Supporting Information

Highly Transparent Polyethylcyanoacrylates from Approved Eco-Friendly Fragrance Materials Demonstrating Excellent Fog-Harvesting and Anti-Wear Properties

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Low vapour pressure solvents

Further experiments were conducted with more solvents comparable to vapour pressure of cyclopentanone that includes 2-butanol, chlorobenzene and anisole. Our results indicate that although 2-butanol instantly reacts with cyanoacrylate therefore it is not a suitable solvent for our proposed research (see figure S1 a & b). Furthermore, to validate our discussion about low vapour pressure solvents, two more solvents were tested with low vapour pressure including chlorobenzene with 7.5 mmHg and anisole with 3.54 mmHg whereas reported solvent cyclopentanone has vapour pressure of 11.4 mmHg. As shown in figure S1 (c & d) by controlling rapid polymerization and limiting interaction of monomers with ambient humidity, it is possible to fabricate transparent films from those solvents as long as they do not react with the monomer.

Figure S1. (a) Instant reaction of 2-butanol with cyanoacrylates. (b) Agglomeration of opaque non-uniform structure. (c) Formation of transparent freestanding ultra-transparent film with chlorobenzene (d) Formation of freestanding transparent film with anisole.

NMR of Benzyl alcohol and PECA

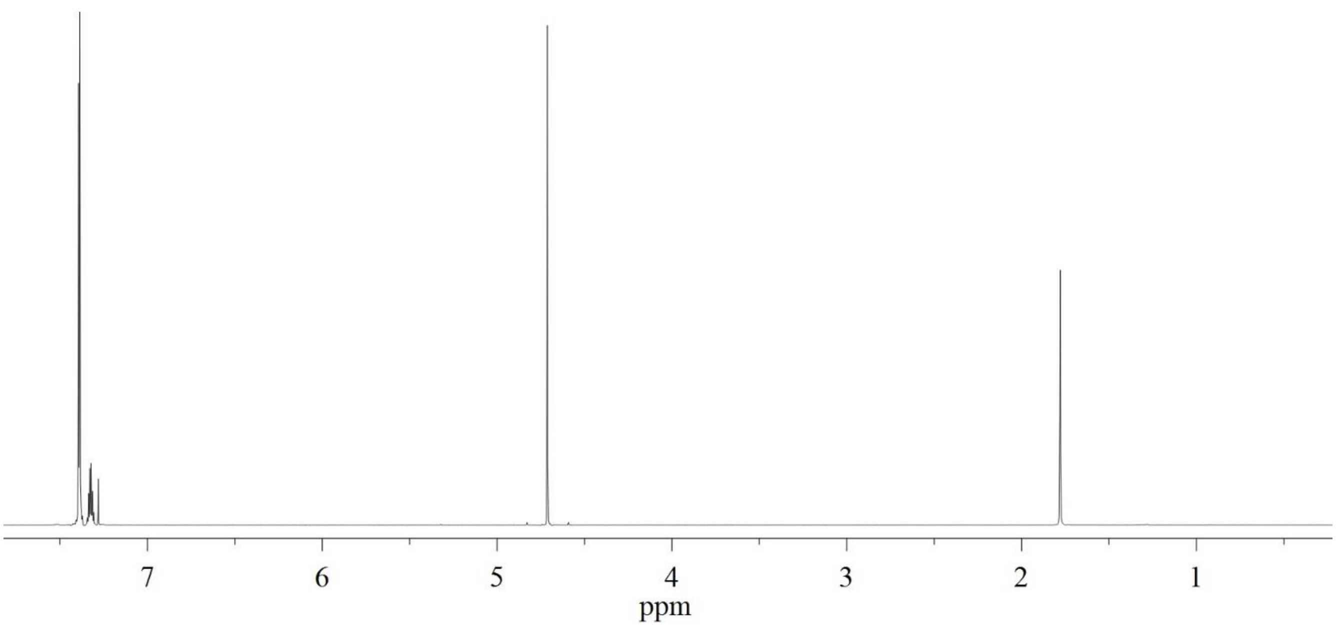

Figure S2. 1H NMR spectrum of reference material, benzyl alcohol, in CDCl3.

