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ORIGINAL PAPER

Synthesis and characterization of novel comb-type amphiphilic graft copolymers containing polypropylene and polyethylene glycol

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Abstract Amphiphilic comb-type graft copolymers containing polypropylene (PP) and polyethylene glycol (PEG) have been prepared. Polypropylene-*g*-polyethylene glycol comb-type thermoplastic amphiphilic copolymers were synthesized by the reaction between chlorinated polypropylene and polyethylene glycol in the presence of a base via a "grafting to" technique. A series of graft copolymers containing PEGs with molecular weights of 600 and 2,000 Da in the range of 4–34 mol% PEG were obtained. The amphiphilic graft copolymers with PEG segments in range between 20 and 30 mol% PEG displayed good film properties with elongation at break 275–440%. The hydrophilicity of the amphiphilic copolymers increases with the increasing PEG content in the copolymer while the mechanical properties decrease. Therefore, PP-*g*-PEG2000 with PEG contents in the range of 20–30 mol% PEG should be useful for medical and industrial applications where good film properties are needed.

Keywords Amphiphilic polymer · Comb-type graft copolymer · Polypropylene · Polyethylene glycol

Introduction

Amphiphilic block copolymers containing hydrophobic and hydrophilic blocks are a class of functional polymers for application in the structural control of materials

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interfaces [1–10]. Their ability to form micelles in water [11–16] also makes amphiphilic block copolymers strong candidates for potential applications as emulsifiers, dispersants, foamers, thickeners, rinse aids, and compatibilizers [17–20].

The last two decades have seen considerable progress in the development of synthetic strategies to prepare amphiphilic block copolymers of various architectures, solubility, and functionality. Architectures comprise diblock, triblock, and multiblock copolymers [21–33] arranged linearly or a star [13, 34–37], dendritic [38–41], hexagram [42], comb- or brush-type [23, 35, 42–52] copolymers. Grafting reactions of the hydrophilic segments with a hydrophobic chain can be performed in three routes [35, 43–46]: "grafting from," "grafting through," and "grafting onto" leading to comb- or brush-type graft copolymers [23, 42, 47–52]. Brush-type graft copolymers usually consist of a linear backbone with a high grafting density of side chains (usually one side chain per repeat unit of the backbone). Comb-type graft polymers consist of a main polymer chain, the backbone with one or more side chains attached to it through covalent bonds, and the branches [23, 42, 47–52]. The backbone length, grafting density, and side chain lengths determine the total molar mass and influence the properties of comb-type graft copolymers.

In the "grafting onto" method the backbone and the arms are prepared separately by a living polymerization mechanism. The backbone bears functional groups distributed along the chain that can react with the living branches. Upon mixing the backbone and the branches in the desired proportion and under the appropriate experimental conditions, a coupling reaction takes place resulting in the final comb shaped polymers. Comb-type graft copolymers contain polymer groups which are suspensed along main chain therefore it causes a very tight structure and a higher density segment to form. Block copolymers having a poly(ethylene glycol) (PEG) comprise a special and interesting category since PEG is a crystalline, neutral, nontoxic, and biocompatible material [10, 45, 47, 50, 53–63].

In spite of the promising results achieved up to now, the synthesis of novel polymers and copolymers is still of importance due to the high demand for new materials with defined architectures and improved properties. Up to now, most amphiphilic polymers were comprised from PEG and vinyl polymers as hydrophobic segment such as polyethylene, polystyrene, and polymethyl methacrylate. Polypropylene (PP) is one of the most important polyolefines due to its wide industrial production, low cost, good mechanical properties, easy processing, and excellent recyclability [64, 65]. Furthermore, it is a very versatile, hydrophobic polymer that has medical and industrial applications due to its good film and fiber properties. In order to obtain materials with advantageous properties, polar groups can be introduced into this polyolefin to overcome its hydrophobic character via free radical post-polymerization reactions. There have been post-polymerization reactions such as peroxide [66], maleic anhydride [67], and acrylate [68] modifications. Hydroxyl [69] and ester [70] functionalized PP have also been prepared by metal-based catalysts to convert terminal C–H bonds into hydroxyl groups.

