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Controlled Photodegradation of Phenyl Vinyl Ketone Polymers by Reinforcement with Softer Networks

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Abstract

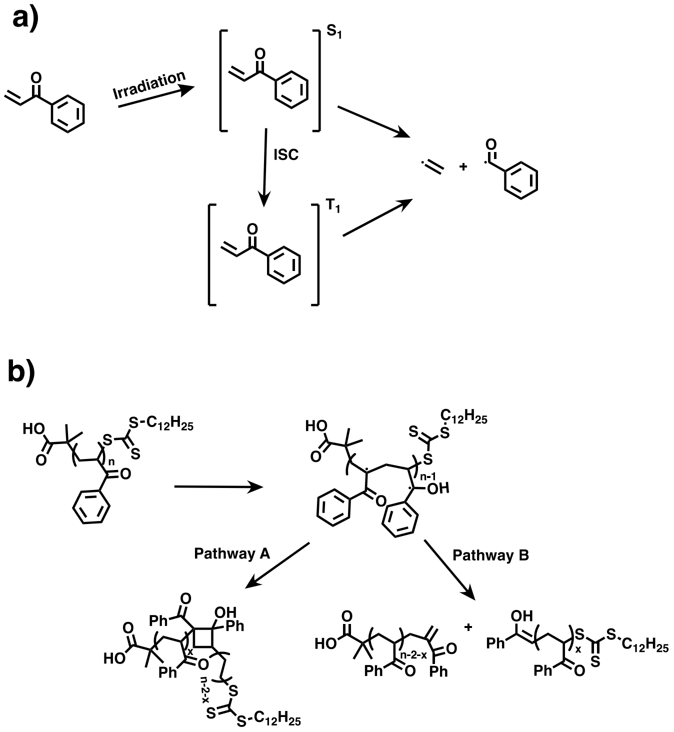
The photodegradation of polymer materials represents a promising solution for addressing the challenges associated with plastic waste management within the environment. Vinyl ketone polymers, such as phenyl vinyl ketone (PVK), exhibit backbone degradation upon exposure to ultraviolet (UV) light. However, this property leads to significant degradation of PVK polymer materials within a few years under simulated sunlight conditions. While this is advantageous for waste management purposes, it can adversely impact the lifespan of these materials in practical applications. This study demonstrates a novel approach to control the degradation of PVK materials by incorporating a secondary network, based on poly(ethyl acrylate), within the polymer matrix. This approach allows for the manipulation of the material's mechanical properties while also enabling the controlled photodegradation of network materials.

Introduction

Research on polymer degradation and end of life for polymers has become an increasingly important in recent years.[1–3] Most importantly, the degradation process of polymers can be triggered by exposure to a variety of chemicals, heat, UV irradiation, solvents, microorganisms among others.[4–8] As a consequence of degradation, polymer materials often experience loss of optical and physical properties, including the shape, strength, color, and weight.[9–12] Due to the widespread use of polymer materials in industrial and consumer applications it is important to develop controlled polymer degradation procedures.[13] However, studies have shown that the degradation process is often random and difficult to control once it starts.[14–17]

Polymers containing ether, carbonyl, or aromatic functional groups undergo degradation under ultra-violet light.[18,19] Phenyl vinyl ketone (PVK) polymers, in particular contain an acetophenone subgroup in every repeating unit, making them highly susceptible to photo degradation under UV light.[20–26] Further, PVK monomers act as intrinsic photo initiators through a proposed Norrish type I process (Scheme 1a). The photodegradation of PVK polymers has been reported in both polymer solutions and in material levels through Norrish II process (Scheme 1b).[27–31] However, the rate of the degradation can vary depending on the power of the UV source, with the degradation times changing from couple of days to few years.[32] In earlier studies, PVK containing thermoplastic elastomers have been synthesized, with fast and substantial degradation (>24 hrs) under strong source of UV light.[32] This is extremely beneficial for the targeted photodegradation of damaged or no longer useful products. Conversely, materials that are still in use will also degrade at same rate, reducing their useful lifetime under UV sources such as the sun.

As a potential solution for this matter, this work develops crosslinked PVK polymers integrated with another polymer network to synthesize an interpenetrated network (IPN) system. This allows for controlled degradation of PVK materials even under strong UV sources.[1] IPNs typically consist of two or more polymer networks in which each polymer component behaves independently within the matrix. Depending on the nature of the networks, the IPNs can be divided into two subcategories.[33–37] An IPN (which can be considered a full or true IPN) contains two different polymer networks with distinct, yet orthogonal crosslinkers. A semi IPNs contains two different networks: with only one of them containing crosslinkers. In this study, PVK polymers are incorporated into both IPN and semi IPN systems and compared to unmodified PVK materials to gain insight into obtaining controlled photodegradation within the materials. Systems contained reprocessable second networks, with either no crosslinks as in the semi IPN or dynamic crosslinks in the IPN, which could be important for sustainable use of these polymers.



