Highly Flexible Poly(ethyl-2-cyanoacrylate) Based Materials Obtained by Incorporation of Oligo(ethylene glycol)diglycidylether

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Summary: Poly(ethyl-2-cyanoacrylate) (PECA) is a polymer with potential medical or technical applications, which are limited due to its high brittleness. In this work, the capability of different ethylene or propylene glycol-based oligomers to provide flexible poly(ethyl-2-cyanoacrylate) films upon blending is analyzed. The used oligoethers have been chosen with different end groups or lateral substituents and their effects the on macroscopic behavior of the obtained materials have been characterized. During its synthesis, in situ blending of PECA was performed with increasing quantities of oligo(ethylene glycol) diglycidyl ether providing homogeneously miscible materials with single T_g's. The T_g's decreased in a concentration dependent manner and showed negative deviation from predictions by the Fox equation, possibly due to specific intermolecular interactions. Remarkably, the mechanical properties could be tailored over a wide range with Young's moduli of 0.2 to 900 MPa, which so far has not been reported for cyanoacrylate-based materials. Therefore, the concept of compatible blends should be further explored to establish flexible cyanoacrylate-based materials for various technical or biomedical applications.

Keywords: blend; glass transition; mechanical properties; polyethers; poly(ethylene glycol) diglycidylether; poly(ethyl-2-cyanoacrylate)

Introduction

Polyalkylcyanoacrylates (PACA) have been employed for a variety of medical and technical applications for several decades.[1] Commonly they have been used as tissue adhesives for wound closure, for dental applications, or proposed as drug delivery systems.[2] PACA polymers are often referred to be non-toxic, non-immunogenic and degradable,[3] with different in vivo degradation mechanisms being discussed.[4–6]

The use of cyanoacrylates (CA) is often limited due to the intrinsic brittleness of the formed PACA.[1] Generally, PACA are amorphous materials with high glass transition temperatures T_g clearly above room and body temperature. Even though longer alkyl side chains can reduce the T_g, pure PACA's as well as PACA copolymers are highly brittle materials at biologically relevant temperatures.[7] In contrast, medical applications often require flexible and degradable materials.[8]

Generally, scientific approaches in polymer chemistry to increase elasticity is the preparation of copolymers. For instance, this concept has been applied to multiblock copolymers as thermoplastic elastomers, which allowed to tailor their mechanical properties as well as their degradation behavior.[9–12] Furthermore, elastic, degradable materials could be realized by

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crosslinking copolyester segments to form covalent polymer networks.[13–14] For amorphous materials, plasticization by solvents, particularly by water, could occur rapidly and soften the material.[15]

In principle, elastic PACA based materials could be prepared by different approaches: (i) PACA homopolymers synthesized from monomers with increasing alkyl-ester side chain lengths[16] exhibit reduced T_g for sterical reasons. However, the lowest T_g observed in medically relevant PACA is 64 °C for poly(octyl cyanoacrylate),[7] which is clearly above body temperature (ii) Anionic copolymerization approaches based on mixtures of CA monomers allowed tailoring of T_g according to expectations of the Fox equation, but were not effective to realize PACA's with T_g's close to body temperature.[7] iii) Binding of flexible chains such as oligo(ethylene glycol) (OEG) to PACA. OEG was either used as as a side chain[18] or as starter for CA anionic polymerization leading to linear di- or triblock polymers.[17] The created amphiphilic polymers were used to prepare core-shell nanoparticles,[2] but their bulk mechanical properties were so far not reported. Furthermore, due to the high reactivity of CA in the presence of traces of water, the synthesis of OEG modified monomers can be expected to be highly challenging due to strong hygroscopy of OEG. (iv) Covalent networks synthesized by radical copolymerization of CA with oligomeric crosslinkers bearing methacrylate endgroups. Cyanoacrylate tissue adhesives crosslinked by linear or branched copolyesters as degradable segments showed reduced brittleness.[19] (v) Plastification of PACA with solvents. Water, but not 2-propanol, could reduce the T_g of PACA. This, however, was an irreversible phenomenon in the case of water and again was not suitable to establish T_g's close to body temperature.[7] (vi) Blending of PACA with elastic polymers rather than synthesis of copolymers or networks may be an alternative approach to obtain elastic PACA-based materials. However, recent reports on blending of PECA with poly[(*L*-lactide)-*co*-(ε-caprolactone)] did not provide a mechanical characterization of the blend.[20]