The synthesis and structural characterization of polyvinyl chloride-*g*-PEG amphiphilic graft copolymers by using PEG200 and PEG600 have been reported without thermal and mechanical characterization [71]. To our knowledge, PP-*g*-PEG amphiphilic polymers have not been synthesized up to now. We recently reported that the antimicrobial efficiency of gold and silver nanoparticles embedded into PP-*g*-PEG amphiphilic comb-type graft copolymers [72]. The present work is an extension of our recent work [72] and refers to the synthesis and thermal and mechanical characterization of a series of the amphiphilic comb-type PP-*g*-PEG graft copolymers by using PEG600 and PEG2000.

Experimental

Materials

Chlorinated polypropylene (PP-Cl) has one chlorine atom in average in three repeating units with MW 147 Da and supplied from Aldrich. NaH 60 wt% in oil, polyethylene glycols with MW 600 Da (PEG-600) and MW 2,000 Da (PEG-2000), were supplied from Aldrich. THF was supplied from Aldrich and refluxed on sodium flakes overnight and then distilled. The middle fraction was used.

Synthesis of PP-*g*-PEG amphiphilic graft copolymers

Experimental procedure

The williamson-ether-synthesis-like reaction between PEG and PP-Cl was performed according to previously reported methods [73]. The synthesis was based on the reaction between chlorine in PP-Cl and the sodium salt of PEG. A typical end-capping reaction was performed as follows: PEG-600 (1.51 g, 2.5 mmol) and PP-Cl (1.43 g, 1.0 mmol Cl) were mixed and dissolved in dry THF (10 mL). To the solution was added NaH (0.12 g, 5 mmol), and the reaction mixture was stirred at room temperature under argon for 3 days. The reaction mixture was poured into 200 mL water containing 1 mL of concentrated HCl. The polymer was filtered, washed with distilled water and dried under vacuum at 50 °C overnight. For the purification, it was redissolved in chloroform and reprecipitated in 200 mL of methanol and then dried under vacuum overnight. Yield: 1.9 g (75 wt%).

Instrumentation

FT-IR and FTIR-ATR (Attenuated Total Reflectance Spectroscopy) spectra were recorded using a Nicolet 520 model FT-IR Fourier Transform Infrared Spectrometer and Perkin Elmer FT-IR Spectrometer 100. ^{1}H-NMR spectra of the samples in $CDCl_3$ as solvent and tetra methylsilane as the internal standard was recorded using Bruker mq 20 Minispec model Pulsed NMR Spectrometer. The molecular weight of the polymeric samples were determined by gel permeation chromatography (GPC) measurements in tetrahydrofuran (THF) with an Agilent 1100 Series GPC Setup as an integrated instrument, including a Zorbax PSM 60 S column (range: 5×10^2–10^4 MW), Zorbax PSM 1000 S (range: 10^4–10^6 MW), a UV (254 nm), and RI detector. The eluent was run at 40 °C and at a flow rate of 1 mL/min. A calibration curve was generated with four polystyrene green standards provided by EasyCal Agilent Technologies Polymer Standards Service (MW's: 696500, 50400, and 2960). The thermal behavior of the samples was investigated using a DuPont 951 thermogravimetric analyzer. Viscosity measurements were carried out by using Brookfield Cone and Plate Viscosimeter.

Stress–strain measurements of the polymer samples were performed on a Zwick Z010 Model Universal Tensile Testing Machine using a 50 kg load cell with a stretch speed of 100 mm/min. The film samples were rectangularly shaped with a size of (0.3–0.4) × 10 × 50 mm. At least four samples were used in the measurement for each experiment.

Measurement of swelling ratio

The degree of swelling of the amphiphilic polymer was measured gravimetrically in distilled water at room temperature. Before the measurement of the swelling ratio, the amphiphilic polymer was incubated in distilled water for at least 24 h at each particular temperature, and weighed after blotting the excess surface water. Degree of swelling was defined as follows [74]:

$$\text{Swelling}\,(\%) = 100 \times (W_\text{s} - W_\text{d})/W_\text{d},$$

where W_s is the weight of swollen amphiphilic polymer at a particular temperature and W_d is the dry weight of amphiphilic polymer after drying under vacuum overnight.

Chlorine analysis

The amount of chlorine in the amphiphilic polymer was determined using a gravimetric method. In a pyrex tube, a piece of polymer sample (30 mg) and a piece of sodium (0.1 g) were fused together on a flame. After cooling at room temperature, the product was dissolved in 20 mL of water and then acidified with 3 mL of the concentrated HNO_3. The solution was filtered from carbonized residue. 2 mL 10 M $AgNO_3$ was used to precipitate AgCl. The amount of chlorine in the amphiphilic polymer was calculated by using dry weight of AgCl.