Scheme 1: Proposed Mechanism of a) self-initiated photo-polymerization of PVK. b) photo-degradation of poly(PVK).

Results and Discussion

Synthesis of Polymer Networks

In the preparation of IPN systems, first crosslinked network was synthesized using ethyl acrylate (EA) as the backbone monomer and 2-(((6-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)hexyl)carbamoyl)oxy)ethyl acrylate (UPyA) as the crosslinker, through free radical polymerization (FRP). The choice of UPyA crosslinker was driven by several considerations, including its ability to form strong quadrupole H-bonds through dimerization,[38,39] which enhances the mechanical properties such as toughness and fracture energy.[38] Judicious choice of UPyA content gives a balance between elasticity and plasticity, and provides nanoscale aggregates of hydrogen bonded units.[40] Further, UPy functional groups have been proven to be stable under UV irradiation, making them a critical component for high performance materials.[41] Most importantly, the hydrogen bonded UPyA centers have been identified as scattering centers against irradiation.[42–44]

The second network comprised of PVK as the backbone monomer and ethylene glycol methacrylate (EGDMA) as the crosslinking agent. Similarly, semi IPNs were synthesized using EA polymer intertwined with poly(PVK-EGDMA) network. All the polymers were analyzed by SEC (Figure S1a and S1b). IPN and semi IPN network systems were prepared by mixing the corresponding polymers with different ratios and changing the crosslink densities (Table S3 and S4) using DMF as the solvent.

The pure PVK materials with 2.5% and 5% EGDMA crosslinkers displayed glass transition temperature (T_g) around 80 °C (Figure S2), while the semi IPN and IPN materials displayed two T_g values at approximately –10 °C and 80 °C which are consistent with poly(EA)/poly(EA-UPyA) and crosslinked PVK respectively (Figure S3a and S3b). Furthermore, all the materials (crosslinked PVK, semi IPN, and IPN) demonstrated a characteristic peak IR absorption around 1680 cm^{-1} corresponding to the ketone C=O stretching in PVK (Figure S1c). The semi IPN and IPN materials possessed another sharp absorption peak around 1730 cm^{-1} corresponding to the ester group in the ethyl acrylate indicating the presence of a second network within their matrix. The properties of each material were also evaluated by temperature sweep dynamic mechanical analysis (DMA). The degradation rate of the IPN and semi IPN networks were compared with the degradation speed of the pristine poly(PVK-EGDMA) system. Each material was irradiated with 310 nm UV light to study their degradation over time. After the irradiation time was completed, the storage and loss moduli of the materials were compared to the pristine samples by DMA temperature sweep experiments.