In this study, thermoplastic elastomers based on PACA should be prepared that allow a systematic tailoring of the mechanical properties and do not require a challenging synthesis of modified monomers. It appears, that even though blending often allows to alter and adjust material properties,[21] this concept so far has not been extensively applied to PACA's. Importantly, miscibility of the blend components is required to systematically tailor the mechanical properties by changing their composition. In the case of a partially miscible blend system, the solubility of the components in each other is limited, possibly resulting in phase separation when the composition of the blend is changed.

Oligo(ethylene glycol)diol [$OEG(OH)_2$] was selected since it has shown its ability to introduce flexibility into some polymeric materials.[23] Considering that miscibility of blend components also depends on end groups, different oligoethers were explored. In addition to $OEG(OH)_2$, the effect of blending with on the properties of PECA films has been evaluated also for oligo(propylene glycol)diol [$OPG(OH)_2$] with a more hydrophobic main chain, OEG diglycidyl ether (OEGDG) with the less hydrophilic end groups as well as trimethylpropane triglycidyl ether (TPTGE) as a non-linear triglycidyl ether of similar molecular weight.

Experimental Part

Materials

Ethyl 2-cyanoacrylate monomer (ECA) Sicomet 40® was from Henkel (Hannover, Germany), oligo(ethylene glycol) diglycidyl ether 526 Da (OEGDG), trimethylolpropane triglycidyl ether (TPTGE), oligo(propylene glycol)diol 425 Da [$OPG(OH)_2$], oligo(ethylene glycol)diol 550 Da [$OEG(OH)_2$], and anhydrous tetrahydrofuran (THF) were from Sigma-Aldrich (Taufkirchen, Germany).

Preparation of Poly(ethyl-2-cyanoacrylate) Based Films

The studied oligoethers have been added to a 25 ml tube with a rubber cap, which was pre-treated with five cycles of high-vacuum/argon-flushing to remove water, resulting in a residual water content of 786 ppm as determined by Karl-Fischer titration. After homogeneous dispersion in 10 ml of freshly distilled THF, 1 ml of ECA has been added. The polymerization of ethyl 2-cyanoacrylate started after a few seconds as observed by an increasing viscosity of the solution. After vigorous stirring for 4–5 h, the samples were casted in petri dishs, allowed to dry at room temperature in a desiccator at 900 mbar, and subsequently exposed to low pressure for one day after gradually decreasing the pressure to 20 mbar within 4 hours. The obtained films have been detached from the dishes and used for the subsequent characterizations.

Depending on the oligoether employed for blending, the samples were named as follows: $OEG(OH)_2$/PECA, $OPG(OH)_2$/PECA, TPTGE/PECA, and OEGDG/PECA. OEGDG/PECA films have been prepared by using different molar ratios X_{OEGDG} of oligoether/ECA monomer ($X_{OEGDG} = 0.5$, 0.33, 0.25, 0.2, 0.13, and 0.06), which correspond to OEGDG weight content ratios μ_{OEGDG} in the range of 0.2 to 0.68 (see Table 1). The concentration of used ECA monomer in THF was kept constant at 10 wt.%. Films of $OEG(OH)_2$/PECA, $OPG(OH)_2$/PECA, and TPTGE/PECA were prepared with $X_{OEGDG} = 0.5$, 0.2, and 0.06.