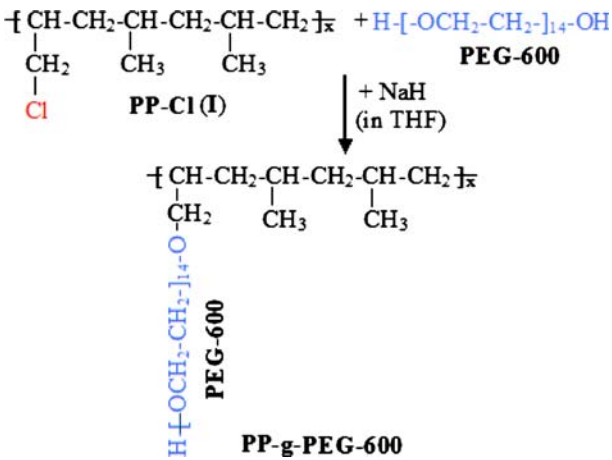
Determination of the PEG content of the amphiphilic polymer by FT-IR spectroscopy

PEG contents of the amphiphilic polymers were calculated by using the FT-IR spectra of the amphiphilic copolymers according to a previously reported [32]. FT-IR spectra of the polymers were recorded from their KBr pellets (150 mg KBr + 2 mg sample). The length of the signal at 1,100 cm^{-1} which belong to the ether bonds of PEG was compared with the calibration curve obtained from that of PEG in a mixture with PP-Cl.