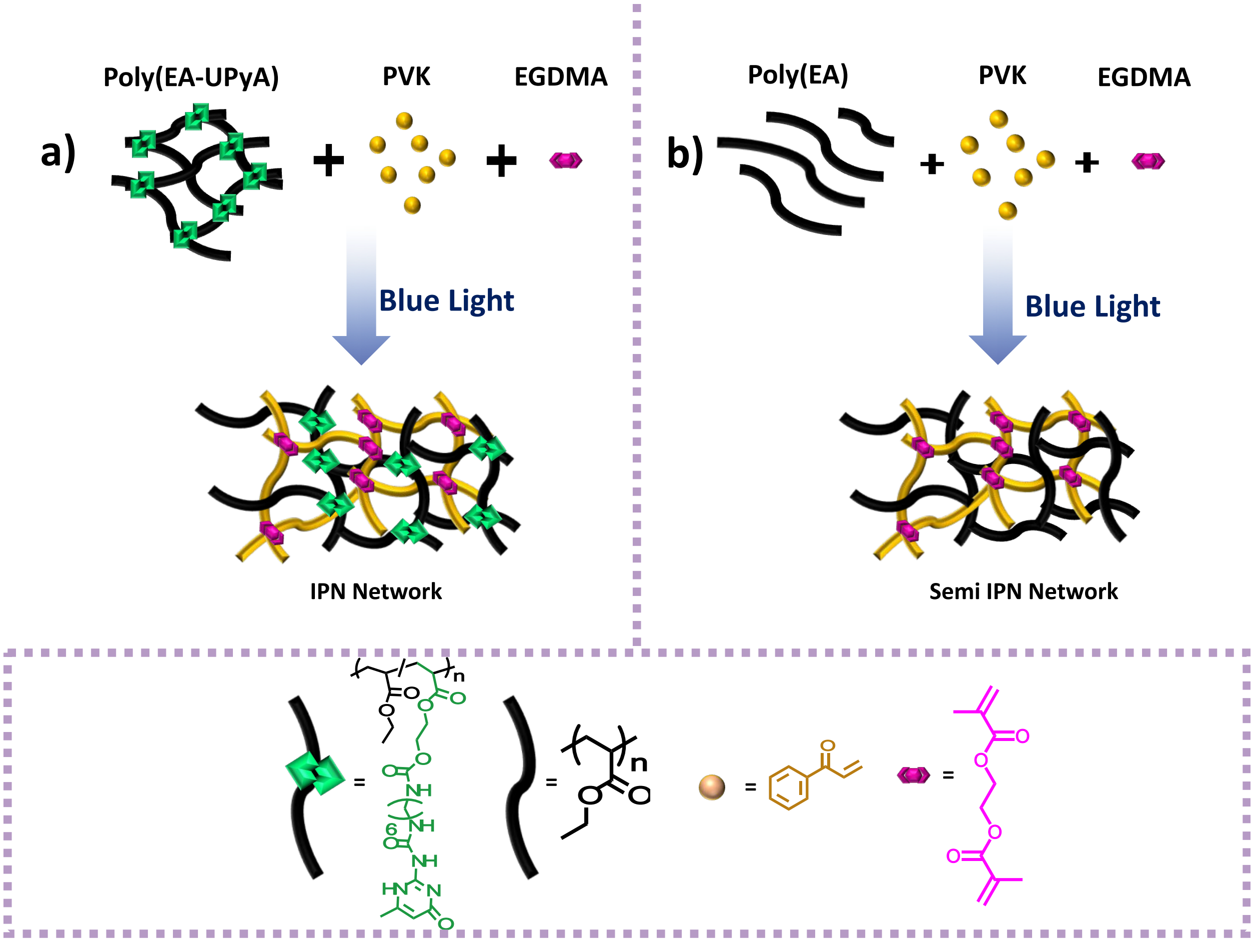


Figure 1: Schematic representation of synthesis of a) IPN and b) semi IPN networks.

It is important to note that the synthesis of the IPN-based materials not only affects their mechanical properties of the materials but also their physical appearance as well. Prior work has shown that the PVK polymer chains can be combined with a monomer having a lower T_g to obtain phase separated block polymers.[32] These block polymer materials displayed degradation under strong source of UV light. However, it is noted that mixing of poly(PVK-EGDMA) networks with another polymer network (poly(EA-UPyA) or poly(EA)) can cause phase separation, as indicated by two T_gs, and affect their light absorbance capabilities (Figure 2a) as well.

The IPN approach offers a straightforward synthetic methodology to effectively modulate the photodegradation of the PVK polymers, eliminating the need for preparation of block polymers. Additionally according to previous reports in the literature,[42–44] the UPyA units can further contribute to scattering phenomena, through nanoscale assembly of the UPy units, resulting a loss of transmittance within the materials. The poly(PVK-EGDMA) systems displayed a strong increase in % transmittance starting from 375 nm wavelength, while the IPN and semi IPN materials displayed 0% transmittance within the entire UV-Visible region (Figure 2a). This decrease in transmittance may arise from either phase separation between the two networks or the inclusion of species (e.g., UPyA units) capable of scattering light more effectively than the unmodified PVK material. However, the introduction of the second network controlled the light absorbance of these materials and modulated their degradability under strong UV sources. Further, mixing with crosslinking or non-crosslinking matrices also expanded their processing temperature range by increasing the crossover points and glass transitions of these materials (Figure 2b). The PVK-EGDMA system displayed E' and E" crossovers around 80 °C, closer to the observed T_g of PVK polymers. IPN and semi IPN systems displayed crossover temperatures around 110-120 ºC , demonstrating an increment in their service temperature and temperature tolerance.

