Influence of length branches in PE copolymer nanocomposites by in-situ polymerization

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Introduction

Copolymerization of ethylene with small hydrocarbon chains, as hexene, is performed using catalyst Ziegler-Natta or metallocene. Ziegler catalyst has a dominant position in the market, but it has the disadvantage of producing copolymers with inhomogeneous branching distribution in his structure, reducing the mechanical properties. However, metallocene catalyst has unique active site, allowing synthesize polymers with a narrow molecular weight distribution and with homogeneous branching distributions. This advantage it has allowed in recent years the growth in the use of metallocene catalyst for ethylene copolymer synthesis.[1]

The present study use the sepiolite as filler and support for catalyst system, this fact has effect in the final polymer structure. Consequently this method has many variables to study, because type and distribution of the branches have an important effect in nanocomposite properties.[2]

This work was designed to study the influence of the length of branches on the final properties of the co-polymer. Three different co-monomers (hexene, octene and decene) with equal concentration of sepiolite and comonomer were studied.

Experimental

Clay pretreatment, polymerization, preparation of test specimens and characterization

Desired amount of dry sepiolite (SEP) was mixed with co-catalyst in different ratio (ml of methylaluminoxane, MAO, solution g^{-1} clay) in 100 ml of dry toluene and afterwards the mixed was stirred for 90 minutes at room temperature, following the procedure explained in our previous work based on optimizing the process of immobilization of the MAO into sepiolite surface.[3] Ethylene polymerizations were carried out in a 1 liter stainless steel autoclave equipped with a mechanical stirrer under the conditions explained in the patent WO2013-167764A1 with 0.1M of comonomer.[4] Finally, the samples were mould in vacuum press and there were cut according to the requirements for each test characterization

Results and discussion

Table 1 shows the thermal and morphological properties of the different copolymer synthesized, and Figure 1 shows the elongation at break of neat PE copolymers and their corresponding sepiolite nanocomposites.

Table 1. Thermal and morphological properties of obtained copolymer

Sample[a]	T_m (ºC)	T_c (ºC)	ΔH_m (J/g)	X (%)	% Clay	% molar co-monomer	Productivity	Mw (g/mol)	P.I.
PE	139.8	108.0	284	96.9	-	0.00	$8.51 \times 10^3 \pm 4 \times 10^2$	1.6×10^5	3.84
CoH0.10PE	126.4	105.1	229	85.8	-	1.54	$9.73 \times 10^3 \pm 2 \times 10^2$	8.6×10^3	3.95
CoO0.10PE	118.5	102.7	183	65.7	-	1.35	$1.58 \times 10^4 \pm 8 \times 10^2$	9.0×10^3	4.30
CoD0.10PE	112.9	102.1	175	62.1	-	0.98	$1.79 \times 10^4 \pm 5 \times 10^2$	9.0×10^3	4.75
N2PE	144.1	180.8	254	92.1	3.5 ± 0.7	0.00	$9.12 \times 10^3 \pm 6 \times 10^3$	1.9×10^5	3.20
N2CoH0.10PE	128.3	105.5	187	67.6	3.0 ± 0.4	2.25	$1.44 \times 10^4 \pm 9 \times 10^2$	6.5×10^4	3.44
N2CoO0.10PE	125.6	104.8	174	61.5	2.5 ± 0.2	1.97	$2.19 \times 10^4 \pm 1 \times 10^3$	1.5×10^4	3.67
N2CoD0.10PE	116.5	105.4	171	57.8	1.3 ± 0.4	1.98	$2.08 \times 10^4 \pm 3 \times 10^2$	5.4×10^3	3.89

[a] Nomenclature: PE: polyethylene matrix, CoH: hexane copolymer, CoO: octene copolymer, CoD: decene copolymer, 0.10: molar% of comonomer, N2: nanocomposite obtained with 2 g of initial clay.
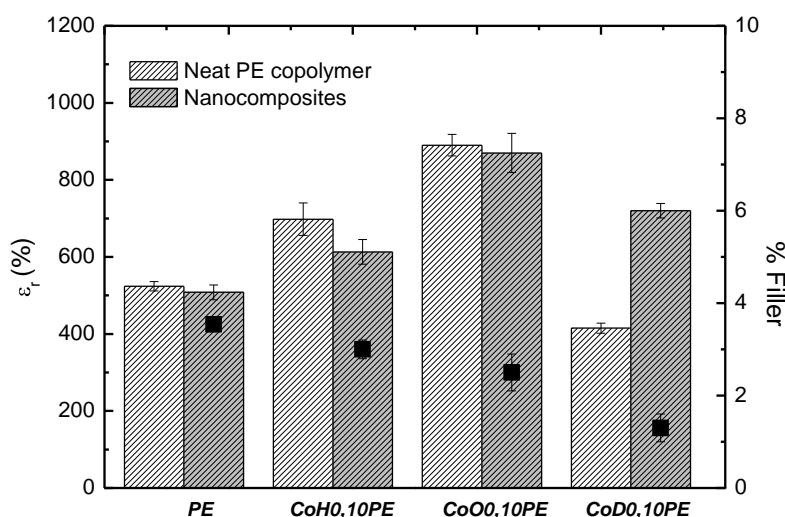
Figure 1. Elongation at break of the copolymers and their nanocomposites obtained.

Conclusion

PE copolymers loaded with sepiolite have been successfully prepared. The neat co-polymers and their nanocomposites have been characterized in thermal behavior and mechanical test. The versatility of the method allows manufacturing from ultra high molecular weight polyethylene up "thermoplastic rubbers". All of them with the advantage that produces a nanofiller presence in the structure: mechanical properties, barrier, thermal stability, flame retardancy and abrasion resistance.

References

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