**Insights into *in situ* Compatibilisation of Polydimethylsiloxane-modified Thermoplastic Polyurethanes by Dynamic Crosslinking: Relating Experiments to the Predictive Models**

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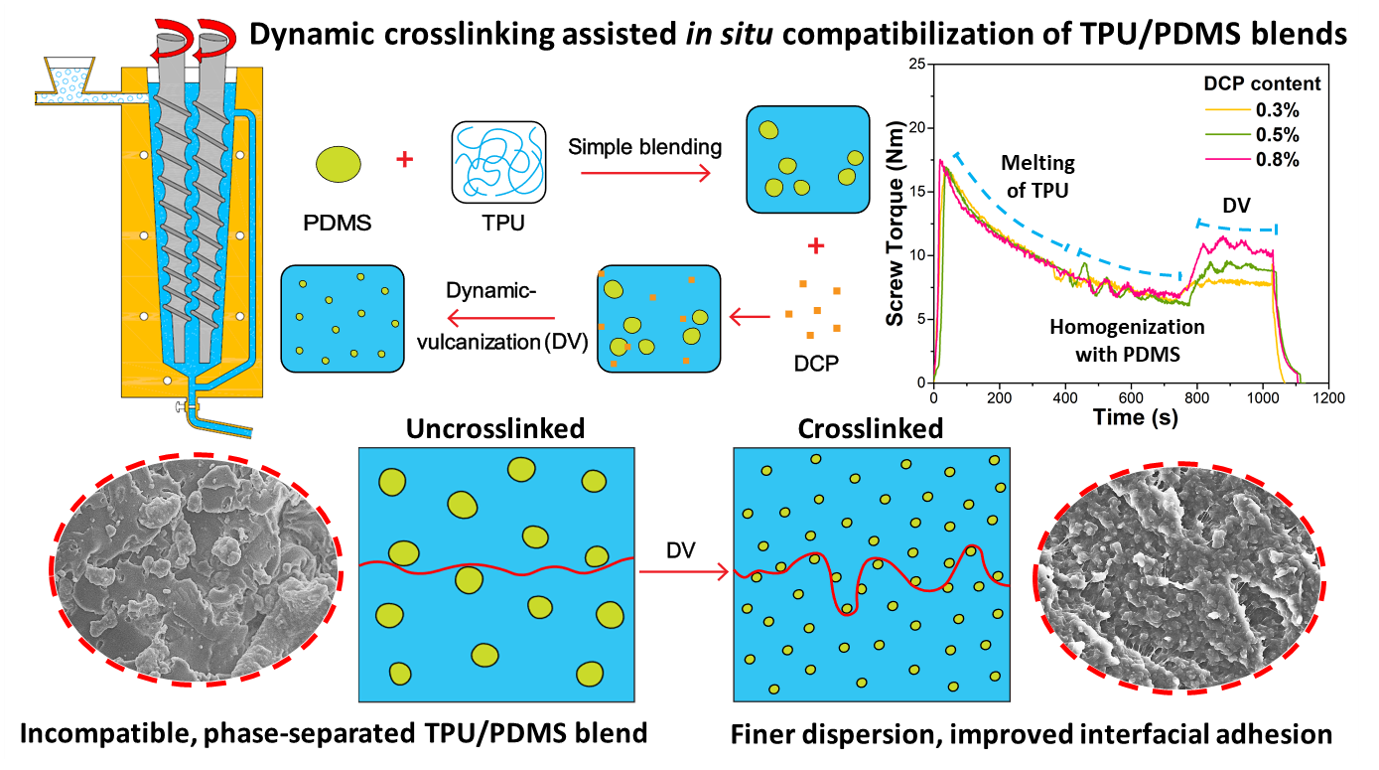
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**Abstract**

Thermoplastic polyurethanes (TPU) based biomaterials are widely investigated in fabricating biomedical implants and devices. The present study describes a dynamic vulcanisation inspired reactive melt-blending methodology to modify TPU with polydimethylsiloxane (PDMS) and ensure the selective *in situ* crosslinking of the PDMS phase. The influence of the peroxide crosslinker during melt-processing was assessed, and, thereupon, a complete set of dynamically vulcanised blends was prepared with varying PDMS content (10-40 weight %). Thus obtained thermoplastic vulcanisates (TPVs) were characterised for their crosslink density, mechanical properties, morphology and thermal stability and benchmarked against the uncrosslinked, pristine blends. The fractographic examination of the blend surfaces demonstrated a remarkable improvement in interfacial adhesion and a more refined microstructure for the TPVs, while a gross phase-separation was evident in the uncrosslinked blends. The experimentally determined tensile/compression response for the dynamically vulcanised system was in good agreement with the theoretical predictions, based upon the Halpin Tsai, Coran and Takayanagi models. The pristine blends, devoid of crosslinking, largely conformed to the lower-bound series model, implying immiscible and uncompatibilised behaviour. The analysis of stress-concentration parameters was also performed to gain further insights into the discontinuities in the stress transfer in the dual-phased blend system. Taken together, the obtained results affirmed the superior properties of TPVs and established the efficacy of dynamic vulcanization for the *in situ* compatibilization of the TPU/PDMS system, in good corroboration with the predictive models.

***Keywords:*** *TPU/PDMS blends;**dynamic vulcanisation; mechanical properties; crosslink density; phase morphology;* *phenomenological models; stress-concentration parameters*

**Graphical abstract**



**1. Introduction**

Thermoplastic poly(ether)urethanes (TPUs) are a highly versatile class of linear block copolymers with a two-phase morphology arising from an unusual, segmented composition of hard and soft units.1 The soft segments (SS) are typically derived from a polyether macro-diol, while the hard segments (HS) constitute a diisocyanate group and a chain extender. The variations in the respective chemistries of these two segments allow for immense structure-property diversity and impart the resultant polyurethane, a combination of excellent mechanical properties, good processability, as well as biocompatibility. In accordance, their application has been investigated for different medical devices and implants such as urethral catheters, ureteral stents, vascular grafts, heart valves, pacemakers.2,3 However, in some instances, particularly those pertaining to more extended indwelling periods in biological milieu, poly(ether)urethanes have been identified to undergo erosion or degradation. This can subsequently lead to surface or bulk environmental stress cracking and stiffening.4,5 The occasional incidences of compromised physical properties and eventual implant malfunction and failure have been primarily associated with the inadequate oxidative stability of the ether linkage within the macro-diols and the hydrolytic susceptibility of the urethane linkage joining hard and soft segments.6

To surmount such limitations, several strategies, like polydimethylsiloxane (PDMS) inclusion, are proposed for improving the biostability of TPU upon long-term *in vivo* exposure.4,7,8 PDMS has a long clinical history as an implantable biomaterial and is recognised for its biocompatibility, low tissue reactivity, good blood-contacting properties, high flexibility, anti-adhesive nature, and wear resistance.9,10 Nevertheless, the insufficient mechanical properties including low tensile strength, modulus and toughness, can often limit its wide range of applications. A secondary disadvantage associated with the conventional silicone elastomers is the requirement of crosslinking to develop desirable properties. Once crosslinked, the resultant thermoset silicone cannot be reprocessed or reshaped. In this context, it is prudent to design a silicone modified polyurethane system that synergistically integrates the favourable characteristics of both the constituent polymers. In the published literature, this has been pursued by introducing PDMS either as a coating, an end-capping agent, or a component of the SS of TPU.11 Such chemical procedures promote a silicone-rich surface due to the high mobility and low surface energy of PDMS. Since biodegradation initiates at the biomaterial surface, a surface layer of hydrophobic PDMS is desirable to prevent or retard initiation. This reduces the overall wettability and generates a protective barrier by the wrapping of flexible and non-polar silicone chains around the labile linkages of polyurethane.4,8,12,13

Among the different routes for silicone enrichment of TPU, the alteration of SS chemistries with PDMS has been most commonly explored (Table 1). Based upon the same concept, the first-generation silicone-based poly(ether)urethane, Avcothane® (Avco-Everett Co.), was developed in 1970s. It was described as a promising block copolymer for cardiovascular applications, with a 10 weight % addition of partially copolymerised and blended PDMS to form a copolymer polyblend.14 Regardless, Avcothane® has been associated with fairly unstable mechanical properties under dynamic loading conditions and gradually stiffened upon cyclic deformation.15 In theory, inclusion of PDMS into the TPU backbone is an appealing solution to integrate the properties of the two polymers. However, owing to the significant differences in solubility parameters and the lack of specific intermolecular interactions between urethane and siloxane sequences, synthesizing acceptably high molecular weight copolymers from a mixture of polar and non-polar monomers has proven difficult in practice.16,17 Many empirical studies have shown extremely weak interactions between the SS and HS domains of the resultant copolymers, compromising the mechanical properties.17 In recent times, this has been overcome by either incorporating ether-functionalized end-group segments into a predominately PDMS macro-diol, or by introducing a second polyether macro-diol into the copolymer.17,18 The terminal units attached to the ends of siloxane oligomers or the polyether-based secondary SS can act as compatibilisers, interjecting an intermediate polarity chemical species between the highly apolar PDMS and the polar HS. These speculations on improved compatibilisation have corroborated well with the clinical performance of various proprietary TPU/PDMS copolymers containing PTMO and PHMO as ‘mixed-macrodiol’ (Table 1).

