The Effect of γ-Irradiation and Reactive Extrusion on the Structure and Properties of Polycarbonate and Starch Blends: A Work Oriented to the Recycling of Thermoplastic Wastes

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ABSTRACT: Polymer materials with improved properties can be obtained through polymer blends. As a polymer mixture is generally immiscible and incompatible, it is necessary to develop new methods to improve the interfacial adhesion. In this study, polycarbonate-based extruded thermoplastic were developed by blending polycarbonate with thermoplastic starch using extensive process engineering based on structure–property correlations. Starch was destructurized and plasticized followed by melt-blending with polycarbonate. The optimal conditions for processing of the thermoplastics blends were found to be 230°C, 2 min of processing time, and 3–6 wt % of glycerol. The effect of γ-irradiation on the fabrication of the blend was studied. Changes in structure, morphology, and properties resulting from γ-exposure in the range 0–150 kGy were investigated. Electron spin resonance results revealed that numerous radicals remained trapped in the materials after irradiation even after a long time enabling reactions between starch and polycarbonate. Results obtained from tensile test, differential scanning calorimetry, and dynamic mechanical analysis revealed the relatively good affinity between the two components after blending in a micro-extruder. Irradiated blends are thermally more stable than those non-irradiated. Mechanical tests also showed that the efficiency of the irradiation depended greatly on the dose applied to the initial materials. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Thermoplastics materials have become an integral part of our life. As it known, these materials have many applications in different industrial as well as domestic area. Many plastics materials, after being used, are still discarded in the landfill together with solid waste, generating a large amount of waste which exceeds the capacity of the deposits in the landfill.

The blending of biodegradable polymers, such as starch, with polymer engineering has received considerable attention. The reasoning behind this approach is that if the biodegradable component is present in sufficient amounts and if it is removed by microorganisms in the waste disposal environment, the plastic or film containing the remaining polymer engineering should disintegrate and disappear.

During the last five decades, study of polymer blends has become a special field of research on polymer materials with the aim of recycling with new properties.[1] Blending of immiscible polymers offers attractive opportunities for developing new materials with useful combinations of properties.[2] A good

balance between properties and processability which allows reuse and upgrading is absolutely necessary in a recycled material. In addition to the academic interest in this system, there exists an industrial interest[3,4]; however, simple blends promote the desegregation of phases; they are also responsible for high interfacial tension, poor adhesion between the phases with poor mechanical properties and unstable morphologies.[5–8] Compatibilization of such blends is necessary.

Polycarbonate has a distinguished role in this context, because it is extensively used in engineering applications, which is due to its relatively high toughness under certain conditions and excellent chemical resistance.[9] However, disposal of used plastic products has become a public concern because of their non-biodegradability.[10–12] At the beginning of the 21st century, plastics were a leading material, providing uncountable useful and inexpensive items for modern life. Some attention to the emergence of bioplastics, a new generation of biodegradable plastics whose components are derived entirely or almost entirely from renewable raw materials is requested. They conserve irreplaceable fossil fuels, contribute little to the already burdensome problems of

waste management, and help prepare us for the time when fossil fuels become exhausted. Usually these polymers are used or recycled in blends. For this reason, it is important to find experimental conditions for mixing different polymers engineering and naturals without losing mechanical properties.

There is more carbohydrate on earth than all other organic material combined. Polysaccharides are the most abundant type of carbohydrate and make up ∼ 75% of all organic matter.[13] Starch is a very abundant biopolymer, utilized by plants as the major storage material for carbohydrates.[14] Starch can also be plasticized with organic plasticizers such as glycol, glycerol, sorbitol, or urea in order to obtain thermoplastic behavior.[15–17] Under the action of thermomechanical energy, the starch granule containing a plasticizing agent will melt at low temperature and at very low water content. Ayoub et al.[16] dealt with plasticizing starch at low water content (microhydric conditions). The major drawback of using thermoplastic starch-based polymers to produce the new generation of plastics is their hydrophilic characteristic and their poor mechanical properties.[17,18]

One of an alternative method for blending is to generate some copolymers *in situ* during the blend preparation through polymer–polymer grafting reactions using functionalized polymers.[19] However, it is often difficult to produce suitable graft or block copolymers for important commercial applications. Irradiation of polymer materials generates some effects depending on the kind of polymer, as well as on the parameters of irradiation and the state of the material under processing.[8,20–22] The two main reactions which determine the final properties of the polymer include (a) scission of main chain and (b) crosslinking. The yield of scission and crosslinking, or more precisely the mutual ratio of these two parameters, is key parameters for the outcome. To achieve the desired objective, irradiation of polymer material can be conducted under special conditions. Some studies[23–25] demonstrated a good enhancement in the final properties of the blends after γ-irradiation exposure. In our research group, after having studied blends of polystyrene and polycarbonate before and after irradiation, we thought that the use of starch and polycarbonate systems with similar radiation sources would help to improve the compatibility and hence the mechanical properties between thermoplastic starches (TS) and polycarbonate. In this work, we report the use of γ-irradiation and reactive extrusion as extensive process engineering to obtain TS/polycarbonate (PC) blends.