Material Characterization

Dry-state tensile tests were performed with dumbell shaped test specimens (20 mm length, 2 mm width, 250–400 μm thickness) using a Zwick Z005 (Zwick, Ulm, Germany) with a load cell of 50 N and a minimum of five standard test samples (ISO 527-2/1BB) at room temperature analyzed at a strain velocity of $5\,mm \cdot min^{-1}$. The Young's modulus (E) was calculated from the first 5% of strain, while the maximum tensile strength (σ_{max}) was determined from the stress–strain curve recorded for the elongation at break (ε_B).

The glass transition temperature T_g of the PECA and OEGDG/PECA films were determined with a Phönix DSC 204 F1 (Netzsch, Selb, Germany) differential scanning calorimeter. The samples were placed in pans with pierced lids and were sealed. Two heating (up to 180 °C) and cooling (−100 °C) cycles at a scan rate of $10\,°C \cdot min^{-1}$ were performed. The T_g was determined from the inflection point of the second heating curve. The thermal stability of materials was studied by thermogravimetric analysis (TGA) with a thermomicrobalance (TG 209C; Netzsch). The TGA experiments were carried out from 20 °C to 600 °C at a scan rate of $10\,°C \cdot min^{-1}$ under constant nitrogen purge.

The extraction of OEGDG from OEGDG/PECA films has been performed

Table 1.
Thermal properties of PECA, OEGDG, and OEGDG/PECA films.

Sample	X_{OEGDG}	μ_{OEGDG}	T_g	ΔT_g*	Δc_p	Fox: T_g**
	–	–	°C	K	$J \cdot g^{-1} \cdot °C^{-1}$	°C
PECA	–	–	146	11	0.349	–
OEGDG/PECA	0.06	0.20	101	18	0.087	73
	0.13	0.35	−49	25	0.269	33
	0.20	0.46	n.d.***	n.d.***	n.d.***	11
	0.25	0.51	−57	13	0.571	0
	0.33	0.58	−58	9	0.679	−12
	0.50	0.68	n.d.***	n.d.***	n.d.***	−28
OEGDG	–	–	−68	8	0.448	–

*Difference between onset and offset of glass transition.
**Mixed-system T_g as predicted by the Fox equation.[27] [7]
***No thermal transition detectable.

by immersing dumbell shaped films in 100 ml of distilled water under gentle stirring for 48 h at room temperature with subsequent freeze drying.

SEM studies of samples coated with Pd/Pt have been performed with a Gemini Supra™ 40 VP SEM (Carl Zeiss NTS GmbH, Oberkochen, Germany) at 3 kV using a secondary electron detector with an aperture size of 30 mm. The samples have been cross sectioned using cutting tweezers in liquid nitrogen.

Results and Discussion

Synthesis of Flexible Materials by Anionic CA Polymerization in the Presence of Oligoethers

Blending polymers to established desired material properties typically is performed, e.g., by coextrusion of their melt after their individual synthesis. In contrast, due to the extremely high reactivity of CA in the presence of traces of water, the anionic polymerization of ECA could be performed in THF in the presence of the dissolved oligoether compound. Importantly, to clarify the material structure and mechanism of potentially improved mechanical properties, it needs to be shown that the oligoethers are not being attacked and covalently bound during polymer synthesis. Clearly, PECA in situ synthesis and blending with oligoethers as a simultaneous one-step process may be advantageous, since it avoids later process steps and may allow homogeneous mixing of the compounds. Subsequently, PECA based films were obtained by casting and evaporation of THF. Such films could also be used to evaluate the mechanical properties by tensile tests after cutting defined test specimens.

Improved mechanical properties of PECA-based materials were postulated to be associated with an efficient reduction of the T_g. In homogeneously miscible blends of amorphous polymers, a mixed phase is formed, which according to the theory of Fox should result in mixed-system glass transitions with the T_g's correlating with the weight fractions of the blended components. In the literature, a few examples of polyether/PECA copolymers are shown and no examples of phase separation were reported. Therefore, the selection of the oligoethers, i.e., $OEG(OH)_2$, OEGDG, $OPG(OH)_2$, or TPTGE (Figure 1) was rationalized by their possible miscibility with PECA and their low T_g (compare Table 1 as discussed below), also including considerations of end or side group effects.

