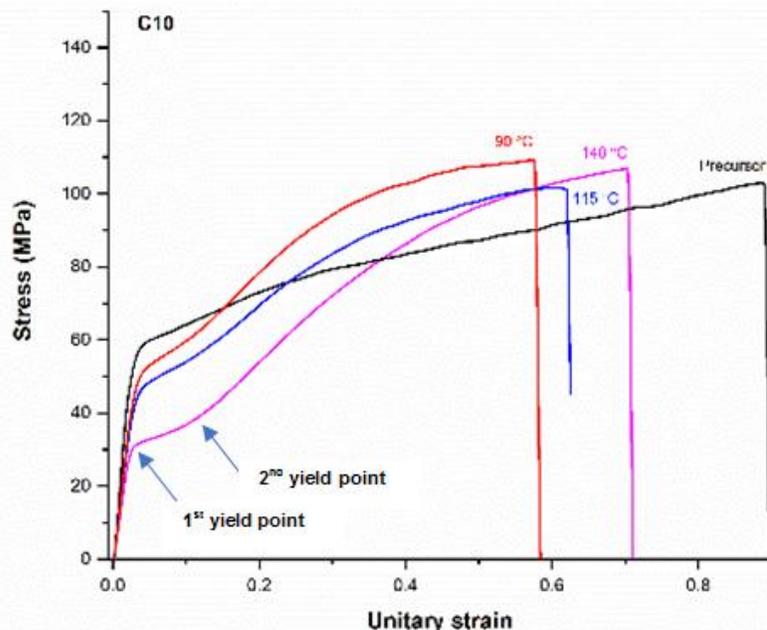
Effect of annealing temperature: As stated in previous sections, a study on the effect of annealing temperature was conducted for calcium carbonate/polypropylene compounds (Figure 5). It is seen that an increase in annealing temperature led, as a general trend, to a decrease in the values of the first yield point (Table 1). This trend is completely reverse to that observed for neat polypropylene for Saffar [21], but the trend is similar as observed by Caihong [26], also for neat polypropylene.

Figure 5: Effect of annealing on stress-strain curves for PP/calcium carbonate precursor films.
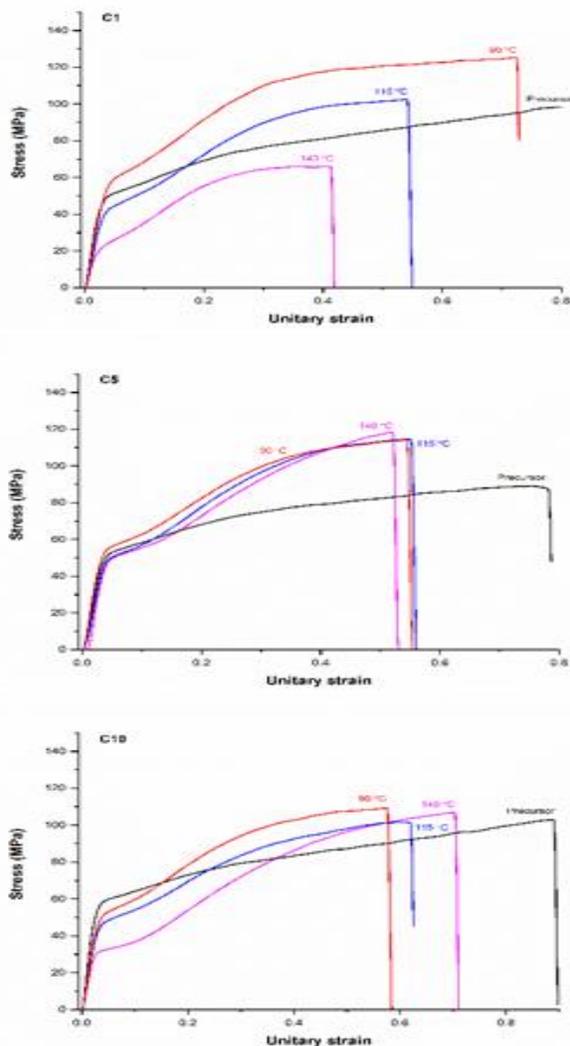

Based on the relationship between the mechanical properties and the fraction of the tie chains in the amorphous region proposed by Nitta and Takayanagi [27] the decrease of yielding point after annealing is related to the fact that some tie chains disappear during annealing. These tie chains during annealing crystallize [28]. The crystallization of these tie chains indicates the occurrence of secondary crystallization during annealing, similar to the conclusion drawn by others. With increasing annealing temperature from 90 °C to 140 °C, the decrease of the yielding point may indicate that more secondary crystals are formed. It can be seen, above all in 10 wt. % calcium carbonate samples that annealed polypropylene/calcium carbonate samples at different temperatures showed a higher slope between first and second yield point that the corresponding precursor film. It is also noticeable how the annealing temperature affects notably to the rigidness of the films (Table 1), as the show a remarkable decrease as the annealing temperature is increased in almost all cases. As annealing increases the size and number of lamellae, precursor films have a large elongation at break than annealed films.

Table 1: Elastic modulus and 1st yield point of the non-annealed and annealed precursor of PP/calcium carbonate.