In this article, we have studied the influence of the processing on the efficiency of γ- irradiation to compatiblize different blends under molten state. Irradiation was applied on the pellets before injection molding. A variety of techniques have been used to identify the behavior of blends versus the irradiation to verify the changes that take place in the polymer structure, e.g., thermal analysis technique and mechanical properties. The reactions were carried out in a bench top twin-screw micro-compounder. This technique was chosen for its simplicity. This compound was transformed in the reactor under controlled thermomechanical conditions. The results presented in this article deal with irradiated modified polymers prepared according to this process. In addition, this work is aimed at recycling domestic thermoplastic wastes in the world. This study was firstly carried on blends prepared from virgin raw materials, which can be considered a model of thermoplastic wastes. However, the blends of recycled polymer engineering as PC with starch should have two environmental advantages: (a) to substitute the virgin synthetic thermoplastic matrix by post-consumer materials and (b) the end product would be biodegradable and cheap.

MATERIALS AND METHODS

Materials
PC was provided by DSM Engineering Plastics Europe (The Netherlands) coming from electrical and electronic equipment. PC was characterized and the obtained results for melt flow index (MFI), density, and Vicat softening temperature (VST) were as follows: For polycarbonate: MFI (230°C/5 kg) = 6.06; density = 1.2 g/cm^3; VST = 139.2°C; melting point = 225°C; molecular weight = 254.3 g/mol. Native corn starch (10.3% moisture) was provided by Roquette Frères, Lestrem (France). Glycerol was purchased from Sigma-Aldrich (L'Isle d'Abeau Chesnes, France). Non-treated hemp fibers were offered by la Chanvrière de l'Aube (France).

Reactor
The reactor (Figure 1) is a device designed for compounding and analyzing the rheological behavior of polymers on a 15 g-capacity DSM micro-extruder (Midi 2000 Heerlen, The Netherlands). It consists of a sealed body containing two corotating conical screws. The system is fed once by compacting the mix loaded in a compartment with a piston at the beginning of the cycle. The system's temperature is regulated by electric resistors and air flow. Via an integrated back flow channel, the filled-in mix can be reintroduced in the system, upstream in a loop. A pneumatically controlled bypass flushes the sample to the air through a die at the end of the cycle after a chosen reaction time. The measurement of the motor torque and pressure from the sensors in the loop channel allow the monitoring of the sample's rheological behavior.

Blends and Sample Preparation
The plasticizer is adsorbed to the starch by a mixture of glycerol (30 wt %) and starch for 15 min prior to adding the PC (Figure 2). The optimal conditions for processing of the thermoplastics blends were found to be 220°C; 2 min of processing time to prevent the thermal degradation (five tests were done under different time conditions from 1 to 5 min), the rotational speed of the screws was kept constant at 200 rpm during all the extrusion cycle and injected in a 100-cm^3 mold at 90°C to obtain dumbbell-shaped specimens. This process was repeated six times under the same operating conditions.

Different formulations of irradiated and non-irradiated PC pellets and TS were prepared (Table I). The blends contain up to 20 wt % plasticized starch. One experiment was attempted with 30 wt % TS and 70 wt % PC but the blending proved to be difficult because the melt was too sticky to be injected. Samples were taken in every extrusion cycle to evaluate the mechanical properties, perform differential scanning calorimetry (DSC) and thermogravimetry (TGA) tests. For molded pieces prepared from irradiated pellets, the time between irradiation and injection-molding was up to 2 weeks.
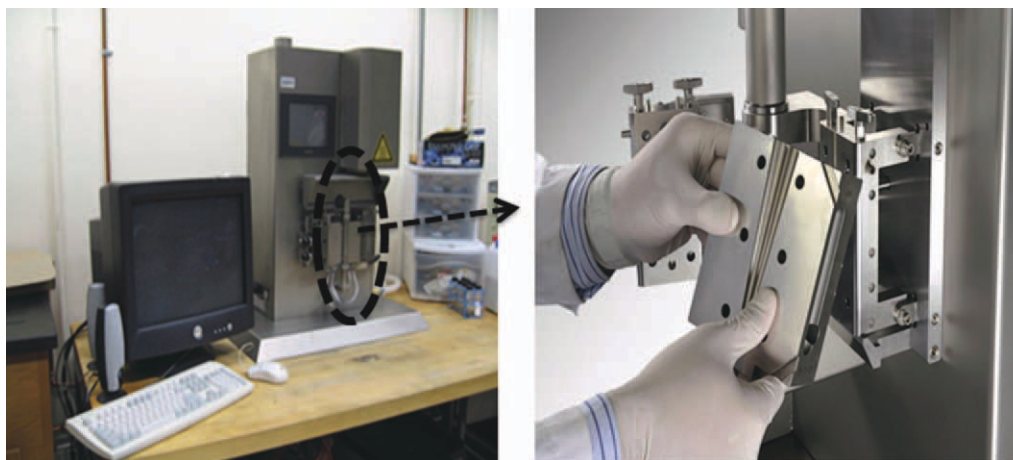
Figure 1. 15-g capacity DSM micro-extruder (Midi 2000 Herlen, The Netherlands). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