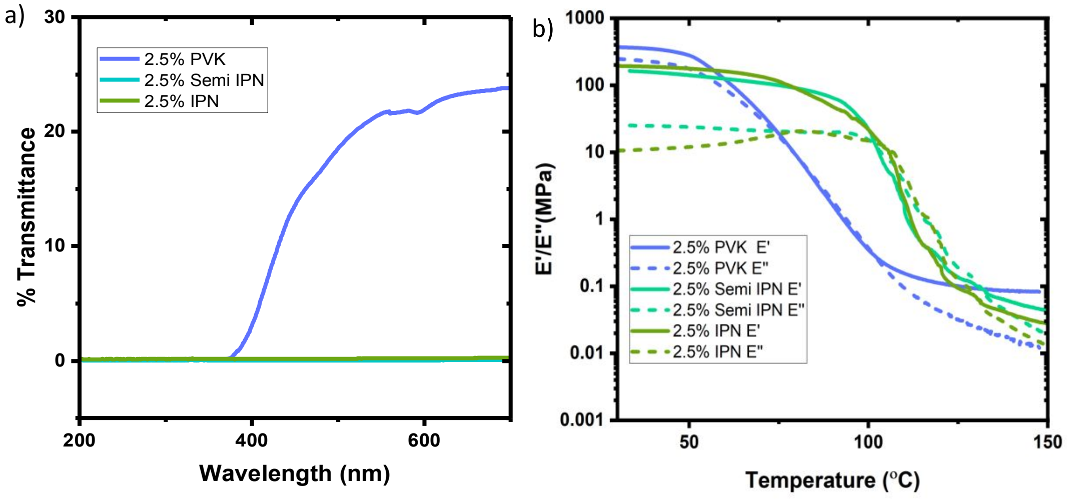


Figure 2: a) % transmittance of poly(PVK-2.5% EGDMA) network, semi IPN system (with poly(EA):PVK=1:1 and 2.5% EGDMA) and IPN system with (poly(EA-UPyA):PVK=1:1 and 2.5% EGDMA). b) Temperature sweeps of poly(PVK-2.5% EGDMA) network , semi IPN system (with poly(EA):PVK=1:1 and 2.5% EGDMA) and IPN system (with poly(EA-UPyA):PVK=1:1 and 2.5% EGDMA).

Upon changing the ratio of PVK to EA in the IPN or semi IPN materials, the modulus of the materials changed. The introduction of higher quantities of the softer network lowered the modulus of the materials (Figure 3a and 3c) while introduction of a higher density of crosslinks with PVK increased the modulus of these materials (Figure 3b and 3d). Additionally, the second networks reduced the material's apparent swelling capabilities compared to the pristine PVK materials in THF (Figure S6). This is most pronounced for the semi IPN containing poly(EA) which can freely diffuse into the network, with the IPN materials crosslinked by UPy in the second network having only slightly lower apparent swelling properties to the pristine PVK network. A potential reason for this observation for the lower apparent swelling in the semi IPN is that solvent replaces some of the volume originally occupied by the poly(EA) chains, as they diffuse into the THF, reducing the apparent swelling ratio. A similar effect, albeit weaker, could be at play in the UPy crosslinked poly(EA) chains in the IPN material.

However, increasing the amount of softer matrix increased the apparent swelling of these IPN materials in THF (Figure S7). Softer segments (poly(EA) or poly(EA-UPyA)) do not contain any permanent crosslinks within their matrix. Therefore, materials containing softer components can diffuse more solvent within the network, resulting a higher swelling ratio. Additionally, the higher content of non-covalently crosslinked polymers can loosen the effective crosslink density in the PVK matrix, causing this network to be able to swell more, especially as the EA based chains diffuse into the solvent. However, when the permanent crosslinkers increase within the matrix, the materials become stiffer and thus are not able to swell as much (Figure S8). Hence, decreased swelling ratios occurred with higher permanent crosslink density.

The materials were degraded under 310 nm UV light which is significantly higher (>500 times) than the typical UVB intensity found in most tropical and non-tropical countries on a sunny day (UVB intensity < 0.15 mW/cm^2).[32] Upon exposure to UV light, the swelling capacity of the semi IPN and IPN materials increased (Figure S6-S8). This is likely due to the scission of the PVK chains within the matrix and a decrement in the chain entanglements as a result of the photo degradation. In contrast, the swelling capacity of the pristine PVK materials decreased upon exposure to UV light. Unlike semi IPN and IPN matrices, theses PVK materials lack support from a second network, such as poly(EA) or poly(EA-UPyA) network within their matrix. Hence, as the PVK chains degrade with the UV light, they tend to dissociate into solvent, causing lower apparent swelling ratios than the original samples. However, the SEM images swelled samples of 5% pristine PVK samples, semi IPN samples and IPN samples did not reveal any discernible morphological changes such as cracks or fissures, following degradation (Figure S11). It is possible that these changes have been obscured by the presence of surface wrinkling resulting from swelling.