Besides the block copolymer synthesis, the melt-processing route is an attractive alternative for TPU/PDMS blend fabrication. Melt state blending is an easily scalable and commercially viable process compared to the block or graft copolymer synthesis of silicone-based polyurethanes. It additionally constitutes a solvent-free, greener approach for the development of reprocessable and recyclable blends. Even so, the selection of suitable blending and compatibilisation strategies remains crucial for heterogeneous systems to maximise synergism.19,20 In some of the earliest reported work, the physical melt-mixing of two immiscible polymers, such as TPU and PDMS, would permit an optimum PDMS concentration of barely 1.5–2.0 % to be incorporated in the blend. Beyond this, the phase separation became significant and mechanical properties reduced rapidly.21 Nonetheless, even at such low concentrations, the inclusion of PDMS was shown to improve chemical stability and wear resistance. Nando and coworkers had also devised the reactive compatibilisation of TPU and PDMS using ethylene methyl acrylate (EMA).22,23 EMA was initially grafted onto PDMS. During the subsequent melt-mixing with TPU, it facilitated specific interactions through hydrogen bonding between its >C=O and the unassociated >NH- of urethane group. This methodology allowed as high as 50 weight % PDMS to be melt-mixed, and the resultant blends were found to display finer morphology and improved mechanical properties, with respect to uncompatibilised blends.

In our previous work, we had reported a unique strategy of *in situ* ordynamiccrosslinking to successfully incorporate PDMS within the matrix of an aromatic poly(ether)urethane for urological applications.24 Unlike other studies that are primarily based upon physical or van der Waals forces assisted melt-mixing process, the three-dimensional *in situ* crosslinking of PDMS within the TPU matrix promotes much stronger interfacial adhesion. This methodology is characteristic of the fabrication of thermoplastic vulcanisates (TPVs).25,26 TPVs constitute a special class of polymer blends with properties and functional performance resembling a conventional vulcanised (crosslinked) rubber, yet they retain the processability and recyclability of a thermoplastic polymer. This dual character is realised through a dynamic vulcanisation procedure, where the elastomeric phase is selectively crosslinked in the presence of the molten plastic phase (Figure 1). Thus, the mixing process needs to be carried out above the melting temperature of the thermoplastic component and under high shear stresses to achieve finely dispersed micron or sub-micron size crosslinked rubber particles distributed in a continuous matrix.

TPVs are associated with remarkably improved structural properties and stability compared to simple blends without dynamic vulcanisation.25,26 A similar observation had been remarked by us for the dynamically crosslinked TPU/PDMS blends that were shown to outperform uncrosslinked counterparts and behave like a compatibilised system.24 To the best of our knowledge, this had been the first time when a TPV inspired methodology was applied to design silicone modified polyurethanes. Accordingly, in the present work, we were interested to carry a fundamental investigation towards the development and structure-property correlation of polydimethylsiloxane-based thermoplastic polyurethane blends. Critical insights are provided into the crosslinking process, microstructural characteristics, and mechanical properties. Furthermore, emphasis has been placed on evaluating and relating the experimental data with theoretical analyses. This was accomplished by adopting different phenomenological models to predict mechanical properties. These custom models assume different interfacial behaviour (e.g., good adhesion and no adhesion between the dissimilar materials), which, in conjunction with material property characterisation, established the interfacial attributes of the polymer blends under consideration.

Table 1. Design strategies for the development of silicone-based thermoplastic poly(ether)urethanes for biomedical applications

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **TPU/PDMS based copolymers** | | | | |
| Compositional features | PDMS  (weight%) | Compatibilisation strategy | Application/ Biocompatibility properties | Reference |
| PDMS: polyorganosiloxanes having reactive end-blocks | 10 | -- | Cardiovascular applications; gradual stiffening and unstable mechanical properties upon cyclic deformation | Avcothane® (Avco-Everett Co., Everett, Massachusetts) |
| SS: PDMS/PHMO | Variable: 12-60 | Mixed PDMS/polyether macrodiol | Cardiovascular; orthopaedic (finger joints); intervertebral discs; and cochlear implants | Elast-EonTM (Aor-Tech Biomaterials Pty, Glasgow) |
| SS: PDMS/PTMO |  | Cardiovascular implants (vascular grafts, blood pumps, artificial heart components, pacemakers, stent and intra-aortic balloon) | Cardiothane® and Angioflex® (Arrow International and Applied Biomedical Corp., Wayne, Pennsylvania) |
| SS: PDMS with hydroxyl-ethoxy propyl terminals/PTMO; HS: MDI; chain extender: BDO; and SME: PDMS | Variable: 10-61 | Cardiovascular; orthopaedic; ophthalmic; and anastomotic implants | PurSilTM (Polymer Technology Group Inc., Berkeley, California) |
| SS: α,ω-dihydroxy propyl-terminated PDMS grafted with MPEG; HS: MDI; and chain extender: EG/DBM |  | PDMS-based PUs with MPEG grafts exhibited least platelet adhesion, displaying suitability for blood-contacting biomedical devices | Park et al.[24] (1999) |
| SS: α,ω-dihydroxy propyl-terminated PDMS; HS: MDI; and chain extender: BDO | Variable: 40-80 | Lowered fibrinogen (FBG) adsorption and favorable endothelial cell adhesion indicating potential for blood‐contacting applications | Pergal et al.[9] (2013) |
| SS: PDMS; HS: HDI; and chain extender: BDO |  | CNC as reinforcing and compatibilising filler | PDMS modified polyurethane bio-nanocomposites associated with good cytocompatibility and significantly improved cellular proliferation *in vitro* | Khadivi et al.[28] (2019) |
| **TPU/PDMS based blends** | | | | |
| Base polymer: TPU containing PTMO (SS), MDI (HS) and ED (chain extender); Additive: TPU containing PDMS(SS), MDI (HS) and BDO (chain extender) | < 3 | PDMS based copolymer as surface modifying additive | VAD, vascular graft | Thoralon®, Thoratec Corporation, Pleasanton, California |
| TPU containing PTMO(SS), MDI (HS) and BDO (chain extender);  PDMS containing diacetoxy silyl terminals | 30 | Semi-IPN formation | Semi-IPN coated vascular grafts noted with improved endothelialisation and reduced thrombus deposition over 24 months of *in vivo* assessment | Soldani et al.[29] (2009) |
| TPU: TEXIN RxT85A;  PDMS: Siloprene | Variable: 10-30 | EMA copolymer as compatibilising agent while solution mixing | Blend with 30 weight% PDMS established with the prospect of cytocompatibility and haemocompatibility; potential application as biostable skin substitutes | Drupitha et al.[30] (2018) |

SS: soft segment; HS: hard segment; PHMO: poly(hexamethylene oxide); PTMO: poly(tetramethylene oxide); MDI: 4,4′‐methylenediphenyl diisocyanate; HDI: hexamethylene diisocyanate BDO: 1,4‐butanediol; MPEG: monomethoxy poly(ethylene glycol); EG: ethylene glycol; ED: ethylene diamine; DBM: diethyl bis(hydroxymethyl) malonate; EMA: Ethylene-methyl acrylate

**2. Materials and Methods**

**2.1. Materials**

Texin RxT85A (TPU), a medical-grade aromatic polyether urethane (melt flow index: 4 g/10 min at 190 °C/8.7kg; density: 1.12 gcm-3), was procured from Covestro (India). Silplus 40 MP (vinyl terminated PDMS), a heat-cured elastomer (density: 1.12 gcm-3), was kindly provided by Momentive Performance Materials (India). Dicumyl peroxide (DCP, 98%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%) were procured from Sigma Aldrich. Toluene and tetrahydrofuran (THF) were of analytical grade and used as-received from SD Fine chemical Limited (India).

**2.2. Fabrication methodology for TPU/PDMS blends**

All samples were fabricated following the processing strategies described in our earlier work.24 Briefly, a two-step sequential melt-mixing route had been adopted to prepare pristine, uncrosslinked blends. Herein, vacuum dried TPU pellets were first fed into the barrel of micro-compounder (DSM Xplore, Netherlands) and, subsequently, PDMS rubber was introduced. Throughout the homogenisation process, the micro-compounder was operated at 90 rpm, and the temperature was collectively maintained at 170 °C for all the heating zones across the screw length.

The second set of dynamically vulcanised blends was prepared in a three-step pre-blending protocol, where the additional third step was meant to ensure the *in situ* crosslinking of PDMS using dicumyl peroxide (DCP) as the thermal initiator. During the initial optimisation, the amount of DCP was varied from 0.3-0.8 weight % of the rubber content in a TPU/PDMS: 80/20 system. Subsequently, a complete library of blends was developed with the DCP concentration fixed at 0.5 weight %. Mixing was continued until an equilibrium platform was obtained, implying completion of the vulcanisation process. The designation and composition of the formulated blends are presented in Table 2.