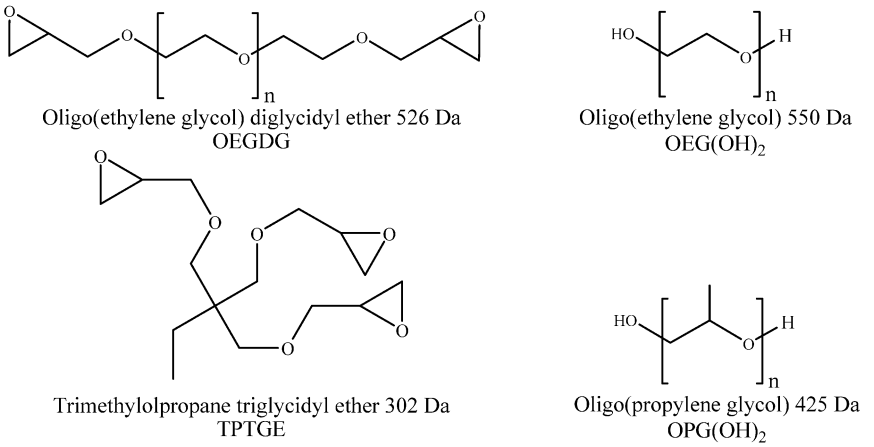

Figure 1.
Structures of oligoethers explored for blending of PECA.

Identification of Oligoethers Suitable to Establish Flexible PECA Blends

In screening studies, the properties of blends of the oligoethers (Figure 1) with PECA were analyzed by first evaluating their macroscopic behavior. In these preliminary studies it was aimed to understand the influence of different end groups or lateral substituents on the compatibility of oligoethers of comparable molecular weights and PECA.

Films from pure PECA synthesized by the described procedure were transparent, colourless, and, as expected, extremely brittle. Pure PECA films could hardly be isolated from the casting dish and could subsequently not be handled, e.g., in tensile tests without fracturing. The macroscopic appearance of the films changed when the synthesis was performed in the presences of oligoethers (Figure 2), but only in the case of OEGDG/PECA blend a highly flexible material was obtained (Figure 2C). In contrast, films of $OEG(OH)_2$/PECA (Figure 2a) and $OPG(OH)_2$/PECA (Figure 2B) showed non-transparent areas, probably due to macrophase separation. $OEG(OH)_2$/PECA and $OPG(OH)_2$/PECA were highly brittle, with particular difficulties to handle $OEG(OH)_2$/PECA samples without breaking. Increasing the molar ratio of oligoether and monomer did not result in improved elastic properties for $OEG(OH)_2$ and $OPG(OH)_2$. Furthermore, for $OPG(OH)_2$/PECA, some droplets of OPG were observed at the sample surfaces after drying the films, indicating macrophase separation and non-compatibility of OPG with PECA. Transparency was observed for TPTGE/PECA films, but the material remained brittle.

From the observation that only OEGDG rather than $OEG(OH)_2$, $OPG(OH)_2$, or the structurally related TPTGE could provide flexible blend materials with PECA, it has been concluded that combination of OEG and epoxy endgroups is required for homogeneous miscibility. Furthermore, it was found that the separate synthesis of PECA and subsequent blending with OEGDG by solvent casting did not provide homogeneous materials. Blending by melt extrusion was not evaluated since thermal decomposition of PECA could be expected from TGA analysis as discussed below. The differences in material properties between in situ blending compared to blending of preformed PECA indicates that there may be physical interactions between the two compounds, which can be established only during but not after PECA synthesis. Preformed PECA dissolved in THF might be partially coiled and therefore could not well interact with OEGDG as in the case of in situ ECA polymerization in OEGDG solution, in which the growing polymer chain should be freely surrounded by OEGDG. In order to learn more on the material structure, OEGDG/PECA materials were comprehensively characterized.