γ-Irradiation

Irradiation was performed by Ionisos SA (France), on the pellets and native starch, using a 2×10^6 Ci ^{60}Co source, under air atmosphere and at ambient temperature. Irradiation dose was controlled with a precision of $\pm 15\%$ for minimum dose and $\pm 5\%$ for maximum dose. The samples were stored in a refrigerator to prevent the recombination of the free radicals before been used. The total number of spins per gram was not changed the first two weeks after irradiation. Dose rate was 2 kGy/h. Final doses ranged from 50 to 150 kGy. Irradiated materials were then stored in a refrigerator to prevent the recombination of the free radicals. γ-irradiation is a very penetrating radiation, which is why no difference should be expected for different thicknesses of samples.[25] This process was repeated three times under the same operating conditions.

For polycarbonate pellet and native starch powder, electron spin resonance (ESR) spectra were recorded using a Bruker Elexsys e500 X-Band (9.4 GHz) spectrometer with a standard cavity, at room temperature.

Differential Scanning Calorimetry Measurements

The first characterization technique consisted in the determination of the thermal transitions such as glass transition temperature (T_g) for non-irradiated samples and for each set of irradia-

tion conditions. This was accomplished using DSC. The instrument used to conduct these evaluations was a TA Q10 DSC. Samples were prepared by slicing sections of unstressed tensile samples used in the tensile tests. The samples measured approximately 3 mm $\times$ 3 mm $\times$ 1 mm thick. The mass of each sample was about 6 mg. Samples were heated at a rate of 10°C/min under nitrogen to 200°C. The T_g for each sample was determined at the second heating ramp by the midpoint data of the endothermic changes associated with the glass transition.

Thermogravimetric Analysis Measurements

TGA was carried out using a TGA Q500 instrument. The heating was carried out at a temperature range from room temperature to 350°C at heating rate of 10°C/min under nitrogen gas atmosphere.

Table I. Proportions Tested for the Blends with Irradiated and Non-Irradiated Pellets

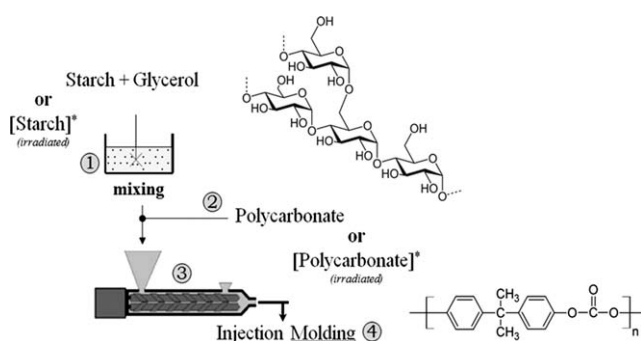| Dose (kGy)	Formulation	Blends proportions (wt %)	
		TS	PC
0	F_1	0	100
	F_2	100	0
	F_3	5	95
	F_4	10	90
	F_5	20	80
50	F_6	0	100
	F_7	100	0
	F_8	5	95
	F_9	10	90
	F_{10}	20	80
100	F_{11}	0	100
	F_{12}	100	0
	F_{13}	5	95
	F_{14}	10	90
	F_{15}	20	80

Figure 2. Schematic of the processing steps from starch plasticizing to injection molding: (1) mechanical mixing; (2) blending; (3) molten medium; (4) screening experiments.
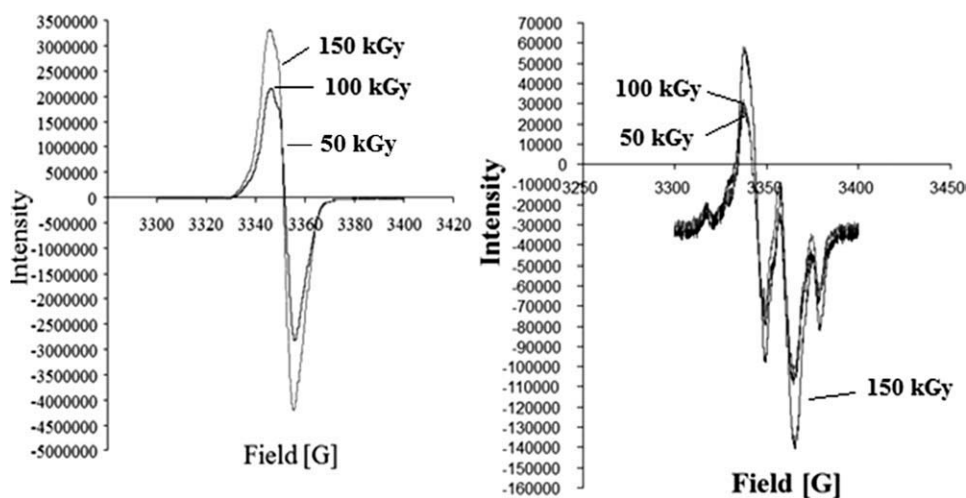
Figure 3. ESR spectra of polycarbonate (on the left) and starch (on the right) irradiated at different doses.