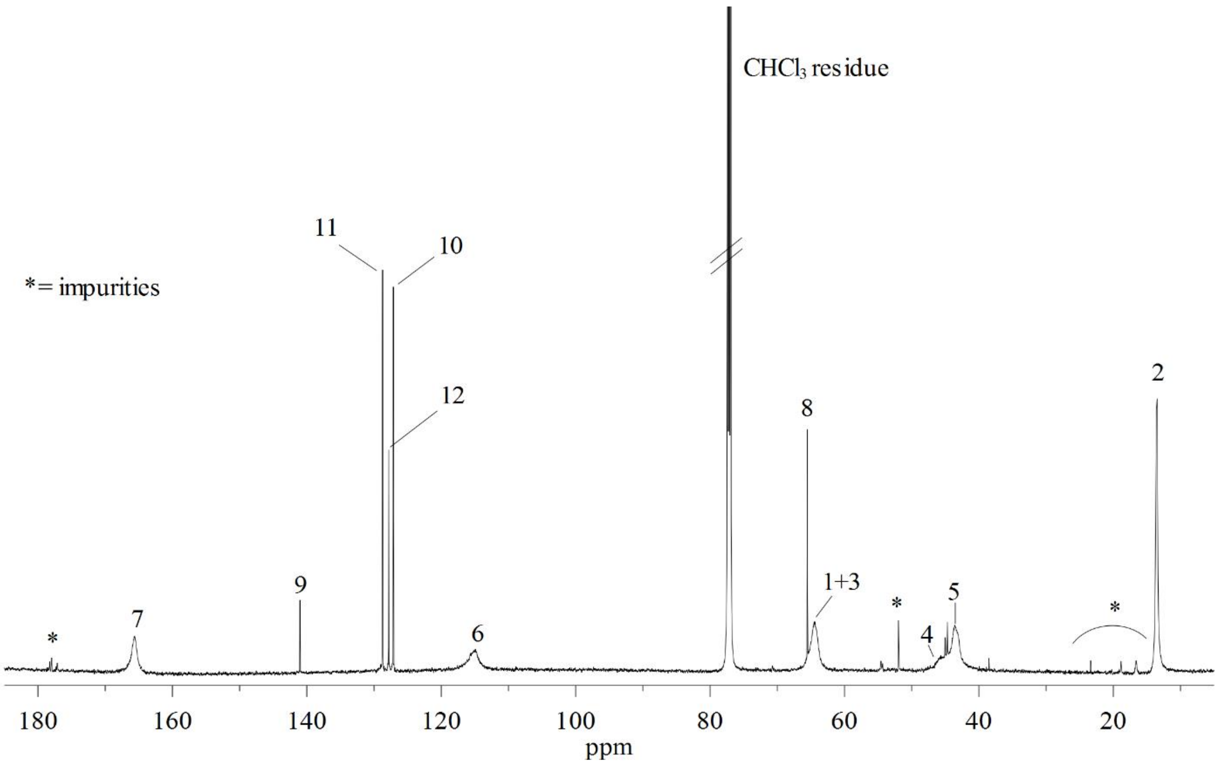

Figure S3. ^{13}C NMR spectrum of PECA in $CDCl_3$.

Benzyl alcohol release kinetics Results

Release kinetics of benzyl alcohol for PECA films inside water were detected by UV-visible spectrophotometer. For release kinetics of the PECA films, 50 mg pre weight of the samples were cut and placed in water solution such as the sample concentration of PECA with benzyl alcohol was 50/50 wt. %. The evaluation of the extracted benzyl alcohol release was detected by UV-Vis spectroscopy after defined time intervals up to 10 hours. UV-visible spectra for kinetic release of benzyl alcohol after 8 hours to 10 hours remained unchanged suggesting that unbounded benzyl alcohol moieties were dissolved in water for the first 8 hours (shown in Fig. S4). Concluding the release kinetics results of benzyl alcohol, we can say that even immersing it for 10 hours in water, still there are benzyl moieties inside PECA structure that is also confirmed by NMR results.