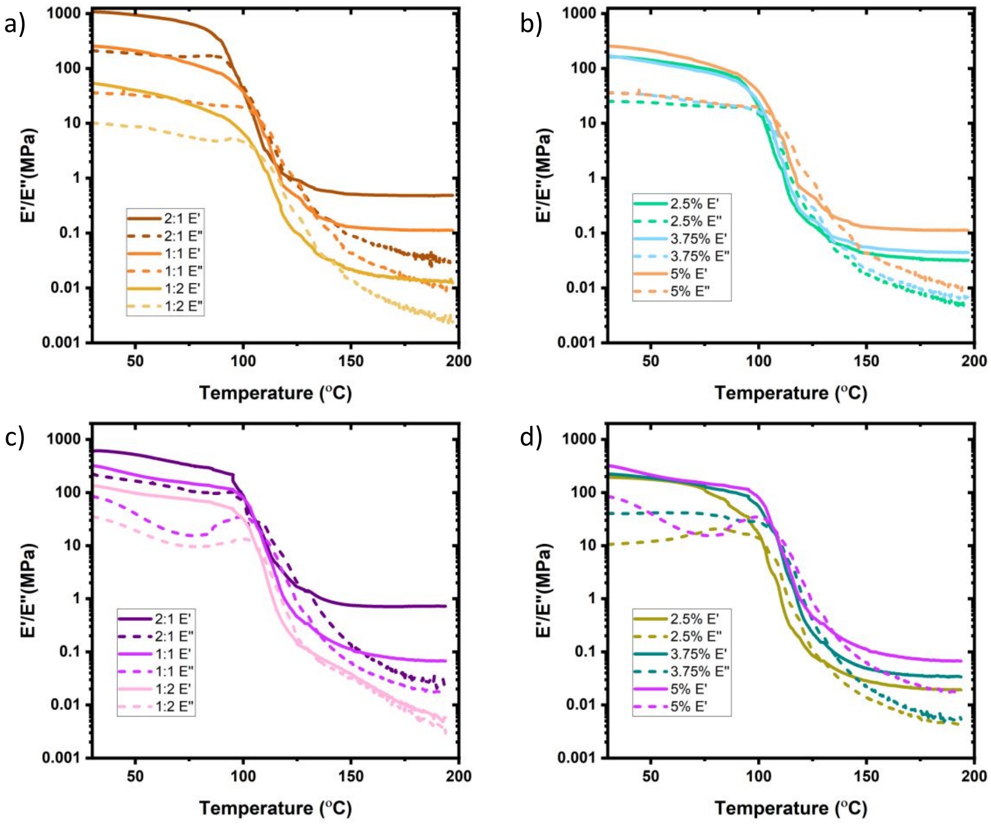


Figure 3: Temperature sweep experiments of a) semi IPN materials by varying the ratio between PVK:poly(EA), b) semi IPN materials by varying the EGDMA crosslink density within PVK network, c) IPN materials by varying the ratio between PVK:poly(EA-UPyA), d) IPN materials by varying the EGDMA crosslink density within PVK networks.

When irradiated with the 310 nm UV source, the pristine poly(PVK-EGDMA) materials displayed faster degradation and lost their original elastic modulus within a few days (Figure 4a). Prior to the temperature sweep experiments, the irradiated material's surface was washed with THF in order to remove the degraded short PVK chain from the surfaces. These degraded short PVK chains cause the materials to have a tacky surface after photoirradiation and display liquid like properties during the temperature sweep experiment (Figure S9). The effect of PVK degradation was also studied by UV-Visible spectrometry. The degraded poly(PVK-EGDMA) materials tend to display higher transmittance when compared to the original samples. The increased transmittance observed in these materials, a result of photodegradation, is indicative of a significant diminution in their absorption efficiency, as well as structural modifications within the material.

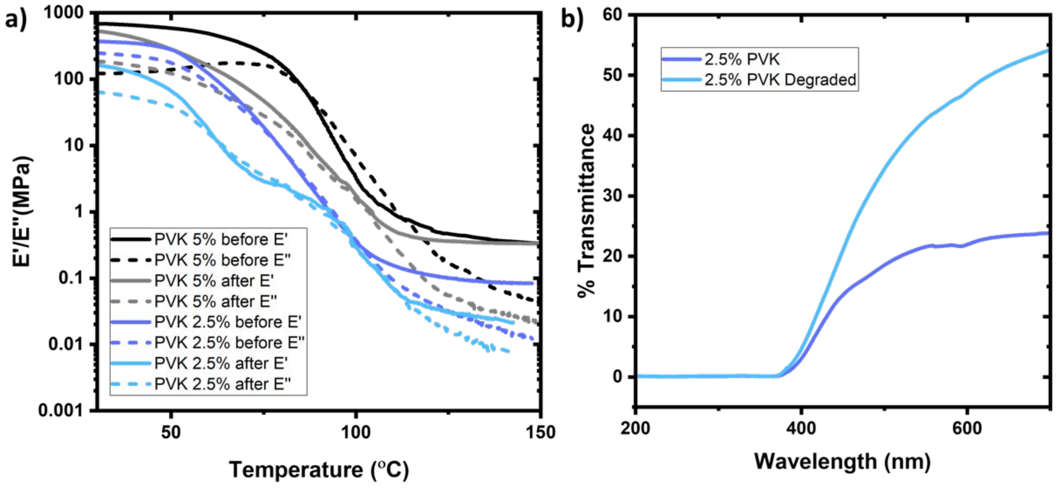


Figure 4: a) Temperature sweeps of PVK materials with 2.5% EGDMA and 5% EGDMA before and after 2 days irradiation with 310 nm UV light. b) % transmittance of degraded and non-degraded 2.5% EGDMA containing PVK networks.