Dynamic Mechanical Analysis

The Rheometric Scientific ARES is a mechanical spectrometer capable of subjecting a sample to a dynamic shear strain (deformation), then measuring viscoelastic properties in the melt and solid state. Loss tangent δ (tan δ) was evaluated through this test. The samples cut from the dumbbell-shaped specimens were subjected to sinusoidal strain in the torsion mode. The temperature sweep experiments were carried out with 3% strain at a frequency of 6.28 Hz. The temperature was increased at the rate of 10°C/min. Samples were conducted at temperature between 20°C and melting point.

Microscopy

The changes in morphology were visualized using scanning electron microscopy (SEM).[26] A Philips XL 20 microscope was used. Before examination, the samples were first microtomed at −150°C using a hammer. Subsequently, the phase was covered with a thin gold layer.

A starch phase etching was also realized on the blend samples in hot water for 6–7 h to reveal the morphology resulting from the interactions between polycarbonate and plasticized starch. This process caused at least the extraction of the starch phase on the surface to be observed. The samples were weighted before and after extraction to determine whether the loss of material did exist. After 7 h in several water baths, the total mass loss corresponded to 10% of the initial weight which is supposed to be sufficient to experiment starch extraction at the surface.

Mechanical Testing

Mechanical properties were determined by means of a universal tensile test machine from Inströn.[27] Five individual dumbbell-shaped specimens were tested for each sample. The values were determined at a crosshead speed of 5 mm/min.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) experiments are carried out on a Bruker Avance II 250 spectrometer operating at 250.13 MHz for ^{1}H and 62.90 MHz for ^{13}C. Liquid NMR spectra are recorded with a 5 mm QNP probe head at room temperature. About 10–15% (w/v) solutions in dimethyl sulfoxide (DMSO) or CDCl$_3$/

DMSO 80 wt %/20 wt % were used as solvent for the samples preparation.

To study the chemical modifications operated on blends, a selective solubilization was first realized to extract the PC phase of the sample and only the starch and eventually the copolymer phase remained trapped in the product.

RESULTS AND DISCUSSION

Irradiation of Polycarbonate and Starch: Production of Free Radicals

In the present investigation, γ-irradiation was the source for free radicals. ESR measurements confirm that the trapped radicals are still present in the irradiated materials (Figure 3). Even 2 weeks after irradiation, radicals are still detected in irradiated polycarbonate pellets and starch powder, probably thanks to the storage in a refrigerator at −20°C.

The irradiation dose has a great influence on the concentration of radicals. The radicals produced initiate further reactions in the molten medium such as crosslinking as proved from the mechanical and thermal properties.

Thermal Properties Analysis

Numerous studies about the thermal properties of starch have revealed that the determination of its glass transition temperature (T_g) was not trivial and no one can establish accurate values of this property. Yu and Christie[28] worked on the importance of the speed ramp, sample preparation, and type of pan used for the test. Many authors reported that the starch thermal transition is usually very difficult to determine because the associated change in heat capacity is weak.[29] The slope obtained in our case is of 0.08 J/g°C. All the samples displayed a unique glass transition temperature, which is shifted to lower values with an increasing amount of plasticized starch incorporated in the formulation (Table II). This observation could indicate the presence of adequate interfacial interaction between the two polymers, suggesting little, if any, separation phase. Though, a single T_g is a necessary but not sufficient condition for a compatible blend. After γ-exposure and under molten medium condition, the loss on the T_g confirms the hypothesis concerning the improvement of

Table II. Evolution of T_g with an Increasing Amount of Plasticized Starch in the Blends Before and After Irradiation

Dose (kGy)	Formulation	Blends proportions (wt %)		T_g (°C)
		TS	PC	
0	F_1	0	100	145
	F_2	100	0	124
	F_3	5	95	143
	F_4	10	90	138
	F_5	20	80	136
50	F_6	0	100	142
	F_7	100	0	102
	F_8	5	95	142
	F_9	10	90	140
	F_{10}	20	80	138
100	F_{11}	0	100	143
	F_{12}	100	0	82
	F_{13}	5	95	141
	F_{14}	10	90	138
	F_{15}	20	80	136