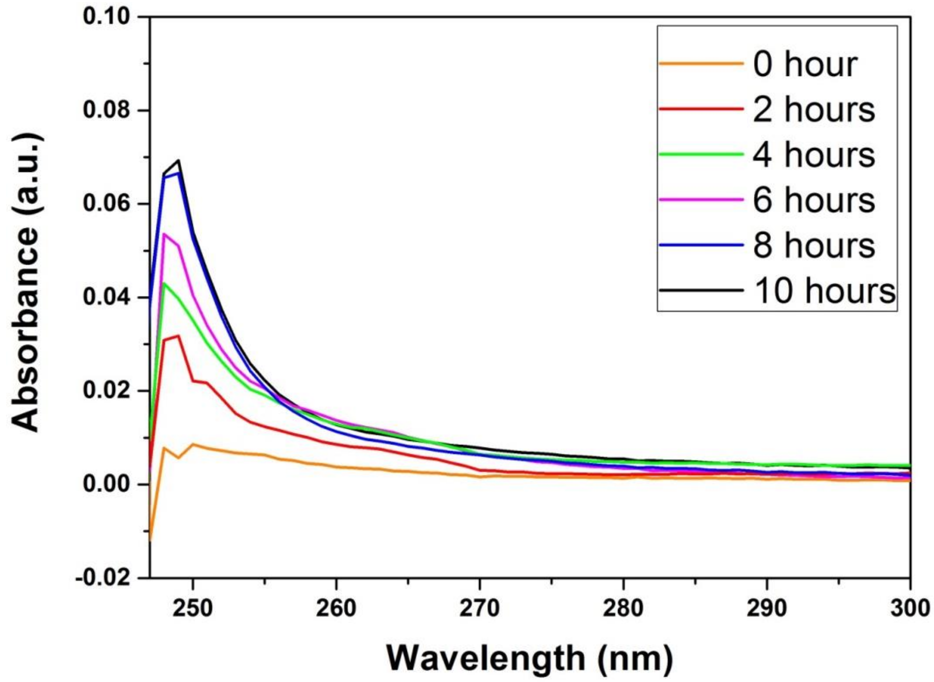

Figure S4. UV-Vis spectral results of PECA 50/50 for kinetic release of benzyl alcohol inside water medium studied at different time intervals.

FTIR of Benzyl alcohol

Pure benzyl alcohol peaks are added in the IR structure for comparison purposes. In addition, peaks for benzene ring in the range of 1400-1600 cm^{-1} are further highlighted in inset of the figure. Shift in the peaks are explained in the manuscript already. Also, collective peaks around 3335 are strong evidence that benzyl alcohol is in the fabricated coatings. In addition, NMR spectrum clearly shows the presence of benzyl alcohol with aromatic signals in its typical region, 7.4-7.3 ppm that can be found in figure S2.