In contrast to the pristine PVK based materials, the IPN and semi IPN materials demonstrated superior stability under 310 nm UV light exposure, even after 2 days of irradiation

(Figure 5a and 5b). When comparing the two IPN systems, IPN materials displayed higher stability than semi IPN materials. These systems displayed similar or slightly higher moduli following degradation in comparison to their original moduli even after prolonged exposure to high strength UV radiation over consecutive days (Figure 5b) due to the support provided by the dynamic bonding from UPyA networks. Despite the degradation of the poly(PVK) network, the presence of H bonding from the UPyA dimerization imparts stiffness to the materials. The semi IPN systems exhibited slightly lower stability under UV irradiation (Figure 5a), although the photodegradation of the semi IPN materials was still substantially slower than the pure poly(PVK) based networks. The incorporation of the poly(EA) network within the crosslinked poly(PVK-EGDMA) network can prevent the disintegration of the degraded poly(PVK) segments and strengthen the matrix.

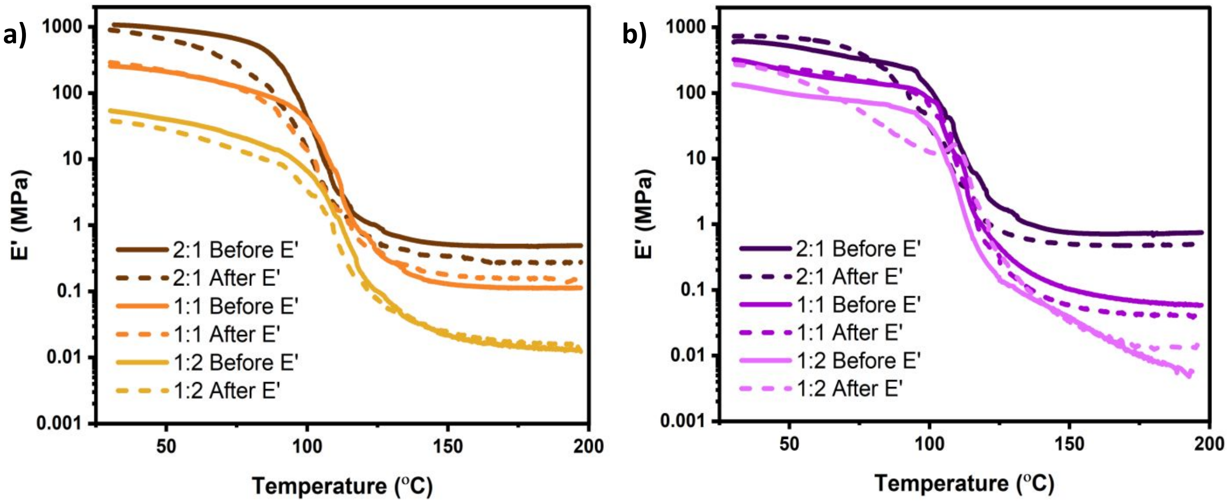


Figure 5: a) Temperature sweeps of semi IPN materials with different constitutions of PVK:poly(EA) ratio with 5% EGDMA crosslinks before and after 2 days irradiation with 310 nm UV light. b) Temperature sweeps of IPN materials with different constitutions of PVK:poly(EA-UPyA) ratio with 5% EGDMA crosslinks before and after 2 days irradiation with 310 nm UV light.

With higher proportions of the UV-sensitive PVK polymer in the IPN matrix, a slight decrease modulus was observed after photodegradation. This could be due to more degradation taking place within the matrix compared to 1:1 system. However, when compared to the degraded pristine poly(PVK) samples, this decrease was minimal, indicating that the semi IPN matrix provided a significant level of protection against UV-induced degradation. Importantly, even though the semi IPN materials do not consist of any permanent or dynamic crosslinks except for the EGDMA in poly(PVK) network, the entanglements of poly(EA) network within the poly(PVK-EGDMA) system avoid the structural disintegration of these materials. Furthermore, it was observed that the systems with 2.5% EGDMA and 3.75% EGDMA had a measurable photodegradation in comparison to the 5% EGDMA samples for the 1:1 PVK:poly(EA) semi IPN materials (Figure S10). This suggests that an increase in crosslink density may prevent the disintegration of the degraded PVK networks in these semi IPN materials, providing a higher level of stability against photodegradation. Overall, the results suggest that increasing the portion of second network, and crosslink density in the IPN materials enhances their stability against UV irradiation.