Table III. Evolution of Mass Loss (%) with an Increasing Amount of Plasticized Starch in the Blends Before and After Irradiation

Dose (kGy)	Formulation	Blends proportions (wt %)		Total mass loss (%)
		TS	PC	
0	F_1	0	100	0.45
	F_2	100	0	85.0
	F_3	5	95	3.70
	F_4	10	90	7.00
	F_5	20	80	15.0
50	F_6	0	100	0.40
	F_7	100	0	55.0
	F_8	5	95	0.80
	F_9	10	90	1.00
	F_{10}	20	80	5.00
100	F_{11}	0	100	0.43
	F_{12}	100	0	53.00
	F_{13}	5	95	0.50
	F_{14}	10	90	1.30
	F_{15}	20	80	6.20

the adhesion between the components as shown in Table II. The comparison of the experimental values for a typical experiment (dose: 50 kGy, PC: 90 wt %, TS: 10 wt %) with theoretical predicting glass transitions in miscible binary blends shows a match with Gordon–Taylor's theory[30] (Figure 4) and proves the affinity existing between polycarbonate and thermoplastic starch. Irradiated plasticized starch endotherm showed a T_g at 102°C, while at 124°C when non-irradiated. This result indicates that starch undergoes chain degradation under irradiation probably resulting in a lower molecular mass.

Thermal Stability

This piece of work was performed in order to determine whether the addition of thermoplastic starch to the polycarbonate formulation would induce a loss in the thermal stability of the sample. Natural polymers are characterized by an important thermal deg-
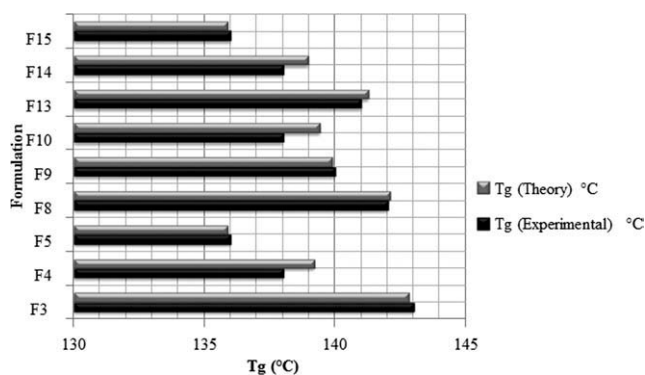
radation and are thus limited in their applications. Moreover, the aim was also to identify the behavior of glycerol under our optimal processing conditions since the boiling point of glycerol is at about 290°C but it can undergo degradation beyond 170°C.

From the TGA data of non-irradiated and irradiated formulation, presented in Table III, weight losses are reported. The polycarbonate showed a high stability when heated to elevated temperatures with an overall weight loss corresponding to 0.45%. Native corn starch, on the other hand, tends to degrade up to 80% above 300°C. When blend F_4 is considered, the total mass loss is less important. This result was expected as polycarbonate is predominant in the formulation. The most relevant degradation occurs after 300°C and corresponds to the

Table IV. Evolution of tan δ with the Irradiation Dose

Dose (kGy)	Formulation	Blends proportions (wt %)		tan δ peak (°C)
		TS	PC	
0	F_1	0	100	151
	F_4	10	90	140
	F_5	20	80	128
50	F_6	0	100	144
	F_9	10	90	142
	F_{10}	20	80	142
100	F_{11}	0	100	145
	F_{14}	10	90	141
	F_{15}	20	80	135