**Table 2.** Sample designation and compounding recipe of TPU/PDMS blends

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Constituents** | **Amount (weight %)** | | | | | | | | | |
| Crosslinker  (DCP) | 0.0 | | | | 0.3 | 0.5 | | | | 0.8 |
| TPU  (ρ: 1.12g cm-3) | 90 | 80 | 70 | 60 | 80 | 90 | 80 | 70 | 60 | 80 |
| PDMS  (ρ: 1.12g cm-3) | 10 | 20 | 30 | 40 | 20 | 10 | 20 | 30 | 40 | 20 |
| Sample designation | T9P1 | T8P2 | T7P3 | T6P4 | D0.3T8P2 | DT9P1 | DT8P2 | DT7P3 | DT6P4 | D0.8T8P2 |

**2.3. Crosslink density measurements**

To determine the degree of crosslinking in the PDMS phase of the binary blend, the solvent swelling method was followed. The estimation of the crosslink density from the volume fraction of the swollen rubber phase has been a standard protocol in literature.31–33 Compression molded specimens (20 mm x 20 mm x 1mm) were pre-weighed before immersion in toluene at 60 °C for 48 h, to achieve equilibrium swelling conditions. The solvent was replaced after 24 h to remove the extracted components.The retrieved swollen samples were gently wiped off the unabsorbed solvent using blotting paper and immediately weighed on an analytical balance**.** To further calculate the mass of de-swollen residuals, vacuum drying was carried out at 100 °C for 12 h**.** The volume swell ratios (Vr) for the samples were determined from the following relation 34;

(1)

where ms and md are the total mass of swollen and de-swollen samples respectively; ρr and ρs represent the density of rubber phase (for PDMS, ρr = 1.12 g/cm3) and extracting solvent (for toluene, ρs = 0.865 g/cm3); and α is the weight content of PDMS in the sample.

Further, the measured Vr was substituted into the modified Flory-Rehner equation for the estimation of overall crosslink density.35 The latter has been calculated relative to the (PDMS + TPU) phases and expressed as ( + TPU) to account for the extracted amorphous TPU 36,37;

(2)

where is the number of moles of effectively elastic chains per unit volume of PDMS in mol/mL (crosslink density); ( + TPU) is the crosslink density of PDMS phase in the presence of TPU (overall crosslink density); Vm is the molar volume (106.3 cm3/mol for toluene); and χ is the polymer swelling agent interaction parameter (0.45 for silicone rubber-toluene system at 20 °C).38

**2.4. Gel content estimation**

The extent of crosslinkable elastomeric phase or the gel-content within the blends was determined by subjecting the samples to a series of solvent extraction. About 2g of polymeric sample was initially extracted for 24 h in toluene to remove the uncrosslinked PDMS phase and low molecular weight TPU fragments. In the subsequent step, exhaustive extraction of the TPU phase was performed for another 24 h with THF, under reflux. After the completion of extraction cycles, the suspension was centrifuged, and the collected insoluble residue was vacuum dried at 60 °C to a constant weight of the sample. The gel content was calculated as the ratio of the final weight (*wf*) of the sample to its initial weight (*wo*) as follows 31,39;

(3)

The average gel content for a given set was reported by analysing three samples.

**2.5. Mechanical property measurements**

Universal Testing Machine (Zwick Roell Z005, Germany), equipped with a 5 kN load cell, was used to determine the tensile properties, including ultimate tensile strength (UTS), elongation at break (Ɛb), and elastic modulus (E). Dumbbell-shaped samples (gauge length: 16mm, thickness: 2mm, width: 4mm) were fabricated as per the ISO 37 type-3 standard with a 5cc Micro Injection Moulder (DSM Xplore Netherland). Five specimens corresponding to each composition were tested at a crosshead speed of 200 mm/min until failure, and the stress-strain response was recorded using interface software (testXpert-III). The mechanical properties of the blends were also characterised via compression tests in accordance with ASTM D695 standards. The same UTM was outfitted with compressive clamps, and the tests were performed on five cylindrical specimens (10 mm x 10 mm) at a crosshead speed of 5 mm/min. All specimens were subjected to a pre-load of 0.2 N and compressed until -50% strain.

**2.6. Microstructure assessment**

To analyse the phase morphology and the interfacial adhesion of the binary blends, fractographic assessment was carried out on the tensile-fractured specimen. The fractured surface were examined with scanning electron microscope (JCM-6000 Plus Benchtop SEM; Jeol), operating at 15 kV in the secondary electron (SE) mode. The polymeric substrates were sputter-coated with gold before imaging to prevent electrostatic charging build-up during observation.

**2.7. Thermal decomposition characteristics**

Thermogravimetric analysis (TGA) was used to evaluate the variations arising in the thermal decomposition behaviour with the blend composition. The measurements were performed using a TGA Q50 unit (TA instruments) from 30-650º at 10 ºC/min. The initial mass of each sample was taken to be ~3 mg, and the experiments were performed under a steady flow of nitrogen gas.

**2.8. Reprocessability**

The remains of the originally tensile tested samples were collected and repeatedly injection molded at the same processing conditions as those of their initial preparation. The obtained specimens were assessed for their mechanical properties in the uniaxial tensile test to determine the reprocessing characteristics. Experiments were carried out for two cycles of remolding and testing for the blend DT8P2.

**2.9. Prediction models**

**2.9.1. Tensile and compression properties**

The applicability of available phenomenological models was tested to predict and validate the composition-dependent variations in mechanical properties, such as strength and elastic modulus, measured under tensile and compression loading. In particular, theoretical predictions were carried out with parallel, series, Halpin Tsai, Coran and Takayanagi equations to analyse the behaviour of the two-phase crosslinked and uncrosslinked blends from the component property data.40–43 The assumptions made regarding the blend structure and the mechanisms and properties of the interface were also assessed. The mathematical expression and the characteristic details of these models are described in Table 3.

**Table 3.** Summarised details for the different phenomenological models used in theoretically predicting the tensile and compression properties of the blends.

|  |  |  |
| --- | --- | --- |
| **Model** | **Governing equation** | **Comments** |
| Parallel [40] |  | Voigt rule of mixture predicting the upper-bound values. ϕ is the volume fraction and subscripts 1 and 2 correspond to the continuous and dispersed phases, respectively. |
| Series [40] |  | Reuss inverse rule of mixture predicting the lower-bound values. ϕ is the volume fraction. |
| Halpin Tsai [41] | ;  *A* | A morphology-dependent model, where ϕ is the volume fraction; l and d are the length and diameter of the dispersed phase, respectively. Herein, l/d is assumed to be 1 for the silicone rubber domains. |
| Coran [42] | ; | f varies between 0 and 1; ϕ is the volume fraction; n relates to the phase morphology;  h and s correspond to the hard and soft phases, respectively. Herein, correlation with the Coran model was determined at n = 7.5. |
| Takayanagi [43] | ; | ϕ and λ are the mixing parameters so that the product ϕλ is the volume fraction of the dispersed phase and relates to the degree of series-parallel coupling. Herein, correlation with Takayanagi model was determined at %parallel = 15% |

*M:* Property of the blend, *ϕ:* volume fraction

**2.9.2. Stress-concentration parameters**

The variations in the tensile strength data were further utilised to develop an understanding of the discontinuities in the stress transfer and the extent of interfacial interactions in the binary uncrosslinked and crosslinked blends. Four differently modified power laws, proposed by Nielsen, Nicolais and Narkis, and Kunori and Geil, were used to calculate stress-concentration parameters, as described in Table 4. A similar application of these models is also reported previously for polymer blends and composites.44–47

**Table 4.** Summarised details for the different predictive models used to investigate the interfacial properties of the blends.

|  |  |  |
| --- | --- | --- |
| **Model fit** | **Governing equation** | **Comments** |
| Nielsen first power law [51] |  |  |
| Nielsen two-third power law [51] |  |  |
| Nicolais and Narkis [52] |  | *∝* |
| Kunori and Geil [53] |  | *∝* |

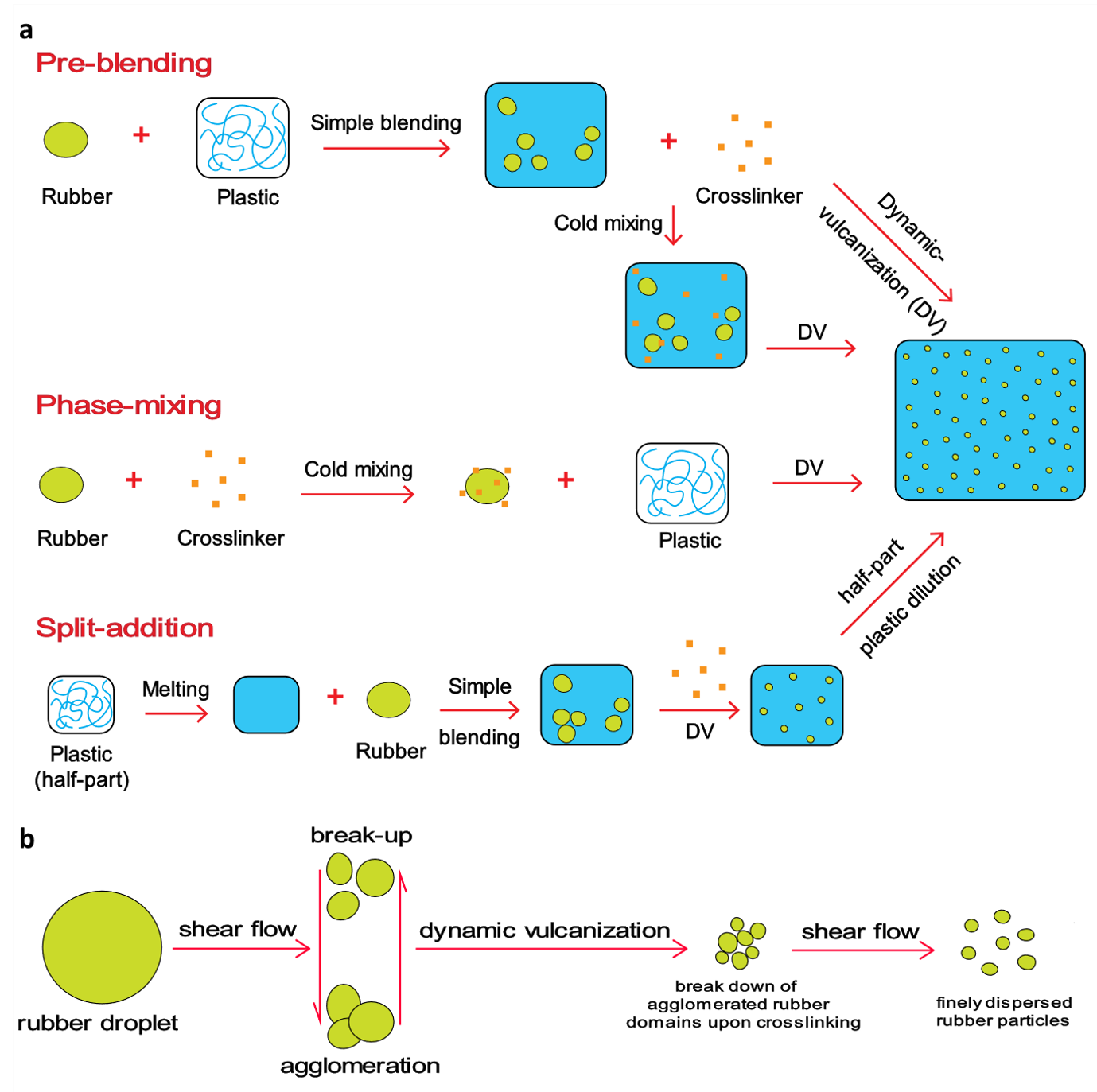
*σ*: Mechanical property of the blend/ matrix; : volume fraction of the dispersed phase