Results and discussion

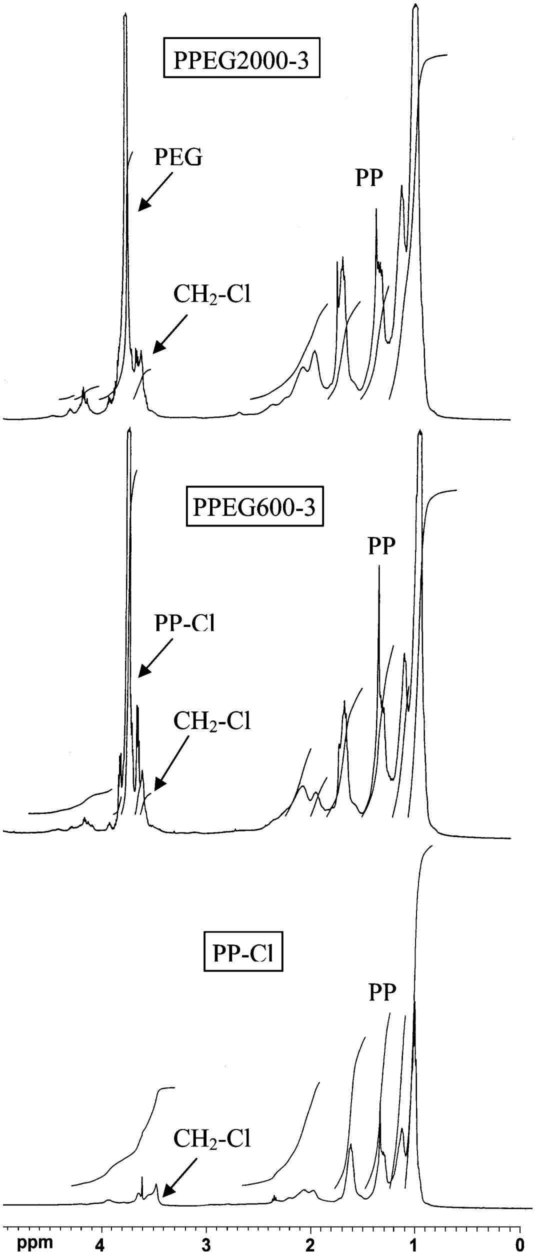
Synthesis of PP-*g*-PEG

Grafting of PEG chains onto chlorinated-PP using a Williamson-ether-synthesis-like reaction was performed. While this reaction was widely used for making macromolecules (i.e., the convergent synthesis of Frechet-type dendrimers relies on this reaction) [73, 75, 76] it has not been used for grafting PEG chains onto chlorinated-PP. PP is an attractive material for PEG grafting to produce amphiphilic graft copolymers with good film properties. Two new series of the amphiphilic comb-type PP-*g*-PEG graft copolymers based on chlorinated PP (PP-Cl) and PEG (MW 600 and 2,000) were synthesized. Scheme 1 shows the reaction between the hydroxyl endgroups of the PEG and the chloride substituents of the PP-Cl in the presence of a base. The end-capping reaction was used to successfully synthesize amphiphilic graft copolymers. PEG units inserted along the PP backbone produce a comb-type graft copolymer structure. The incorporation of hydrophilic units increased the polymer hydrophilicity due to the strong interaction between water and the PEG in the polymer. Figure 1 shows typical ^{1}H-NMR spectra of the PEG-*g*-PP block copolymers with their characteristic sharp signal of PEG segments at 3.6 ppm. The other characteristic signals at 0.9–2.1 ppm for PP units and at 3.5–4.0 ppm for –CH_2–Cl groups for the precursor PP-Cl and for –CH_2–Cl residues in the graft copolymers. Figure 2 shows the FT-IR spectra of the precursor PP-Cl, PP-*g*-PEG600, and PP-*g*-PEG2000 graft copolymer samples. The characteristic signals at 1,100 cm^{-1} for PEG and 657, 725, 757 cm^{-1} for –CH_2–Cl residues in the FT-IR spectra of the graft copolymers were observed. Since the signals of –CH_2–Cl groups (at 3.5–4.0 ppm) partially overlaps with the PEG signal in ^{1}H-NMR, we have used the FT-IR spectra of the graft copolymers to determine PEG content of the graft copolymers. The reaction conditions, PEG content, chlorine (Cl) content, and swelling ratios of the amphiphilic graft copolymers are given in Table 1. The PEG



Scheme 1 A typical reaction design on the synthesis of PP-*g*-PEG graft copolymers

Fig. 1 [1]H-NMR spectra of the PP-Cl, PP-*g*-PEG600, and PP-*g*-PEG2000 graft copolymers



contents of the graft copolymer series were varied between 6 and 25 wt%. Increasing the PEG content causes increasing swelling degrees in water as expected. The highest swelling degrees were observed at 91% for PPEG2000-4 containing 25 wt% of PEG2000 and 71% for PPEG600-4 containing 25 wt% of PEG600 when the hydrophilic unit (PEG) in the gel was the highest. One can conclude that the

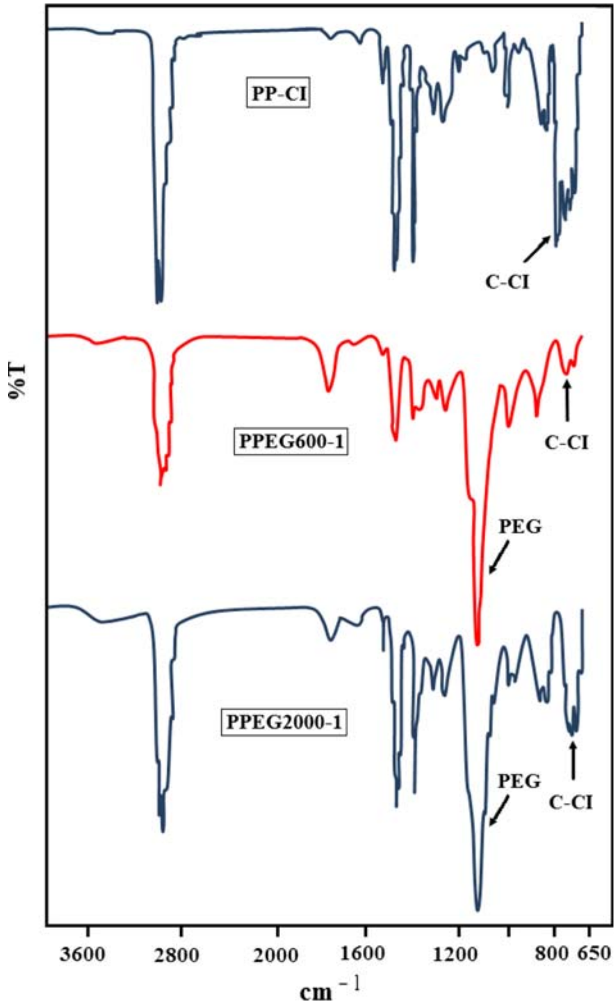


Fig. 2 FT-IR spectra of the precursor PP-Cl, PP-*g*-PEG600, and PP-*g*-PEG2000 graft copolymer samples

hydrophilic character of the PEG units increases with the increasing molecular weight of PEG. Due to the overlapping PEG and –CH_2–Cl signals in their ^{1}H-NMR spectra, chlorine content of the graft copolymer was determined gravimetrically. The variation of PEG content with swelling degree and chlorine content in graft copolymer have been plotted in Fig. 3. The Cl content of the graft copolymers were found to be in range between 9 and 30 wt%, corresponding to the attached PEG units.