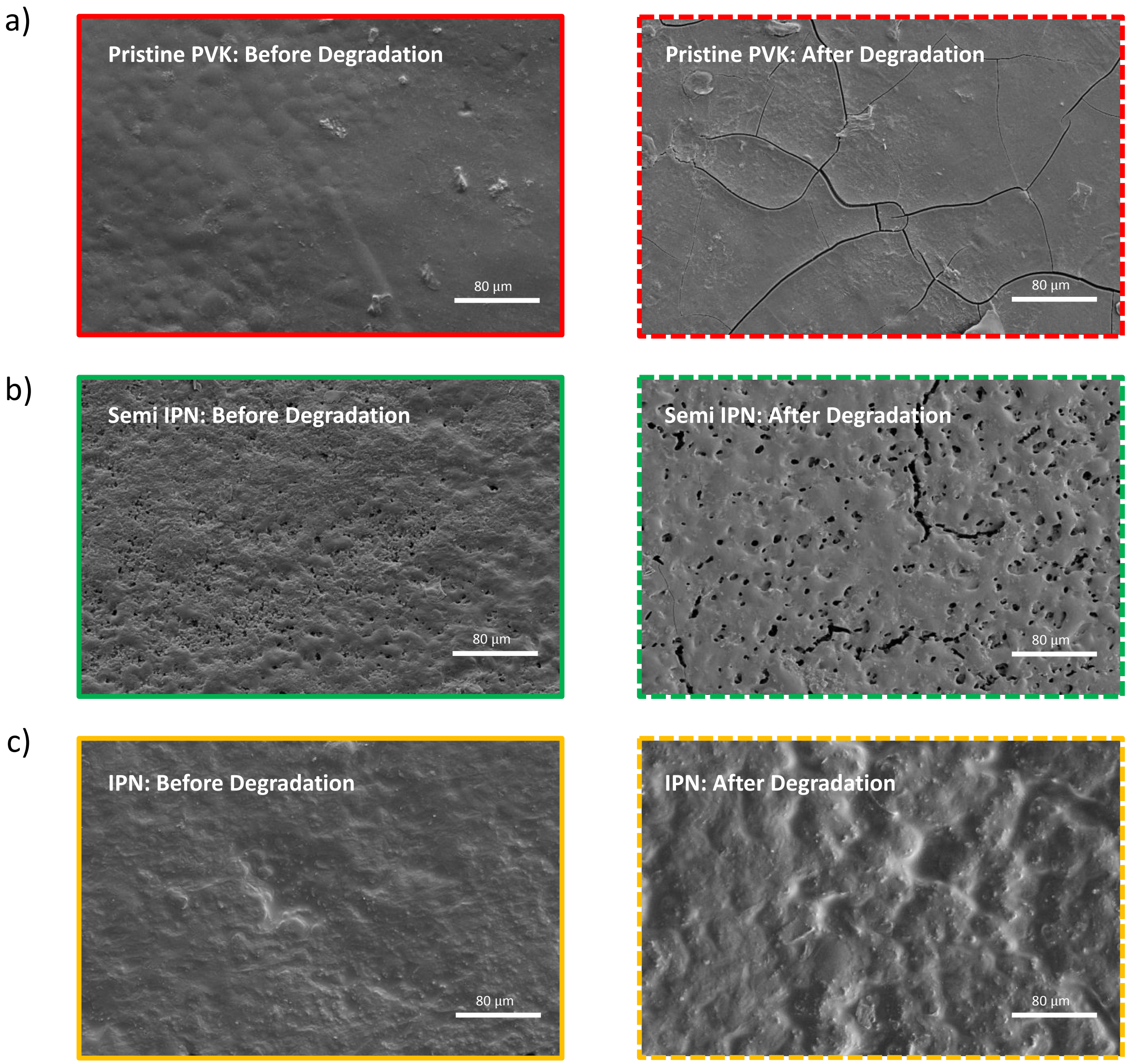


Figure 6: SEM images for a) pristine PVK materials with 5% EGDMA, b) semi IPN with 5% EGDMA and, c) IPN with 5% EGDMA. The solid colors indicate the images before degradation while the dashed colors indicate the images after 2 days of degradation.