**3. Results**

**3.1. Mixing strategy and melt-processability**

Four feeding procedures are typically followed in the preparation of TPVs, and their respective methodologies have been schematically explained in Figure 1a. Methods 1, 2, and 4 represent different variations in pre-mixing of the rubber and the thermoplastic by simple melt-blending.25 Curing agents and other additives are then added into the pre-mixed blends under the same processing conditions to promote the dynamic vulcanisation (DV) of the rubber phase and further homogenisation of various components. Subsequent intensive mixing leads to fine and uniform dispersion of rubber micro- or nanoparticles inside the thermoplastic matrix (Figure 1b). The difference between the three methods is that in method 2, curing agents are added into the cooled-down rubber/thermoplastic (R/P) pre-mix at room temperature before DV. This allows for good dispersion of the curing agents primarily in the rubber phase of the pre-mix, as the plastic phase is solid at this temperature. As such, the crosslinking of the rubber phase is favoured during the subsequent DV, and the degradation of the plastic phase is avoided.

Method 4 follows a dilution protocol; wherein half part of the thermoplastic is first pre-blended with full part rubber. The crosslinker is then added to the molten mass to allow DV. Once the vulcanisation is completed, the blend is diluted further with the addition of the remainder half-part of the thermoplastic component. Often the final TPVs are associated with poor mechanical characteristics. This is attributed to the inefficient dispersion of the thermoplastic matrix phase added at the final stage of mixing. Even upon increased mixing time, the dispersion of the thermoplastic matrix phase is difficult, and the final morphology remains essentially unchanged.51 TPVs can also be prepared through another route, as illustrated through method 3. Here, the rubber phase is initially cold-mixed with curing agents at room temperature and afterwards, this mixture is simultaneously melt-blended and dynamically vulcanised with the plastics and other additives. However, in this approach, the crosslinking of the rubber phase proceeds fast because of the pre-mixing of the curing agents with the rubber phase. In contrast, the mixing time for the rubber and plastics in the molten state is short. As a result, the rubber phase domains in the resultant TPVs may not be fine enough. Therefore, we had been keen on adopting the pre-blending approach (method 1) that allows a sufficient melt-mixing period between TPU and PDMS prior *in situ* crosslinking to generate a more refined morphology.

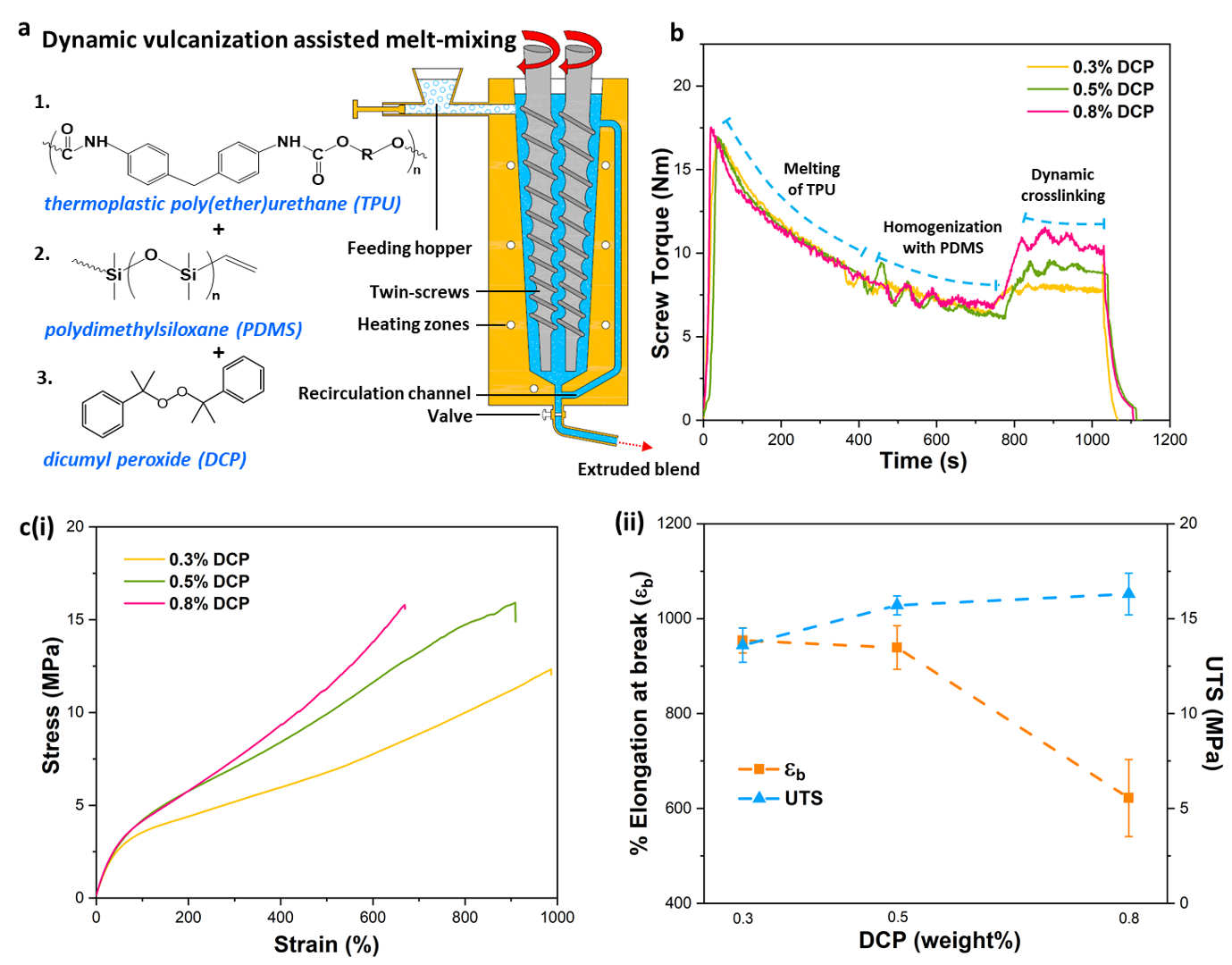


**Figure 1. (a) Schematic diagram of the preparation of thermoplastic vulcanisates by different methods.** Method 1and 2 are pre-blending processes wherein thermoplastic, and elastomeric phases are initially melt-mixed to develop a homogeneous blend. The crosslinker is added afterwards to the molten mass at the processing temperature or cold-mixed at room temperature before dynamic vulcanisation. Method 3, a phase-mixing strategy, involves pre-blending of the crosslinker with the elastomer at room temperature to form a curative masterbatch. The masterbatch is added to the molten thermoplastic phase at elevated temperature to form TPV. Method 4 is a split-addition protocol. The half part of the thermoplastic and full part of the elastomer are processed before the incorporation of the crosslinker to the molten mass. The remaining part of the thermoplastic is melt-mixed with the already vulcanised blend; **(b) Mechanism of dynamic vulcanisation.** The rubber droplets reversibly breaks-up and agglomerate under shear stress. As dynamic vulcanisation is carried out, there is a shrinkage of the rubber particles and the breakdown of the agglomerates at a high crosslinking density. The crosslinked micro-and nano-rubber cannot coalesce and are finely dispersed within the thermoplastic matrix.