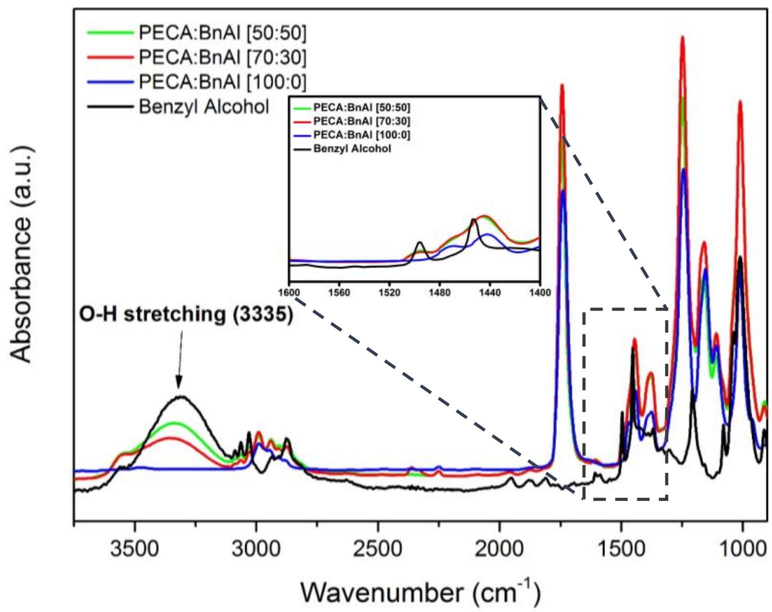

Figure S5. FTIR-spectra of pristine PECA with different concentrations of benzyl alcohol and of pristine benzyl alcohol.

Nano-indentation Results

Hardness and elasticity of the coatings were characterized by nanoindentation on an Anton Paar UNHT equipped with a diamond Berkovich tip. Maximum load was 1 mN whereas loading and unloading time was 30 s, with a dwell time at maximum load of 30 s to allow viscous relaxation. Hardness H of the materials were calculated by the Oliver & Phar method[1] with at least 10 repetitions for each material. As indicated by results, hardness of the coatings decreased as we introduced benzyl alcohol inside matrix. Conversely, elastic energy of the coatings increased after addition of benzyl alcohol (Fig. S6).

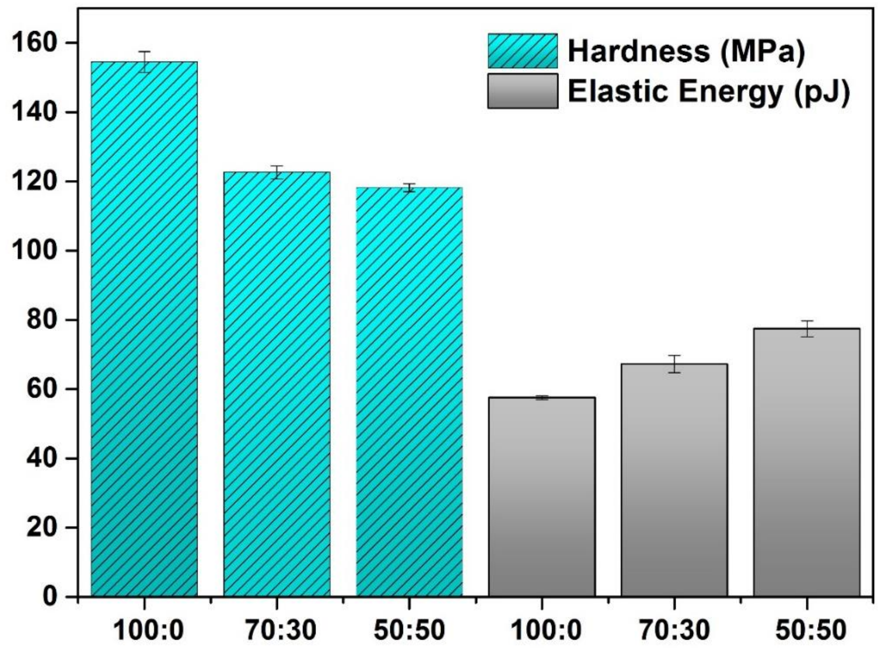

Figure S6. Nano indentation results for hardness and elasticity of PECA coatings with variant concentration of benzyl alcohol.

Biodegradability Results

Biodegradability was evaluated on selected plasticizers, added in PECA, through a standard biochemical oxygen demand (BOD) test that is an indirect method that estimates mineralization by measuring the oxygen amount consumed during a degradation reaction [2,3]. The tests were performed on PECA with benzyl alcohol whereas plasticizers were added including glycerol and poly-ethyl-glycol (PEG). For each sample, three measurements were conducted and weighted samples were carefully cut in small pieces and immersed in 432 mL bottles containing seawater collected from Genova area shorelines. The solutions in the bottles were stirred with magnetic anchors for 30 days in the dark, mimicking the pelagic marine environment. Consumed oxygen in biodegradation reaction was detected by OxiTop caps (monitors changes in oxygen level) and was recorded at different time intervals. For reference, BOD from blank bottles filled with only sea water was measured.