Characterization of Polymer Structure

FT-IR studies have been performed to characterize the chemical composition of the obtained materials. In particular, it should be considered that the polymeriza-

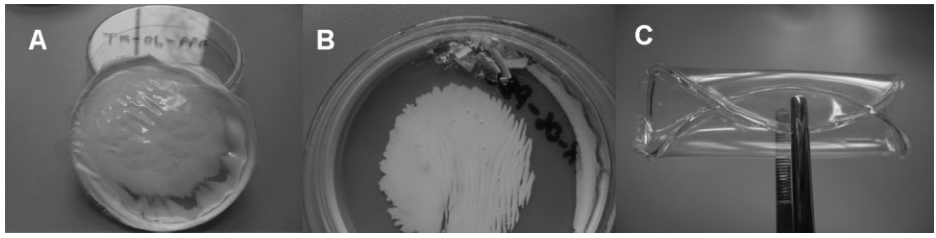

Figure 2.
Macroscopic appearance of (A) $OPG(OH)_2$/PECA films (B) $OEG(OH)_2$/PECA films, and (C) OEGDG/PECA films. In all cases $X_{OEGDG} = 0.2$.

tion of ECA at the employed conditions is an anionic polymerization, possibly resulting in reaction of the living anion of cyanoacrylate with the epoxy ring of OEGDG. FT-IR spectra showed that the peak at 910 cm^{-1}, which corresponds to the epoxy ring vibration, was still present in all the samples. On a qualitative level, this indicates that the epoxy groups are not involved in the ECA polymerization. Additionally, under the same reaction conditions without the presence of ECA, no polymerization of OEGDG was observed. For quantitative determination of the amount of epoxy groups remaining unaltered after the ECA polymerization, ^{1}H-NMR studies (Figure 3) have been performed. Additionally, ^{13}C-NMR studies were conducted to further confirm the presence of epoxy groups.

The ^{1}H-NMR spectra in acetone showed: 4.31 ppm ($-O-\underline{CH_2}-CH_3$), 3.92–3.47 ppm (3 + 4), 3.34 ppm (3'), 3.07 ppm (2), 3.05–2.60 ppm (PECA main chain, overlap 1), 2.56–2.36 ppm (2), 1.37 ppm ($-O-CH_2-\underline{CH_3}$). From these studies, the amount of epoxy groups could be quantified by the ratio of the integrals corresponding to the proton 1 of the epoxy ring (3.07 ppm) and the protons of the OEGDG main chain (3.92–3.47 ppm). All the tested samples showed an epoxide content of OEGDG similar to the starting material, meaning that the epoxy groups were not reacting during the ECA polymerization.

The ^{13}C-NMR spectrum in acetone showed: 164.91 ppm (C=O), 114.34 ppm (C≡N), 69.85 ppm (OEG main chain), 63.07 ppm ($-O-\underline{CH_2}-CH_3$), 49.82 (epoxy 2), 44.93–42.68 ppm (PECA main chain, overlap 1), 12.30 ppm ($-O-CH_2-\underline{CH_3}$). Also by this characterization it was possible to confirm the presence of the epoxy ring by the peak at 49.82 ppm, which was corresponding to the carbon 2 and was not shifted compared to starting OEGDG.