**3.2. Fabrication of dynamically vulcanised TPU/PDMS blends**

Pristine TPU/PDMS blends were processed following a two-step mixing strategy. Within these blends, the PDMS content was varied from 10 to 40 weight %. A corresponding set of dynamically crosslinked blends was also prepared as per method 1. Moreover, the influence of crosslinking agent on the dynamic vulcanisation process was investigated, taking TPU/PDMS: 80/20 as a model system (Figure 2a). To this end, the amount of crosslinker, i.e., dicumyl peroxide (DCP) was varied from 0.3-0.8 weight % of PDMS content. Figure 2b illustrates the evolution of screw torque with time during the entire process of melt-mixing for different concentrations of DCP. A rapid rise in torque is observed as TPU is gradually fed into the mixing chamber. It attains maxima once the complete batch of TPU pellets is transferred. Thereupon, the polymer melting occurs and is also reflected in the continual decrease in the screw torque. Further addition of PDMS as a secondary phase introduces insignificant variations in the torque profile due to the low melt-viscosity of uncrosslinked silicone rubber. For the next few minutes, the shear assisted mixing of the binary blend is carried on until both the polymeric components are homogenised in the molten state. In the next step of processing, DCP is incorporated, causing the torque to rise rapidly. The distinct escalation in melt torque after the addition of peroxide crosslinker is noted for all the TPVs and confirms the incidence of dynamic vulcanisation of the PDMS.32,34,52 Though the trend of rapid ascent is detectable even with the lowest concentration of the crosslinking agent, i.e., 0.3 weight %; it becomes more prominent with the progressive increase of DCP to 0.8 weight %. This consequently demonstrates the systematic improvement in the extent of crosslinking within the silicone phase.

Similar observations have been made in the previously reported literature. Therein, the *in situ* vulcanisation reaction was observed to start earlier, and the torque peaks were noted to reach faster and higher with increasing concentration of the curing agent, catalyst and temperature.32,34,52–54



**Figure 2. (a) Schematic representation of the polymer melt-blending within the twin-screw mixing chamber of the micro-compounder:** A two-step mixing strategy was adopted for the pristine blends while a three-step protocol, involving peroxide-initiated crosslinking, was followed for the fabrication of dynamically vulcanised blends; **(b)** **Evolution of melt-torque profile as a function of time in the course of reactive mixing:** The incidence of successful *in situ* vulcanisation reaction is confirmed by the rapid rise in the screw torque uponthe introduction of the crosslinking agent; **(c) Uniaxial tensile properties:** (i) stress-strain curves; (ii) Variations arising in ultimate tensile strength (UTS) and % elongation at break (εb) with the increasing concentration of peroxide crosslinker (DCP).

As the melt-mixing continued, a new equilibrium platform was reached, implying the completion of the crosslinking process. The levelling off of the mixing torque at the end of dynamic vulcanisation also elucidates the thermal stability and melt processability of the blend, even after the formation of a crosslinked structure in the silicone rubber phase. At this stage, the crosslinked rubber particles are dispersed in the thermoplastic matrix and help attain higher elasticity. However, the shear rate acting on it is insufficient to facilitate further break-down of the elastic network. Therefore, it eventually ends with a constant torque level due to the slippage of crosslinked rubber particles at the rotor surface and the chamber wall while still floating in the TPV matrix.

In order to understand and determine the optimal concentration of crosslinking agent for the TPU/ PDMS system, the uniaxial tensile properties of blends D0.3T8P2, DT8P2 and D0.8T8P2 were investigated. The measurement of the tensile response of the tensile properties of blends is also a way to estimate how the compatibilisation, and thus the interfacial adhesion, is improved by the dynamic vulcanisation strategy. Figure 2c represents the tensile stress-strain properties for the 80/20 blends at different curative levels. The ultimate tensile strength (UTS) and elastic modulus (E) improved consistently with the increase in the DCP content. The respective values of UTS and E were observed to increase from 13.6 ± 0.9 MPa, 8.1 ± 0.3 MPa in D0.3T8P2, to 15.7 ± 0.5 MPa, 8.4 ± 0.1 MPa in DT8P2 and 16.3 ± 1.3 MPa, 8.5 ± 0.2 MPa in D0.8T8P2. This enhancement in the mechanical characteristics was ascribed to a greater crosslinking density of the PDMS chains at higher concentrations of DCP. Such behaviour also reasserts the notion that a higher torque value during melt-processing is suggestive of the higher melt-viscosity, which in turn is usually proportional to the stiffness and strength of the polymer system. While the progressively higher amounts of DCP assist in increasing the extent and rate of PDMS crosslinking, the excessively generated free radicals also encourage a competing reaction of TPU degradation through chain-scission. The previously reported studies on TPVs have reported that the UTS and E values increase successively, stabilise, and thereupon demonstrate a decreasing trend.33,55 The improvement in mechanical properties of these TPVs represents the rubber crosslinking induced strengthening of the blend structure, whereas the subsequent reduction at higher concentrations of peroxide is attributed to the degradation of the thermoplastic phase. In the present work, the mechanical properties continue to improve with the incremental addition of DCP. However, a near saturation in terms of tensile strength and modulus between 0.5-0.8% implicates the exhaustion of the crosslinkable PDMS content in the blend. It can also be anticipated that at even higher concentrations of DCP, the temporarily stabilised properties are likely to decline due to the onset of TPU degradation.

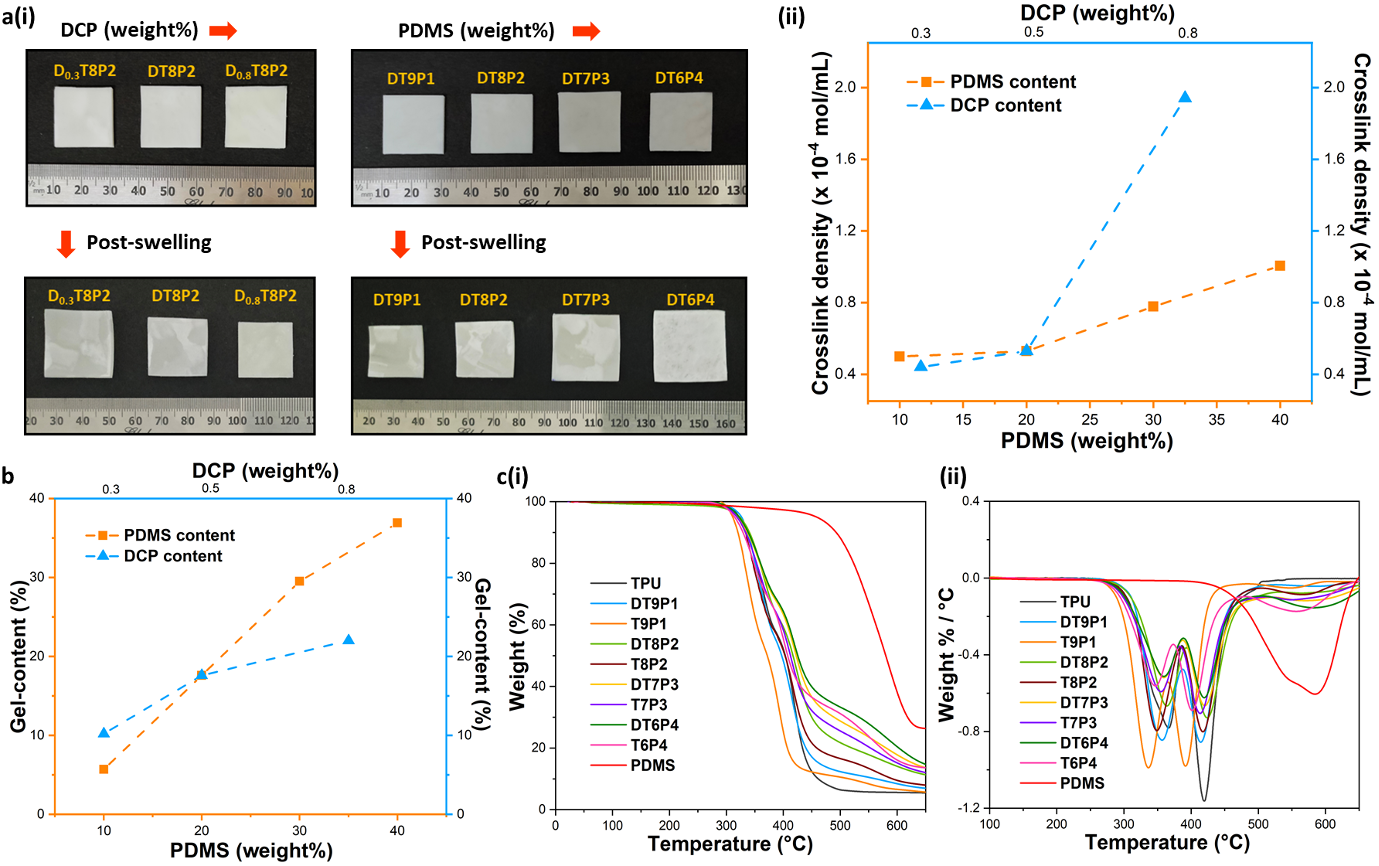
An overall elastomeric response could be established for all the three compositions as they displayed higher than 500% elongation at break (εb). Nevertheless, the εb values were found to be inversely correlated with the concentration of DCP and reduced from 954 ± 26.6% in D0.3T8P2 to 622 ± 81.0% in D0.8T8P2 (Figure 2c(ii)). This is because the crosslinked bridges within the rubber molecules anchor and arrest the flexibility of polymer chains.56 As the crosslinking density is speculated to be maximum in the case of D0.8T8P2, the corresponding constraining effect that restricts the molecular chain mobility and, thereby, the elongation is also most pronounced. In conjunction, these observations indicated DT8P2, with 0.5 weight % DCP, to be an optimum composition. The DCP loading was also fixed at 0.5 weight % of PDMS phase for all the other blends and its actual content varied as per the different TPU/PDMS ratios.