Fig. S7 shows biochemical oxygen demand (BOD) measurements for PECA containing benzyl alcohol and plasticizers. Oxygen consumption for all the PECA samples started after day one and continued to increase until 6 days. Total amount of oxygen consumed was around 40 mg that gives a significant degradation kinetics in bacterial and enzymatic conditions. PECA with benzyl alcohol had a linear increase in oxygen consumption that lead to days 5. Whereas PECA after addition of PEG increased the degradation kinetics and oxygen consumption was more exponential. Contrary, PECA with glycerol had a linear oxygen consumption and lasted till day 6. Ensuring the degradability of waste plastic material especially in sea water helps to avoid environmental pollution and to sustain a contaminated free ecosystem.

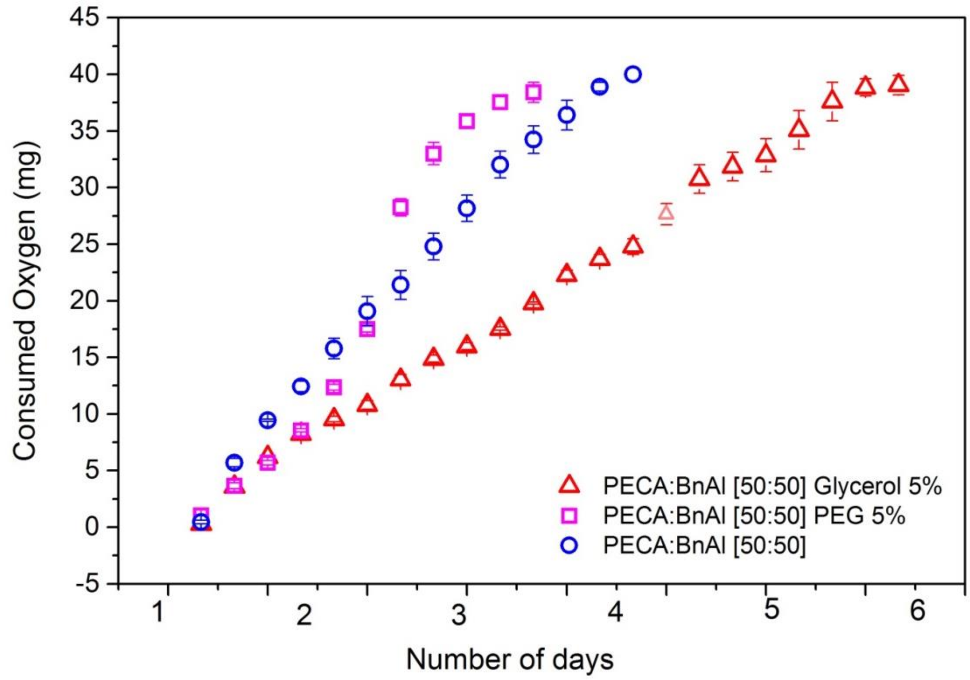

Figure S7. Oxygen consumption data for PECA with different plasticizers content immersed in Mediterranean seawater maintained in dark water.

References

(1) Oliver, W. C.; Pharr, G. M.; Introduction, I. Experiments. **1992**.

(2) Tosin, M.; Weber, M.; Siotto, M.; Lott, C.; Innocenti, F. D. Laboratory Test Methods to Determine the Degradation of Plastics in Marine Environmental Conditions. *Front. Microbiol.* **2012**, *3* (JUN), 1–9.

(3) Ceseracciu, L.; Heredia-Guerrero, J. A.; Dante, S.; Athanassiou, A.; Bayer, I. S. Robust and Biodegradable Elastomers Based on Corn Starch and Polydimethylsiloxane (PDMS). *ACS Appl. Mater. Interfaces* **2015**, *7* (6), 3742–3753.