To provide additional evidence regarding the temperature sweep data, scanning electron microscopy (SEM) was utilized to capture images of the materials before and after degradation. Figure 6 demonstrates that the pristine PVK 5% samples exhibited a comparatively smoother surface when contrasted with the semi IPN and IPN 5% materials, which displayed a rougher and more rutted texture. However, after photodegradation, the PVK 5% materials exhibited fissures that propagated throughout their previously smooth surfaces. In contrast, the semi IPN materials exhibited relatively smaller and localized cracks within their inherently rough surface. Remarkably, the IPN materials showcased minimal changes on their surfaces after undergoing degradation after 2 days.

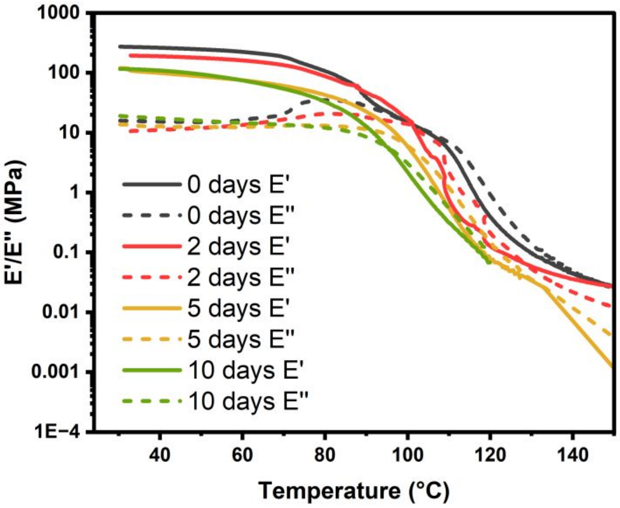


Figure 7: Temperature sweeps data for the IPN materials (with PVK:poly(EA-UPyA)=1:1 and 5% EGDMA) before degradation and 2 days, 5 days, 10 days after irradiation.

To explore their long-term stability, the IPN materials were subjected to additional irradiation for 2 days, 5 days and 10 days (Figure 7 and Figure S12). Following 5 days of irradiation, the temperature sweep data in Figure 7 displayed a decrement in the elastic modulus and crossover temperatures. By comparing the initial modulus from the temperature sweep plots, equation (3) was used to compute the degree of degradation (% degradation). The calculations revealed a minimum degradation of 8% of 5% IPN materials after 2 days, while more substantial degradation occurred with prolonged exposure (55% for 5 days and 58% for 10 days). Most importantly, the majority of the degradation predominantly occurs at the surface due to irradiation-induced surface degradation, which can lead to some variability of the observed bulk degradation rate. Furthermore, in a natural environment the degradation should accelerate as degraded surfaces are removed by natural forces such as rainfall, and abrasion by airborne particulates.

Both temperature sweep and SEM provide complementary evidence of photodegradation. The SEM analysis both complements the temperature sweep data, and the SEM data unveiled minute cracks after 5 days of consecutive days of irradiation. Upon reaching 10-day mark, these cracks had propagated throughout the material and were even visible to the naked eye. Furthermore, the material’s structural integrity was compromised at higher temperatures, as evidenced by its failure during temperature sweep experiment at 120 °C. However, the addition of the second matrix in the PVK materials enhanced the protection against their known susceptibility to degradation under UV light up to 10 days under extreme UV conditions, thereby prolonging the material's lifespan. The inclusion of UPyA in the second matrix further enhances the material's defense against degradation under UV light by means of extended scattering effects.

Conclusions

In conclusion, the photodegradation of PVK based materials was investigated by combining the PVK network with a poly(EA) based network through the synthesis of semi IPN and IPN materials. The pristine PVK materials exhibited rapid photodegradation (within just 2 days) under 310 nm UV radiation, resulting in a substantial loss of mechanical properties. In contrast, when the PVK based network was combined with poly(EA) or poly(EA-UPyA) polymers, the materials displayed significant surface degradation on the outer surfaces that were exposed to the UV irradiation. Further, the incorporation of poly(EA) and poly(EA-UPyA) into PVK networks enhanced their opacity and prevented the light transmittance through the materials, ultimately reducing the degradation of the PVK matrix in the middle. These findings suggest that when PVK materials were combined with other types of networks in the form of semi IPN or IPN, their photodegradation can be controlled. This study suggests that engineering of rapidly degrading materials with non-degradable materials can result in the control of degradation for the overall materials, as well as the mechanical properties.

Conflicts of Interest

The authors declare no competing conflicts.

Author Contributions

N.D.A.W. was involved in conceptualization, data acquisition, formal analysis and wrote the first draft of the manuscript. M.A.S.N.W was involved in data acquisition, formal analysis, editing and revising the manuscript. Z.O. was involved in data acquisition formal analysis and editing the manuscript. D.K. was involved in conceptualization, formal analysis, supervision and editing the manuscript.

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