**3.3. Crosslink density and gel-content analysis**

The improvement in the mechanical properties of the TPU/PDMS: 80/20 with an increase in the DCP concentration is conferred to the corresponding increase in the crosslinking density of the silicone rubber phase. Similarly, the superior performance of the complete set of dynamically vulcanised formulations over their respective pristine counterpart is also accredited to the crosslinking induced strengthening of the binary blends. In the present study, two different methods were thus explored to determine the crosslink density: solvent swelling and gel-content determination. In the former, equilibrium solvent swelling measurements were carried out for the crosslinked TPU/PDMS blends to measure volume swell ratios (Vr) (Figure 3a(i)). The Vr values were then utilised to calculate the overall crosslink density. Since PDMS is embedded in the relatively stiffer matrix of TPU, it swells against the compressive force exerted by the TPU.55 Thus, the overall crosslink density was calculated relative to the (PDMS + TPU) phases and expressed as (υ + TPU), as shown in Figure 3a(ii). From these results, it is clear that the Vr also increases with DCP content. Considering that Vr is defined as a reciprocal to swell ratio, it is directly correlated to the crosslinking efficiency and indicates an increase in crosslink density with a decrease in solvent swelling. This can be explained by the changes arising in the free volume between the polymer molecules. As stated earlier, the formation of a crosslinked network restrains the molecular movement. Consequently, it becomes more difficult for the solvent molecules to penetrate through the rubber phase with a greater extent of crosslinking.

On the other hand, a lower crosslinking density is associated with a loosened network structure and therefore, more solvent absorption and swelling can occur. Similarly, it is observed that the degree of crosslinking in the blends DT9P1, DT8P2, DT7P3, DT6P4 increased progressively with the increasing amount of PDMS. This is likely to be a result of incorporating higher DCP weight % with higher rubber content. Thereby, the contact probability between the free radicals produced by DCP and the PDMS radicals is raised and enhances the apparent crosslinking density of the rubber phase. The more substantial presence of the rubber phase further facilitates the production of heat and relatively lowers the cage effect, acting as a side effect to hinder the initiation of crosslinking.57 Together, these factors improve the crosslinking rate and crosslinking density of the PDMS and thus endow the blends with improved strength properties.

The apparent values of overall crosslink density are obtained for the PDMS phase in the presence of the TPU, and accordingly, the latter's contribution is also accounted for. However, in the estimation of gel-content, the samples are subjected to sequential solvent extraction, wherein the uncrosslinked silicone and low molecular weight TPU are removed first, followed by the high-temperature dissolution of the insoluble TPU matrix. From the experimental measurements, it is concluded that the gel fraction increases with the increasing concentration of peroxide (Figure 3b).



**Figure 3. (a) Crosslink density estimation:** Equilibrium swelling experiments were performed with toluene to determine swell ratios (i) Photographs of the dynamically vulcanised blends before and after solvent-swelling for 48 h; (ii) Overall crosslink density values as a function of PDMS content and peroxide concentration; **(b) Gel-content measurement:** Polymeric samples were subjected to sequential extraction in toluene and THF to determine the fraction of crosslinked phase in the dynamically vulcanised blends; **(c) Thermal degradation profile:** (i) TGA and (ii) DTG curves for the uncrosslinked blends, dynamically vulcanised blends and the constituent polymers TPU and PDMS.

It varies from 10.2% in D0.3T8P2 to 17.6% in DT8P2, and the maximum value of 22.0% is recorded for the blend D0.8T8P2. The improvement is minor; even so, the differences correlate to the PDMS phase's crosslink density. In the same way, the gel-content is also noted to increase from 5.7% in DT9P1 to 29.5% in DT7P3 and 36.9% in DT6P4. Therefore, it can be regarded as a measure of the crosslinkable fraction of the blends, which correspondingly increases with the constituent PDMS fraction. Furthermore, the highest value in the DT6P4 suggests that crosslinking reaction proceeds predominantly in the PDMS phase with less influence of the TPU phase.

It is further interesting to note that the gel-content remained lower than the actual weight % contribution of the silicone phase in the blend, for all the compositions. Thus, it can be deduced that the silicone rubber within the blend is only subjected to partial crosslinking. Additionally, it should also be acknowledged that the solvent extraction method can account for some discrepancies, particularly for the lower concentration of the rubber phase.36 Nevertheless, the results conjunctly indicate that the gel-content in the blends, characterising the extent of crosslinking or the crosslinking efficiency, improves with the concentration of DCP and PDMS. Collectively, these observations are also are in agreement with the overall crosslink density estimated from the equilibrium solvent swelling experiments.

**3.4. Thermal degradation behaviour**

The thermogravimetric analysis (TGA) was performed to confirm the thermal stability and assess the degradation response of the constituent polymers as well as the pristine and dynamically vulcanised blends. Figure 3c(i) displays the thermograms for the different compositions from 30-650 ºC. In the case of TPU, the onset of thermal degradation occurred above 300 ºC. The mechanism of thermoplastic poly(ether)urethane degradation is known to be influenced by the presence of hard and soft segments.58 The degradation initiates with the labile urethane linkages to produce carbon dioxide. A much more complex mixture of products originating from the polyether-polyol segment is generally identified in the subsequent stage. An improved thermal profile was associated with PDMS, which remained stable up to 400°C and exhibited only slight weight loss (<5%) with increasing temperature up to 450 °C. Afterwards, the networks undergo rapid, one-stage thermal decomposition with over 60% weight loss. The thermal degradation products are reported to be cyclic oligomers in the low degradation temperature range and methane and oligomers in the high-temperature range.59 The residue left after the degradation of silicone rubber at 800 ºC consists of traces of silica.

A multi-step degradation profile was identified in the binary blends. In fact, the magnitude of mass loss at the different steps varies in accord with the blend formulation, and an almost quantitative relation with the TPU and PDMS weight% is recognisable. The low-temperature decomposition is more pronounced with higher TPU content, while the percentage of high-temperature decomposition events increases with increasing PDMS content. Moreover, the percentage residue for the different melt-mixed compositions also varies with the blend ratio and is observed to increase with an increment in PDMS content.

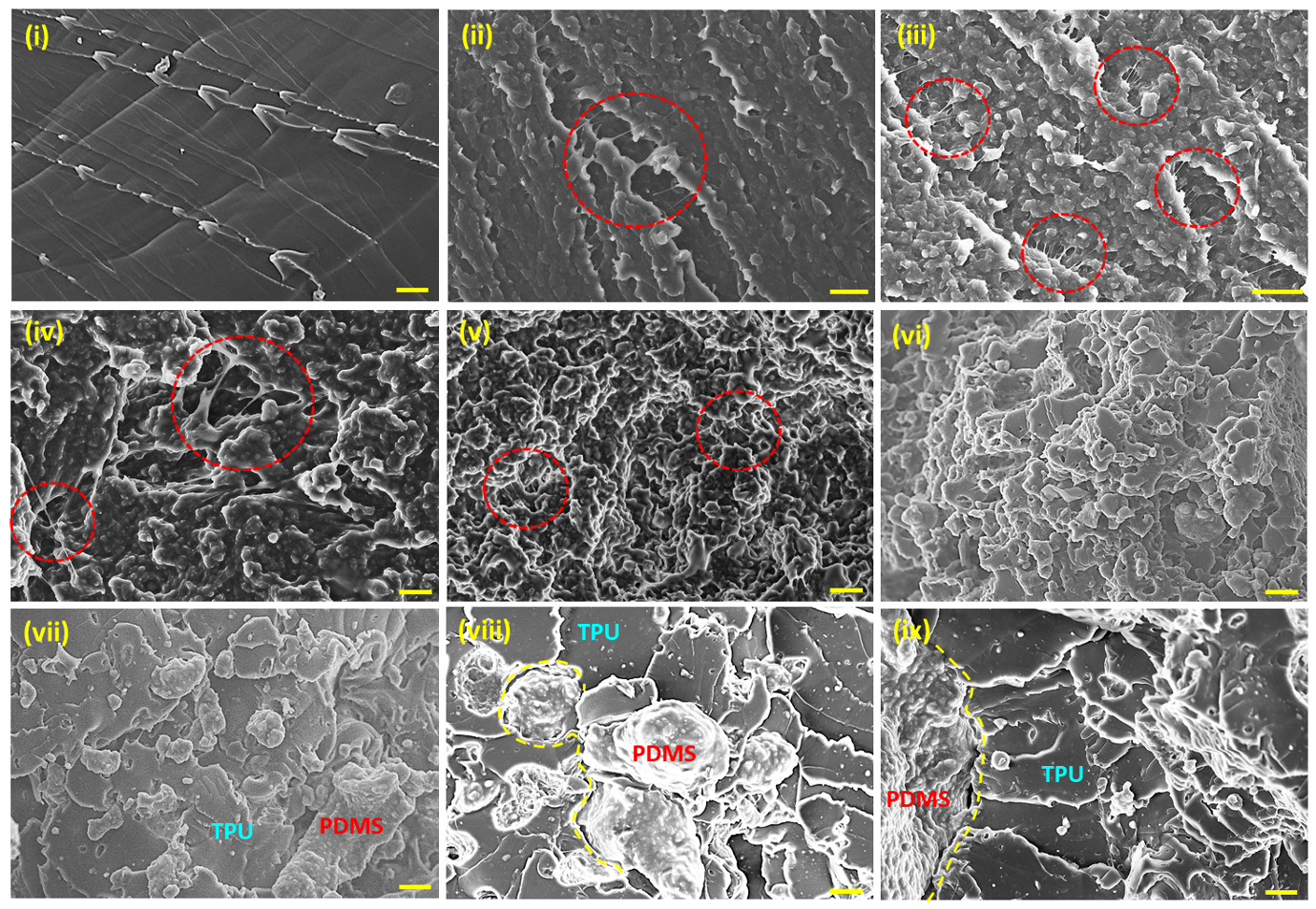
For further insights into the effect of crosslinking and composition on degradation, corresponding DTG curves were analysed (Figure 3c(ii)). The degradation of TPU is evident in two sharp and clear steps, which include the degradation of soft segments (TSS: 366 °C) and hard segments (THS: 419 °C). A single broad peak is identified for PDMS (TPDMS: 584 °C). All the blends expressed three-distinct regions of weight loss, implying a three-step degradation process from the averaged presence of TPU and PDMS. It is easily notable that with the increase in PDMS concentration from 10-40 weight %, blends display a progressive intensification of TPDMS peak. A reverse trend of de-intensification is observed with respect to the degradation of SS and HS of TPU with PDMS enrichment.