Figure 4. Comparison of experimental T_g with theoretical predictions of glass transition in miscible binary blends.
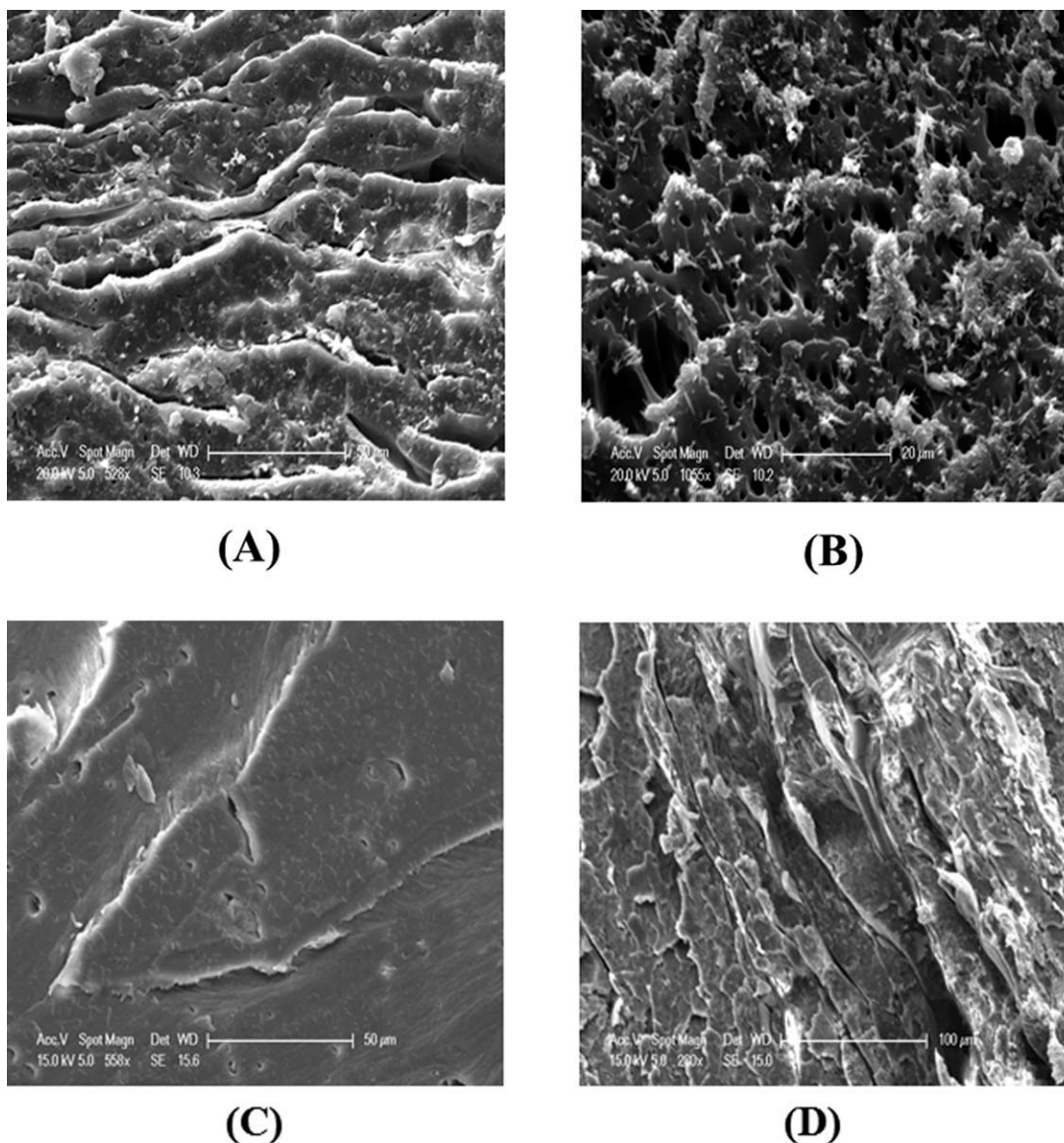
Figure 5. (A) Morphology of boiled [80%PC+20%TS] sample observed on the edges, scale 50 μm; (B) morphology of boiled [80%PC+20%TS] sample observed at the center, scale 20 μm; (C) irradiated (80%PC+20%TS) sample, 50 kGy, scale 50 μm; (D) irradiated [80%PC+20%TS] sample, 100 kGy, scale 100 μm.

alteration of amylose contained in starch. The total loss observed was 7% and we can assume that the association between PC and starch enhances the thermal stability of the second. The temperature of the most apparent degradation is also shifted toward higher values. However, the effect of irradiation on the thermal stability of this blend appears to be remarkable as the overall mass loss is about 1% of the initial weight instead of 7% without irradiation. γ-irradiation has thereby a positive effect on the adhesion between the components related to the general decrease of the degradation experimented herein.

As for the degradation of glycerol, the experiment showed that it is totally annihilated after 20 min at 230°C which corresponds to the extrusion temperature condition. This thermogravimetic curve gives indication on the admissible residence time in the twin-screw extruder.

Viscoelastic Behavior

Table IV shows the variation of tan δ for control, unirradiated, and irradiated blends. The results reveal the presence of a single major relaxation correlated to the T_g of the samples. With an increasing amount of plasticized starch in the samples, the T_g of the blend is shifted toward lower temperature. When initial materials are irradiated, the dynamic mechanical analysis reveals the preservation of the thermal properties. We can notice a slight increase of the T_g for irradiated materials. The evolution of the glass transition temperature is more obvious in this case and the 50 kGy irradiated sample presents the higher T_g among all the conditions tested. From these results, we can assume that the effective physical modification induced by irradiation enables to improve the adhesion inside the blends. This improvement is due to the recombination of the free radicals created during the irradiation.
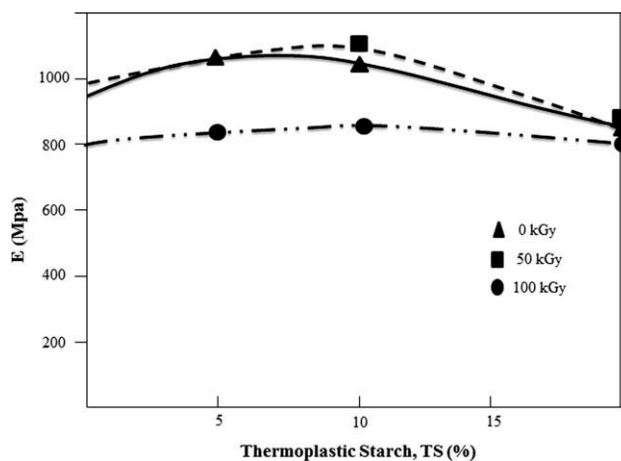
Figure 6. Effect of irradiation on the variation of young's modulus for different amount of starch contained in the blends.