In order to further proof that the materials flexibility was due to OEGDG blending rather than copolymerization, the material properties should be evaluated after removal of the oligoether. Since OEGDG is well water-soluble while PECA is not water-soluble, the samples were incubated in water for 2 days at room temperature. After subsequent drying, the materials exhibited the high brittleness being characteristic for PECA. ^{1}H-NMR confirmed that only minor quantities of the employed OEGDG, e.g., ≈3 mol% for $X_{OEGDG} = 0.5$ or $X_{OEGDG} = 0.2$ remained in the bulk after aqueous extraction. This portion of OEGDG was not

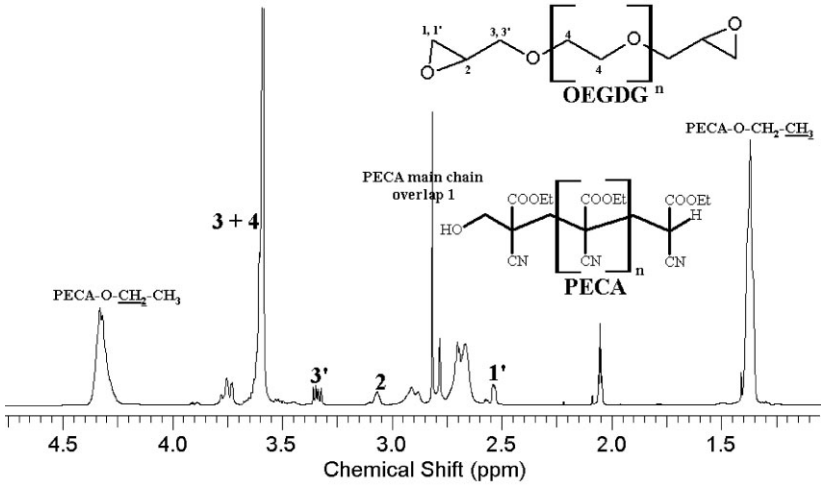

Figure 3.
^{1}H-NMR spectrum of the sample OEGDG/PECA at $X_{OEGDG} = 0.2$.

suitable to preserve the flexibility of the material. The remaining OEGDG may not have been extracted from the material for different reasons such as entanglements, a too short extraction time, or, at a low extent (compare unaltered epoxide content as detected after synthesis by ^{1}H-NMR), covalent binding. Based on the extractability of OEGDG and the associated loss of material flexibility, it was concluded that the prepared material is a blend rather than a covalent network of OEGDG and PECA.

Impact of the OEGDG Content on the Blend's Thermal Properties

The existence of a single glass transition is a widely applied criterion to confirm the miscibility of different polymers in a multicomponent system.[24] The T_g of pure PECA was detected at 142 °C (Table 1), which well corresponds to previously reported results.[25–26] The decreasing T_g values for OEGDG/PECA films could be clearly related to the increasing molar amount of OEGDG used in the synthesis. Interestingly, the samples with the lowest OEGDG amount ($X_{OEGDG} = 0.06$) exhibited a T_g as high as 100 °C, while the T_g for $X_{OEGDG} = 0.13$ substantial decrease to −48 °C. This indicates a major contribution of PECA to the thermal transition at low OEGDG content, which strongly decreases at higher X_{OEGDG}. At the same time, tensile tests as discussed below revealed a substantial decrease in E modulus when increasing X_{OEGDG} from 0.06 to 0.13. Importantly, single T_g's were observed, strongly indicating the presence of one homogeneous amorphous phase.

In this context it should be noted that the glass transitions of OEGDG was very well-defined and clearly observable. In contrast, for PECA the glass transition at 146 °C was broader and close to the onset of thermal decomposition at 150 °C as identified by TGA (mass loss: 1 wt.% at 100 °C; 2 wt.% at 150 °C; 13 wt.% at 170 °C). For OEGDG/PECA films, the width of the thermal transition by trend decreased with increasing X_{OEGDG}. An exception was found for the samples OEGDG/PECA at $X_{OEGDG} = 0.5$ and $X_{OEGDG} = 0.2$, where it was not possible to observe a clear thermal transition even when applying various modified heating conditions.

When considering the initial assumption that more flexible materials would be achieved by reducing the T_g of PACA-based materials closed to or below body temperature, this hypothesis appears to be proven by the presented data. Still, it may be surprising that despite the reduction far below body temperature to values as low as ≈−60 °C, the obtained blends were not liquid. The reason for that may be the entanglements of the long PECA chains, which preserved the shape of the film samples.