The thermal stability of polymer blends is related to the extent of chemical interaction occurring between the component polymers and is acknowledged to improve upon successful compatibilisation. A similar observation is made towards dynamically vulcanised system. The peak degradation temperatures were significantly higher for thecrosslinking compatibilised formulations when compared with the uncrosslinked counterparts (Table S1). In the case of TPU/PDMS: 90/10 blends, TSS, THS and TPDMS rise respectively from 336 °C, 392 °C and 548 °C in T9P1 to 357 °C, 415 °C and 584 °C in DT9P1. Likewise, degradation is demonstrated to be delayed in DT6P4 (360 °C, 419 °C, 583 °C) with reference to T6P4 (347 °C, 402 °C, 557 °C). A shift towards higher TSS, THS and TPDMS is also observed for the intermediate compositions DT8P2 and DT7P3. This confirms that the thermal stability of the blends is effectively improved upon dynamic crosslinking.

**3.5. Fractography and strengthening mechanisms**

In order to understand the mode of failure and to explain the relevant physical properties, the tensile fractured surfaces of pristine and dynamically vulcanised blends were assessed using scanning electron microscopy (Figure 4). Neat TPU is identified with a relatively smooth surface, and the appearance of peaks and ridges on the fracture surface indicate a predominantly ductile failure with plastic deformation. In contrast, it is evident that the uncrosslinked pristine blends exhibit a brittle fracture. The irregular fracture paths in different planes and the absence of microfibrils on the fractured surface further reaffirm this notion.34,60 A closer examination reveals the gross phase separation of the immiscible binary components, and their debonding is a likely cause of this brittle response. Equally noteworthy is the fact that the extent of phase separation alleviates with the increasing PDMS content in blends. The uncrosslinked blend surface demonstrates a droplet-matrix morphology, and the dispersed domain of PDMS enlarge and dissever from TPU as the composition varies from T9P1 to T6P4. The presence of large, irregular domains of the dispersed phase and their widespread distribution are characteristics of an incompatible blend. They arise because of the coalescence of the uncured PDMS in the absence of dynamic vulcanisation assisted stabilisation of the morphology. Moreover, as the fracture cracks are expected to run along the phase boundary of the thermoplastic matrix and the rubber droplets, a debonded interface restricts the dispersed silicone phase from absorbing and dissipating the tensile energy.

Unsurprisingly, the crosslinked blends exhibited a coarse surface with typical toughening characteristics. It is not possible to distinguish the PDMS and TPU phase from the images, and no clear phase boundary could be confirmed (Figure 4(ii-v)). Moreover, the debonding or internal cavitation phenomenon of the PDMS domains, as apparent in the new blends, is absent from the cross-sections of the DT9P1, DT8P2, DT7P3 and DT6P4. These observations are implicative of the superior compatibility between the two polymeric phases. The significant amount of plastic deformation that has occurred due to the breaking of molecular chains is also characterised by the presence of microfibrils.34,61–63 While the extent of microfibrillar formation changes with the blend ratio of rubber and the size and shape of the rubber phase, it is particularly conspicuous in the DT8P2 blend, containing 20 weight % PDMS. The generation of these soft phase microfibrils accounts for the absorption and dissipation of the deformation energy and arrests the crazes and macro-crazes consisting of nano- or micro-voids. During the fracturing process, the TPU phase is likely to rupture first. The elastomeric network of the silicone rubber at the craze openings are elongated until they break or form microfibrils, thereby absorbing a significant of tensile strain energy in this process. Meanwhile, the interfacial adhesion transfers the energy effectively from the TPU phase to the PDMS phase, further assisting in its dissipation. It must also be remarked upon that the roots of the elongated silicone microfibrils are firmly bonded within the TPV matrix, and no viewable delamination can be recognised, yet again confirming the excellent interfacial adhesion between the PDMS and the TPU phase. Taken together, these qualitative insights are consistent with the conjectured mechanism of dynamic vulcanisation assisted *in situ* compatibilisation of the crosslinked blends and the subsequent improvement of their microstructure and interfacial adhesion.



**Figure 4. Representative SEM micrographs of the tensile fractured blend surface:** Dynamic vulcanisation compatibilises the TPU/PDMS blends, leading to an improved microstructure and interfacial adhesion. (i) TPU; (ii) DT9P1; (iii) DT8P2; (iv) DT7P3; (v) DT6P4; (vi) T9P1; (vii) T8P2; (viii) T7P3; (ix); and T6P4. Encircled regions indicate the presence of microfibrils on the fractured surface. Scale bar: 10 μm.

**3.6. Reprocessability**

One of the most distinct advantages associated with the dynamic crosslinking methodology is the characteristic trait of reprocessability, without inflicting any significant change in the physical properties. Considering the fact that the conventional thermosetting rubbers and blends with higher rubber content can be very difficult to reprocess, the inherent recyclability of thermoplastic vulcanisates proclaimsthem as a refreshingly greener alternative. Therefore, we have also been interested in investigating this characteristic property for the present TPU/PDMS blends post *in situ* crosslinking. Accordingly, the residuals of the originally tensile-tested DT8P2 specimens were repeatedly injection molded and re-evaluated for the uniaxial tensile behaviour after each cycle. The results indicated good reprocessability with high stability in the mechanical properties that largely remained comparable to the original specimen. A minor increase in the tensile strength (UTS) was observed after the first cycle of remolding and testing to 15.9 MPa, while the % elongation at break was determined as 890%. This can be attributed to a further increase in the crosslinking density, which occurs during high-temperature reprocessing. Post the second cycle of repetition, the UTS and εb were measured to be 13.5 MPa and 725%, respectively.

**3.7. Mechanical properties: Experimental results vs theoretical predictions**

The mechanical behaviour of a dual-phase polymer system can be investigated by adopting several successful models. Among these, parallel and series models are the simplest and define the upper and lower bounds of the concerned physical property. In the case of the parallel model (Table 3), an iso-strain condition is assumed to exist for both phases, whereas for the series model, stress is understood to be uniform in both phases. Accordingly, the former is more appropriate for materials, where the blend components are arranged parallelly to one another such that the applied stress elongates each component to the same extent, and the Voigt rule of mixture (ROM) makes the property prediction. In the latter, blend components are arranged in series, vertical to the direction of the applied force, and Reuss inverse rule of mixture (IROM) defines the overall property. However, the mechanical behaviour of isotropic, heterogeneous blends and composites lies between the upper and lower bound values and can not be accurately represented by a simple parallel or series expression. This is because the blend properties are affected not only by the volume fractions of the dispersed and matrix phase, but also by their interconnecting and mixing pattern. Accordingly, several derived models have been proposed for analysing the properties of a polymer system and account for non-ideal conditions and inhomogeneity.40–43 For instance, the Halpin Tsai equation is a semi-empirical relationship that enables the overall property of a binary system to be expressed in terms of the properties of the matrix and dispersed components, together with their proportions and geometry.41 For this, it includes an adjustable shape parameter, *A*, that accounts for the aspect ratio of the dispersed phase. The constant *A* is distinguished by the morphology of the blend system. As *A*→0, the expression reduces to the lower bound; conversely, it attains the upper bound when *A*→∞. Initially developed for fibre or particulate reinforced polymer composites, the Halpin Tsai model is shown to be equally valuable in establishing the properties of polymer blends.64–66 Similarly, the relationship presented by Coran is a simple combination of series and parallel models and is particularly well studied in the context of the rheological and mechanical behaviour of thermoplastic elastomers.42 The factor *f* is a function of phase morphology and varies between 0 and 1. As the morphology of the hard phase approaches a continuous form, the value of *f* gets closer to unity. On the other hand, a lower value of *f* suggests continuity in the soft phase. The magnitude of *n* in the Coran equation is also described to account for the aspects of dispersed particulate shape, wetting behaviour, molecular interpenetrability, thermodynamic compatibility and inter-domain interference.42 The viscoelastic characteristics of a heterogeneous polymer blend can be estimated using Takayanagi model as well, that introduces the concept of percolation.43 This model includes components connected partly in series and/or partly in parallel. A typical setting of the model assumes that a portion of the reinforcing phase is continuous and connects to the rest of the structure in parallel, while the remainder portion is connected in series to the matrix.43 Parameters *ϕ* and *λ* are geometry factors representing the phase morphology and, thereby, the extent of series and parallel characteristics of the system. Their product, *λϕ*, constitutes the volume fraction of the dispersed phase. Both these parameters vary with composition and with variations in the state of dispersion. For spherical particles independently and homogeneously dispersed in a matrix, it can be assumed that *λ* is equal to *ϕ*.