Blends Morphology

The cryogenic fracture surface morphology of the blends was observed with the scanning electron microscope to study the nature of the interface between the polymers. Blends made of
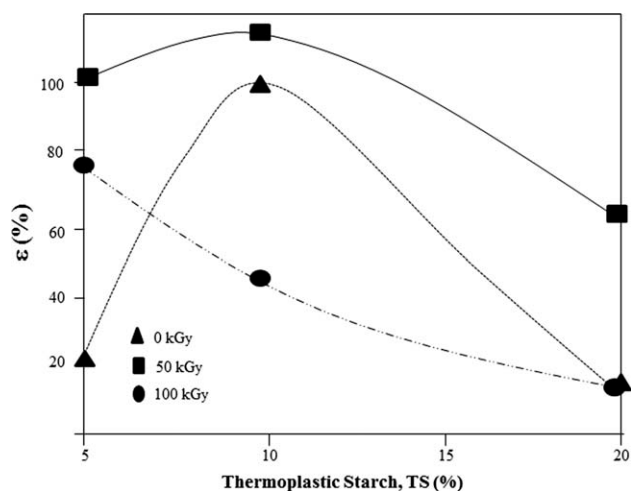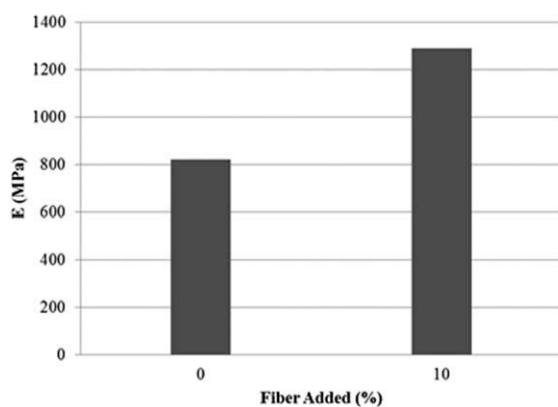

Figure 7. Evolution of elongation at break with varying irradiation dose as a function of plasticized starch added.

(80% PC+20% TS) showed a fluid orientation at the sample edges probably due to the speed gradient existing during the injection-molding process. The morphology reveals a co continuous structure. When we consider the center of the fractured dumbbell-shaped specimens, a nodular morphology is encountered with inclusions of starch in the polycarbonate matrix. After the starch phase extraction, holes of varying sizes can be observed. Their size can be evaluated at 20 μm approximately [Figure 5].

As for the blend made of (90% PC+10%TS), the general structure is quite similar to that of (80% PC+20% TS). The affinity between the two polymers is a consequence of their "polarity" and especially their interfacial tensions that are supposed to be close. Lu and Tighzert have reported monophasic morphology for some specific proportions of PU/starch blends.[31]

After irradiation, the overall morphology of the blend (80% PC+20 % TS) seems to be more homogeneous and presents a unique phase [Figure 5]. The images show a real compatibility between the two components as it was really hard to distinguish one from another.

Tensile Strength

The effect of irradiation on the mechanical properties was also investigated through this test.

A very little increase of Young's modulus can be observed for the samples irradiated at a 50 kGy dose. As for the 100 kGy dose, the exposure seems too drastic and tends to degrade the materials (Figure 6). The evolution of the elongation at break (Figure 7) with varying irradiation dose indicates that an intermediate dose will be preferred to enhance the adhesion of the species.

Best blends were obtained for the composition (90%PC+10%TS) irradiated at 50 kGy. Natural fibers have further been added to the formulation to study their efficiency as a reinforcing technique for the blends. The tensile results indicate an improvement of 40% on the Young's modulus even without any surface modification of the fibers, correlated to a decrease of the elongation at break (Figure 8).