For non-phase separated polymers such as certain amorphous random copolymers or compatible polymer blends, the mixed-phase glass transition temperature can be predicted by the Fox equation.[27] For blends, the weight content (μ) of the two compounds as well as their individual T_g's are taken into account to determine the predicted $T_{g,calc}$ as shown in equation 1:

$$\frac{1}{T_{g,\,calc}} = \frac{\mu_1}{T_{g,\,1}} + \frac{\mu_2}{T_{g,\,2}} \quad (1)$$

Apparently, the Fox equation provided a rather poor prediction of experimental values (Table 1), which is in line with frequent reports in the literature showing negative deviations from the Fox equation.[24] This is, because the theories of Fox as well as of Gordon-Taylor and others often consider only selected events such as an additive behavior of rotation freedom or free volumes. However, intermolecular interactions between the blend compounds or excess volume formation are neglected. Based on that, the observed strong deviations might be a hint that such mechanisms are possibly involved and are affecting the glass transition of the presented material. Furthermore, the reported in situ approach of PECA synthesis and blending, which may enable physical interactions between the growing PECA chains and the OEGDG, might have supported such mechanisms.

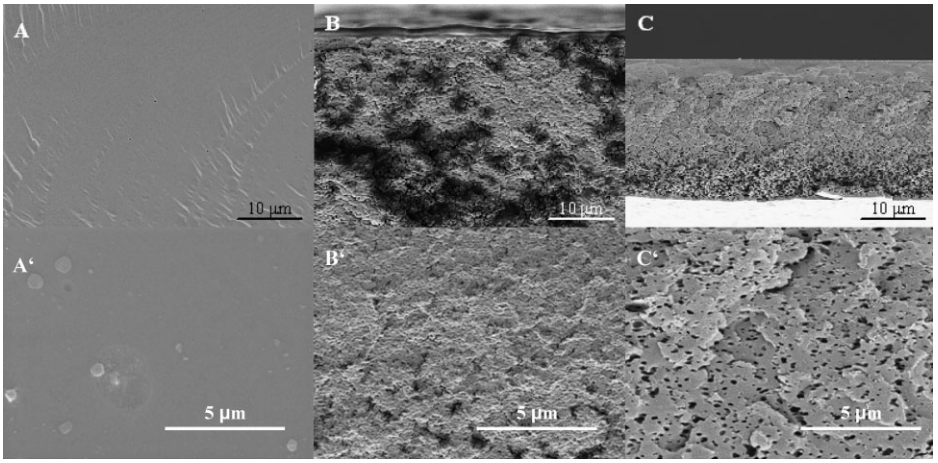

Figure 4.
SEM pictures showing cross-sections of (A, A') OEGDG/PECA film $X_{OEGDG} = 0.2$, (B, B') $OEG(OH)_2$/PECA film $X_{OEG(OH)2} = 0.2$, and (C, C') PECA films.

Morphology of Polymer Films

SEM analysis has been performed to study the morphology of the polymer films. A particular focus was to evaluate a possible phase separation and the porosity of the obtained materials (Figure 4).

As illustrated in Figure 4A, the OEGDG/PECA samples were characterized by a highly uniform cross-section surface with neither porosity nor evident phase separation being detectable. In contrast, samples containing OEG with a different end-group, namely $OEG(OH)_2$/PECA, showed an evident phase separation (Figure 4B). As mentioned before, this material has been observed to exhibit a high brittleness similar to that of pure PECA. The macrophase separation in $OEG(OH)_2$/PECA probably occurred during the solvent evaporation and was caused by a the lack of miscibility of the two compounds. Also, for films from pure PECA prepared by the same procedure, a substantially different morphology with a large porosity formed during solvent evaporation was observed (Figure 4C). In contrast, the homogeneity of OEGDG/PECA films well agrees with previously discussed findings and indicates good miscibility of the two blended components, PECA and OEGDG.