TGA is used for the evaluation of the thermal stability of polymers. The shapes of the all weight-loss curves of all the amphiphilic graft copolymer samples were almost identical. Figure 4 shows the TGA curves of the PP-*g*-PEG600 and

Table 1 Reaction conditions, polymer analysis, and mechanical properties of PP, PPCl, and PP-*g*-PEG graft copolymers

Sample	End-capping reaction				PP-*g*-PEG graft copolymer			
	PP-Cl (mol, Cl)	PEG2000 (mol)	PEG600 (mol)	NaH (mol)	PEG (wt%)	–Cl (wt%)	Stress (MPa)	Elongation (%)
PP	1.00	–	–	–	–	–	26	680
PPCl	1.00	–	–	–	–	34	18	350
PPEG600-1	1.00	0.30	–	0.30	10	25	36	380
PPEG600-2	1.00	0.33	–	0.33	16	22	13	355
PPEG600-3	1.00	0.50	–	0.50	20	20	13	440
PPEG600-4	1.00	0.67	–	0.67	25	19	3.3	275
PPEG2000-1	1.00	–	0.24	0.30	15	30	22	670
PPEG2000-2	1.00	–	0.50	0.60	20	22	12	424
PPEG2000-3	1.00	–	0.75	0.80	22	20	2.2	128
PPEG2000-4	1.00	–	1.00	1.20	24	19	1.0	56

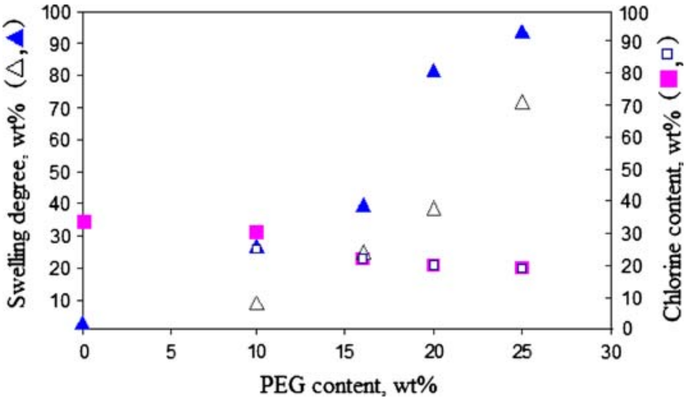


Fig. 3 The plot of the swelling degree and the chlorine content versus the PEG600 content and PEG2000 content (PEG600: *square*, *triangle*, PEG2000: *filled square*, *filled triangle*)

PP-*g*-PEG2000. Two decomposition steps for the PP-*g*-PEG600 series were observed at 253–333 and 477–482 °C, which can be attributed to the PEG segment and PP segment, respectively. Alternatively, one can argue that there is the apparent observation of a single thermal transition for the PPEG2000 at 391–471 °C. The TGA results of the graft copolymers were also listed in Table 2.

The stress–strain curves for the PP-*g*-PEG amphiphilic graft copolymer plastic sheets are shown in Fig. 5. The stress at break and elongation at break of the copolymer samples are also listed in Table 1. In the case of PP-*g*-PEG600 series, the graft copolymer having the highest PEG600 segment had the highest stress