	CaCO₃ wt. %	E (MPa)				1st Yield point (MPa)			
		Non-annealed. precursor film	Annealing temperature °C			Non-annealed. precursor film	Annealing temperature °C		
			90	115	140		90	115	140
Neat PP		1478			820	43			22
PP/Ca CO₃	1	1802	1645	1413	859	57	53	41	22
	5	1701	1588	1498	1076	51	45	46	41
	10	1733	1717	1224	1146	47	44	50	42

Effect of filler addition: Figures 6 show the comparison of annealed precursor films of neat polypropylene with the calcium carbonate/polypropylene compounds studied. Results of elastic modulus and first yield point are collected in Table 1 Here a combination of two effects is observed. Although first yield point of polypropylene has one of the lowest values of all the studied materials (which would help to have a first micropores creation), in all cases, the total elongation at break of neat polypropylene annealed precursor films is more restricted than in filled annealed precursor films. It suggests that the stage of stable pore growth is more enhanced when the filler is added to the polypropylene matrix, as stated by the values of pore density and porous area recorded for filled systems. No significant differences are found in the slope between the first and second yield point between filled and non-filled polypropylene.

Figure 6: Effect of filler content on stress-strain curves for filled PP annealed precursors with calcium carbonate.
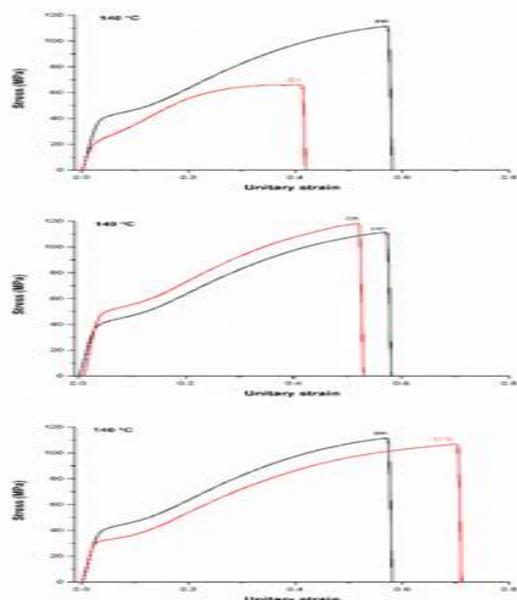
A logical pattern of increasing elastic modulus as filler content does is found in calcium carbonate compounds.

Conclusions

In this work, we studied the mechanical properties of calcium carbonate filled polypropylene microporous films. The different weight percentage of calcium carbonate was used for improving stiffness and mechanical properties. These were shown by tensile testing, Table 1 and Figure 5 and 6. Different tests with various temperatures were performed on different PP/CaCO$_3$ samples with a different weight percentage. Values of 1st yield point and elastic modulus were calculated. Table 1 listed the mechanical values of the filled annealed calcium carbonate films with different contents of calcium carbonate with strain rate (50 mm/min). With increasing the amount of calcium carbonate content to 10 wt. %, the mechanical values were improved than the neat PP film. There was a significant increase in the modulus, as we could predict, which might be because of the inclusion of fillers in the polypropylene matrix leads, which is around each particle, affected by a stress concentration. If these zones join together and form a percolation network, the distance between particles will small enough which increases the modulus.

Moreover, for constant filler loadings, the total volume affected is bigger and the distance between particles shorter if the particles are fine and well dispersed. Therefore, the percolation network develops more easily and the modulus increases. Figure 5 showed the stress-strain curves of the as-extruded PP/CaCO$_3$ precursor film and films annealed at 90, 115 and 140 °C temperature for 15 minutes. a great difference can be observed among these films as expected. Different from that of the as-extruded polypropylene precursor film, two distinct yield points can be seen in the stress-strain curves for the annealed films. The first yield stress and strain show decline, which it might be due to annealing temperature, while the second yield stress and strain keep increasing. Besides, the slope of the curves between the two points increases continuously. The first and second yield points correspond to the beginning of macropore formation in the amorphous region and disruption of the lamellar structure, respectively, and the lamellae are stretched apart along the tensile direction between these two yield points [32]. Thus, the results indicate that creation of micropores happens more easily in the amorphous phase while the ability of the lamellae to resist damage becomes stronger for the films annealed at higher temperatures.

It is reasonable because annealing leads to perfection of the lamellae as well as a decrease of the molecular chain entanglements in the amorphous phase. In addition to, in view of the increased slopes of the curves upon annealing, it suggests more lamellar separation instead of interlamellar slippage happens during the stretching process [28-32].

The mechanical test was performed on different PP/CaCO$_3$ annealed films with a different weight percentage of calcium carbonate (1, 5, 10 wt. %). It was shown that with an increase in calcium carbonate content up to 10 wt. %, the mechanical values were improved than that the neat polypropylene film. There is a significant increase in the modulus, which might be because of the inclusion of fillers in the polypropylene matrix leads which is around each particle, affected by a stress concentration. According to the mechanical results, it seems reasonable that creation of micropores, happens more easily in the amorphous phase, because annealing leads to perfection of the lamellae as well as a decrease of the molecular chain entanglements in the amorphous phase, while the ability of the lamellae to resist damage becomes stronger for the films annealed at higher temperatures. Additionally, as a result of the increased slopes of the curves upon annealing, it suggests during the stretching process, more lamellar separation instead of interlamellar slippage happens.

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