Adjustable Mechanical Properties of OEGDG/PECA Films

In order to experimentally prove that choosing OEGDG for blending with PECA is a suitable approach to adjust the mechanical properties of the blends, X_{OEGDG} was systematically changed to cover $X_{OEGDG} = 0.06–0.5$ (corresponding to $\mu_{OEGDG} = 0.20–0.68$). This range has been chosen based on observations in preliminary studies, showing, on the one hand, that materials with X_{OEGDG} values smaller than 0.06 were too brittle to be mechanically tested. On the other hand, X_{OEGDG} values larger than 0.5 resulted in extremely soft, almost semi-liquid materials at room temperature probably due to decreasing concentration of PECA allowing for less chain entanglements.

The elastic modulus E, the elongation at break ε_B, and the maximum tensile strength σ_{max} of OEGDG/PECA films are shown in Figure 5. It is apparent that alterations in the OEGDG content are a powerful tool to tailor the mechanical properties of OEGDG/PECA materials over a remarkably wide range. In particular, E of OEGDG/PECA was strongly depending on the amount of used OEGDG with

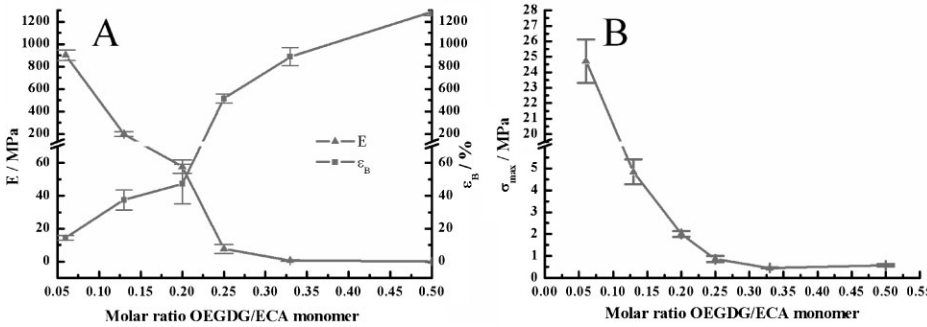

Figure 5.
Effect of the molar ratio X_{OEGDG} of OEGDC/PECA on the mechanical properties as determined by tensile tests at room temperature (n = 5, mean, S.D.). (A) Elastic modulus (E) and elongation at break (ε_B). (B) Maximum tensile strength σ_{max}.

substantial changes, e.g., when X_{OEGDG} was stepwise increased from 0.06 to 0.2. Also, a further increase, e.g., from $X_{OEGDG} = 0.2$ to $X_{OEGDG} = 0.25$ was still useful to alter the materials' mechanical properties. In this way, it was possible to obtain a set of materials with E values covering the range of 900 to 0.2 MPa. At the same time, ε_B could be adjusted from 15 to $\approx$1300%, while σ_{max} decreased from $\approx$25 to 0.6 MPa. Overall, by the concept of blending PECA with OEGDG, a tailoring of the mechanical properties of PECA-based materials over a remarkably wide range has been established.

Conclusion

In order to obtain flexible PECA-based materials by a blending approach, different oligoethers have been explored for their potential to increase the material flexibility. It was shown that the compatibility of OEGDG with PECA was neither solely derived from the OEG main chain nor from epoxide end groups attached to oligoethers, but apparently was depending on a combination of both, the linear OEG chain and the epoxide endgroups. It could be excluded that a hydrolytically non-degradable, covalently crosslinked network was formed or that macrophase separation occurred. The deviation of decreasing experimental T_g's with increasing OEGDG content from predictions by the Fox equation may hint on specific interactions between the blend components beyond the concept of T_g additivity. Remarkably, the mechanical properties of this set of materials could be altered over a wide range, which so far not established for PECA-based materials. This motivates further studies based on the herein reported concept of homogeneously miscible blends to establish flexible polycyanoacrylate materials for various technical or biomedical applications.

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