Nuclear Magnetic Resonance Spectroscopy

The polycarbonates were analyzed by NMR spectroscopy to elucidate their chemical structure and to support the expected
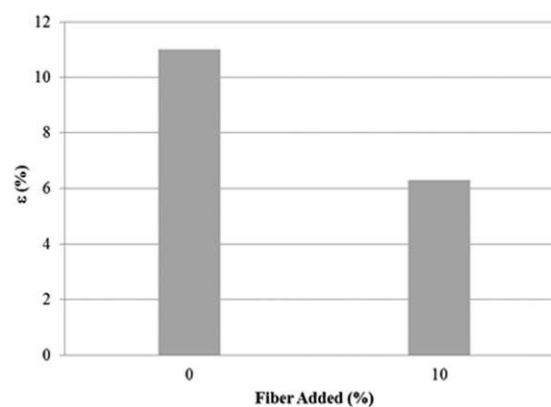

Figure 8. Improvement on the tensile strength and elongation at break with addition of natural fibers in the formulation (80% PC/20% Starch).
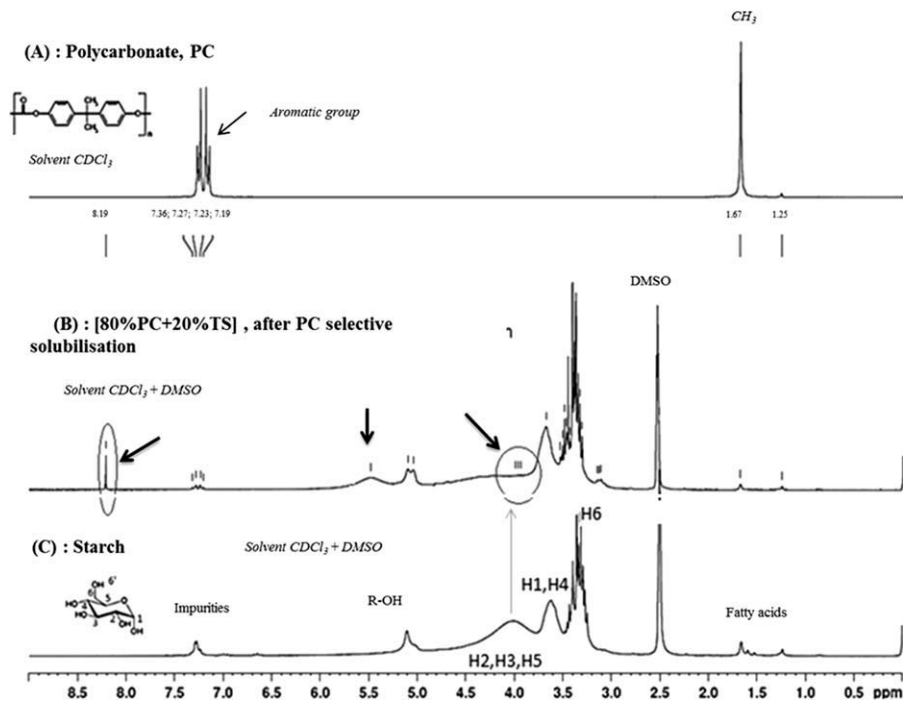
Figure 9. Comparison of NMR spectra for non-irradiated materials and 80%PC + 20% TS.

reaction. ^{1}H-NMR spectra can be used to obtain more direct evidence for any reaction between PC and TS in molten medium, as shown in Figure 9, along with peak assignments.

There were typical chemical shifts of starch and PC segments. In addition, two new peaks appeared in the spectra.

These results can be explained by the formation of copolymers in the transesterification of PC/TS blends. The new peaks may correspond to those of copolyesters formed in the reactions. Transesterification reaction is possible between the polycarbonate ester groups and reactive alcohols from polyols, especially at 220°C. Moad[32] has shown this type of reaction was possible even without catalyst and was highly dependent on the reactivity of the species involved and may lead to increase in miscibility between polymers.

CONCLUSIONS

The article describes the mechanical and thermal behavior of an immiscible binary blend of the polycarbonate and thermoplastic starch through the γ-irradiation and reactive extrusion.

On the basis of the obtained results the following conclusions were drawn:

(a) When irradiation is performed and is followed by extrusion in molten medium, the free radicals could react: the effect of irradiation is enhanced and lower irradiation times are sufficient. The process is more cost-efficient.

(b) Numerous radicals created by irradiation could react and enhance the modification of structure if a new processing step is performed. The crosslinking by combination of two macroradicals is an intermolecular reaction which depends on radical mobility. Irradiation could lead to a new material in the point of view of the structure and mechanical behavior.

(c) The lack of miscibility will be observed both by the presence of two different T_g and lower mechanical properties. The good miscibility of the polymer is demonstrated through the creation of a unique glass transition temperature when polymers are melt-mixed (both observed with the DSC and DMA) and through a homogeneous dispersed morphology as shown by SEM images. Including natural fibers in the formulation enables to increase the tensile strength of 40%.

(d) The NMR experience revealed that a trans-esterification reaction could have occurred during the process and would have been the result of the contact between ester groups of polycarbonate and reactive alcohols of starch.

(e) It is possible to conclude the extrusion; injection molding processes and γ-irradiation are effective enough to obtain homogenous blends since heating processes ensure good mixing conditions and final macroscopic homogeneity.

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