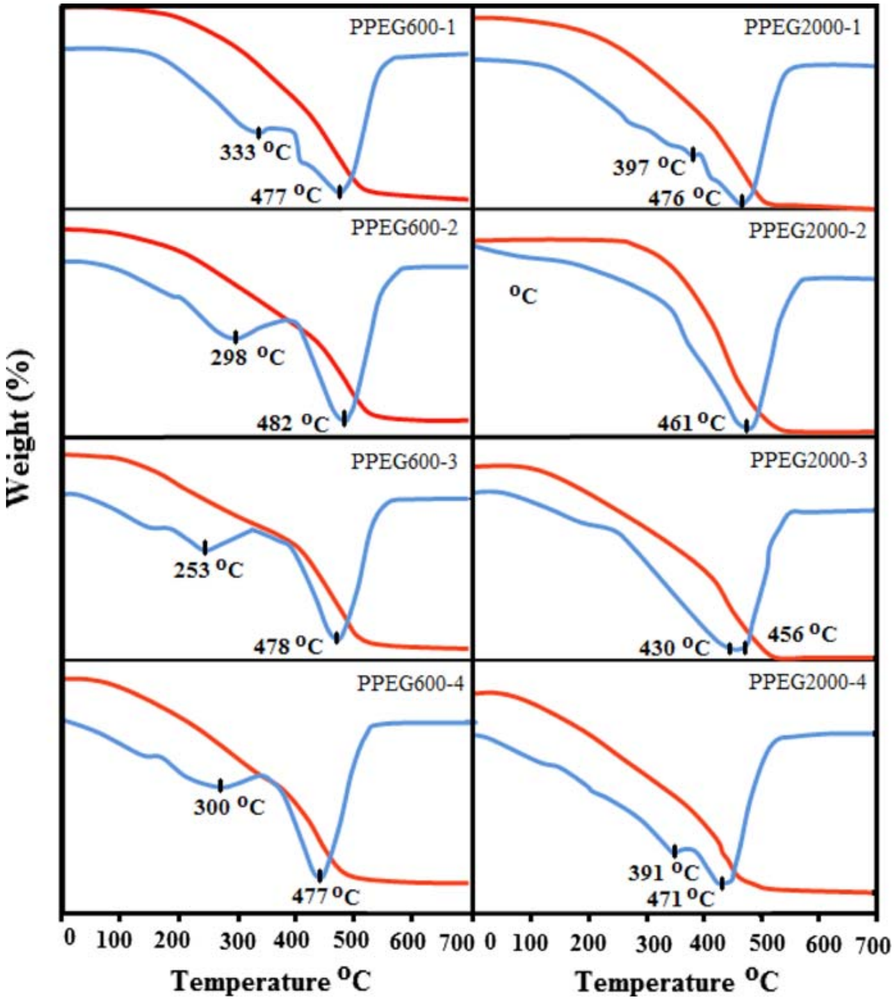


Fig. 4 TGA curves of the PP-*g*-PEG600 and PP-*g*-PEG2000 series

(ca. 36 MPa) and elongation at break 380%. The other samples of the series displayed stress at break in range between 3.3 and 13 MPa and elongation at break in range between 275 and 440%. Interestingly, in the case of PP-*g*-PEG2000 series, the PEG content in copolymer was inversely proportional to the stress–strain values. For medical and industrial applications, PP-*g*-PEG2000 amphiphilic copolymers with PEG contents in range from 20 to 30% should be prepared when amphiphilic copolymers with good film properties are needed. Figure 6 shows the smooth decrease in mechanical properties by the increase in the PEG content in the amphiphilic graft copolymer.

Table 2 Thermal properties of the PP-*g*-PEG graft copolymers obtained from TGA analysis

Sample	TGA (°C)		
	T_{d1}	T_{d1}'	T_{d2}
PP		–	481
PPEG600-1	333	–	477
PPEG600-2	298	–	482
PPEG600-3	253	–	487
PPEG600-4	300	–	477
PPEG2000-1		397	476
PPEG2000-2		–	461
PPEG2000-3		430	456
PPEG2000-4		391	470

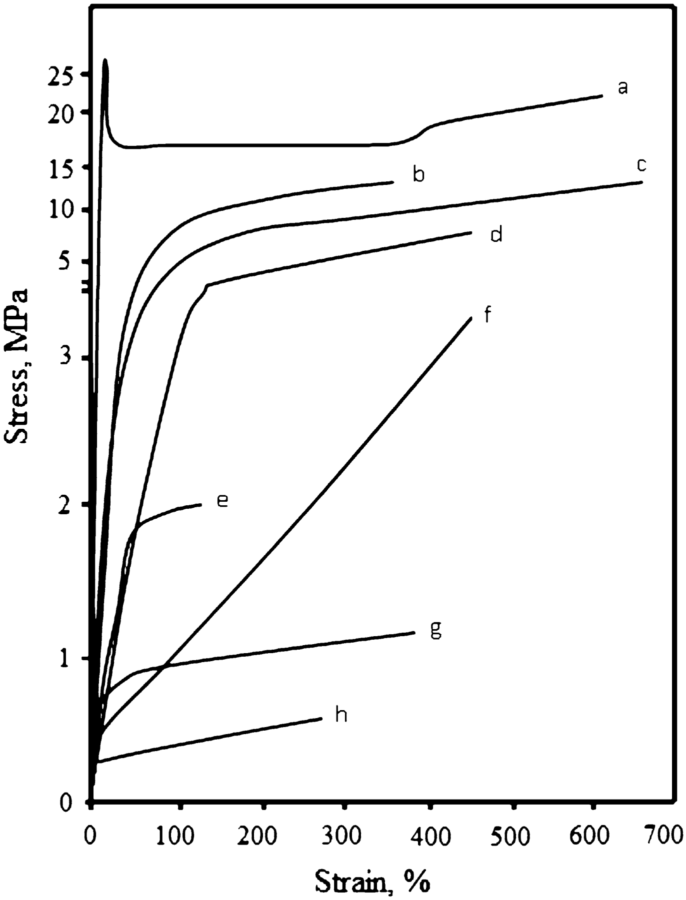


Fig. 5 Stress–strain curves of the precursors PP (*a*) and PP-Cl (*b*); and PPEG600 and PPEG2000 graft copolymer series: (*c*) PPEG2000-1, (*d*) PPEG2000-2, (*e*) PPEG2000-3, (*f*) PPEG600-1, (*g*) PPEG600-2, and (*h*) PPEG600-3

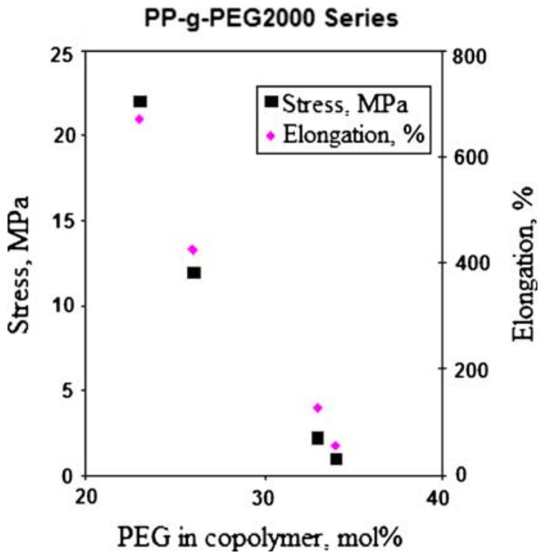


Fig. 6 Dependence of the mechanical properties of the PP-*g*-PEG2000 amphiphilic graft copolymers on the PEG content

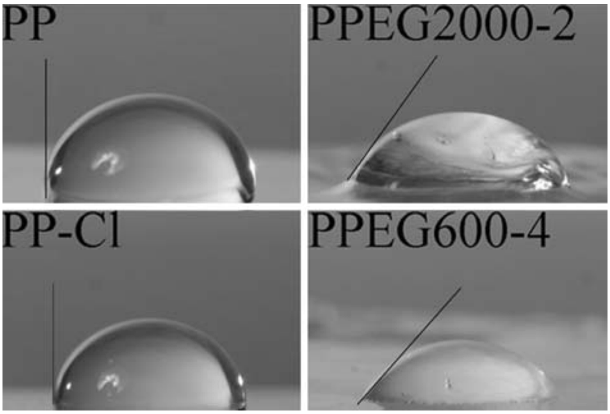


Fig. 7 Photographs of the water drop on the PP, PP-Cl, PPEG2000-2, and PPEG600-4 film surfaces after 1 min

Surface properties of the graft copolymers

The solution properties of the graft polymer differ greatly from the parent backbone polymer, providing further evidence of the formation of the grafted structures. We have also observed that the behavior of a water drop on the PP-*g*-PEG film surfaces. Figure 7 shows the photographs of the water drops on the amphiphilic polymer films and the hydrophobic templates. The hydrophilic PEG segments of the amphiphiles strongly interacts with water drops on the polymer surface and the water drop expands on the surface while water drops on the hydrophobic surfaces of PP and PP-Cl do not expand.

Conclusion

New PP-*g*-PEG comb-type copolymers containing PEG side-chains with molecular weights of 600 and 2,000 Da were synthesized, which are promising materials for medical and industrial applications. The hydrophilicity of the amphiphilic copolymers increases by the increasing PEG content in the copolymer while mechanical properties decrease with increased PEG content. Therefore, PP-*g*-PEG2000 with PEG contents in range between 10 and 25 wt% should be useful for medical and industrial application when good films with hydrophilic properties are needed.

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