**3.7.1. Tensile properties**

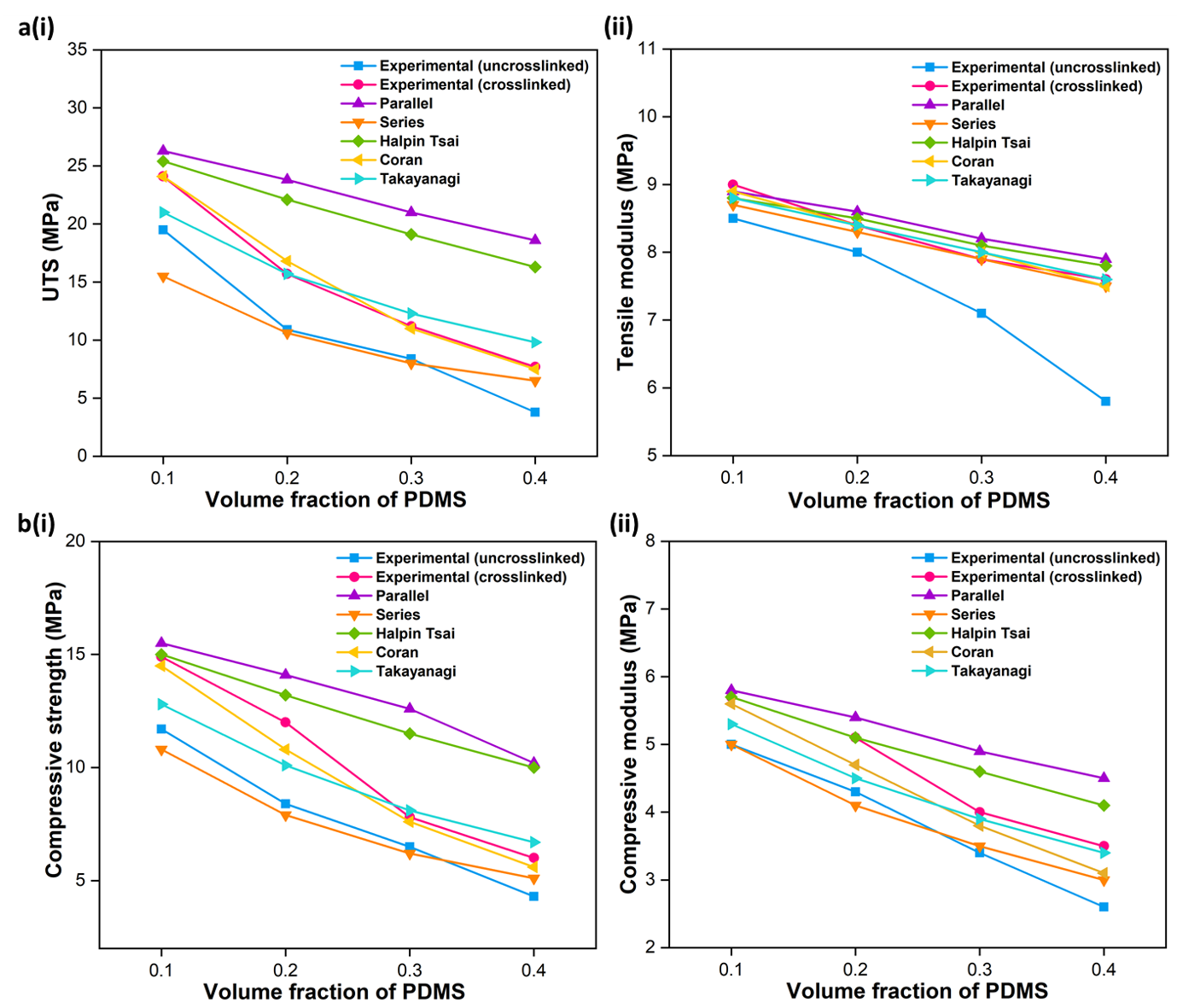
The theoretical estimation of the elastic properties of the TPU/PDMS blend system from the properties of their constituent phases was carried out in reference to ultimate tensile strength (UTS) and tensile modulus. As reference, it is worth mentioning that the pristine TPU is characterised with UTS of 29.0 ± 3.5 MPa, modulus of 9.2 ± 0.3 MPa and 1315 ± 72% elongation at break. The experimental and theoretical curves for the dynamically vulcanised and uncrosslinked blends are illustrated in Figure 5a. Considering the UTS data first, it is evident that for either of the two sets of the blend system, the experimental results lie within the window of the upper and lower-bound values (26.3-6.5 M Pa), as defined by the parallel and series models. It is also noted that while the obtained values for DT9P1 conformed to the Halpin Tsai model, the predictions from the Takayanagi equation were better suited for blends, DT8P2 and DT7P3. Regardless, it is the Coran model (n=7.5) that could most consistently fit and justify the experimental results across all compositions of the crosslinked blends (Table S2). In the case of the uncrosslinked TPU/PDMS system, the experimental data appeared to comply with the theoretical values determined using the inverse-rule-of-mixture or the series model. Even so, some discrepancies were noted at the 0.1 (T9P1) and 0.4 (T6P4) volume fraction of PDMS, where the values tended to be higher and lower from the series estimation.

Evaluation of tensile moduli also established the improvement in tensile properties upon dynamic vulcanisation. Interestingly, the modulus for DT9P1 was in accord with the upper-bound estimation using a parallel equation. The crosslinked blends with the higher concentrations of PDMS continued to be consistent with the Halpin Tsai, Coran and Takayanagi models. It is worth mentioning that the theoretically determined values of modulus were mostly concurrent for all three models. A more prominent trend was recognised for the uncrosslinked blends. While the experimental outcomes for crosslinked blends remained well within the theoretical range of 8.9-7.5 MPa, a significant negative deviation was observed for the uncrosslinked blends from the lower-bound series prediction. Together, these results ascertain the poor tensile properties of the uncrosslinked blends and their characteristic behaviour as a highly immiscible and uncompatibilised system. This conviction is further strengthened considering the fact that the negative deviation, as recorded in the moduli values, is evident at all the volume fractions of the PDMS.

**3.7.2. Compression properties**

The experimental results for compression tests and the data fitted with the different theoretical models are plotted in Figure 5b, as a function of the percentage volume fraction of the PDMS phase. The compressive strength (CS) and modulus for TPU were determined to be 17.0 ± 1.8 MPa and 6.3 ± 0.2 MPa. Similar to tensile properties, the CS and moduli values obtained for the blends conformed largely to the respective range of 15.5-5.1 MPa and 5.8-3.0. MPa, as defined by the parallel and series models (Table S3). Moreover, the dynamic vulcanisation process was yet again established to improve mechanical behaviour. In particular, the blends constituted with lower concentrations of PDMS (DT9P1 and DT8P2) are speculated with the most effective crosslinking induced compatibilisation as their measured strength and moduli are primarily comparable to the values calculated by the parallel model. Such a trend was also identified for the Halpin-Tsai model, which could closely predict the modulus at lower volume fractions of PDMS (0.1-0.2). The deviations become more significant from the parallel, and the Halpin Tsai model fit with progressively increasing PDMS content. For the blends, DT7P3 and DT6P4, the Coran (n=7.5) and Takayanagi equations could more accurately justify the compressive response with reference to both modulus and strength. It may be assumed that below 0.2 volume fraction, the presence of PDMS is still inconsequential, while TPU is determinant in defining the overall properties. However, the analogous behaviour is not reflected in the uncrosslinked blends, T9P1, T8P2, T7P3, T6P4, where the properties remained considerably below the upper-bound predictions for the complete range of PDMS concentration. In fact, the experimentally determined CS values for the uncured PDMS based blends are in the closest agreement with the series model that does not account for interfacial interactions. Likewise, a drop in the compression properties of the uncrosslinked blend is also reflected through the moduli data. Unlike the case of the tensile test, where the experimentally determined values remained invariably below the lower bound, such a lowering in compressive modulus is noted only for blends T7P3 and T6P4. T9P1 and T8P2, on the other hand, tend to be well-matched with the series prediction.

Collectively, these findings suggest that the formation of a crosslinked network and higher chain entanglements within the dynamically vulcanised blends causes the deformation to occur at higher stress than in the unvulcanised system. Similar improvement in mechanical properties upon the dynamic crosslinking is also documented in the previously reported literature on TPVs.25,26



**Figure 5. Correlation with phenomenological model predictions allows better** **mechanistic understanding of polymer blend properties: (a) Uniaxial tensile test:** (i) ultimate tensile strength and; (ii) tensile modulus as a function of the volume fraction of PDMS; **(b) Compression test:** (i) compressive strength at -50% strain and; (ii) compressive modulus as a function of the volume fraction of PDMS. The plots indicate the comparative analyses of the experimentally determined data for the uncrosslinked and crosslinked (dynamically vulcanised) blends with the theoretical predictions from Parallel, Series, Halpin Tsai, Coran and Takayanagi models. The properties of the uncrosslinked blends commensurate with the estimations of the lower-bound values from the series model. The enhanced mechanical characteristics of the crosslinked blends are in closer agreement with the Coran and Takayanagi model, suggesting the dynamic vulcanisation induced strengthening of the dual-phase polymer system.

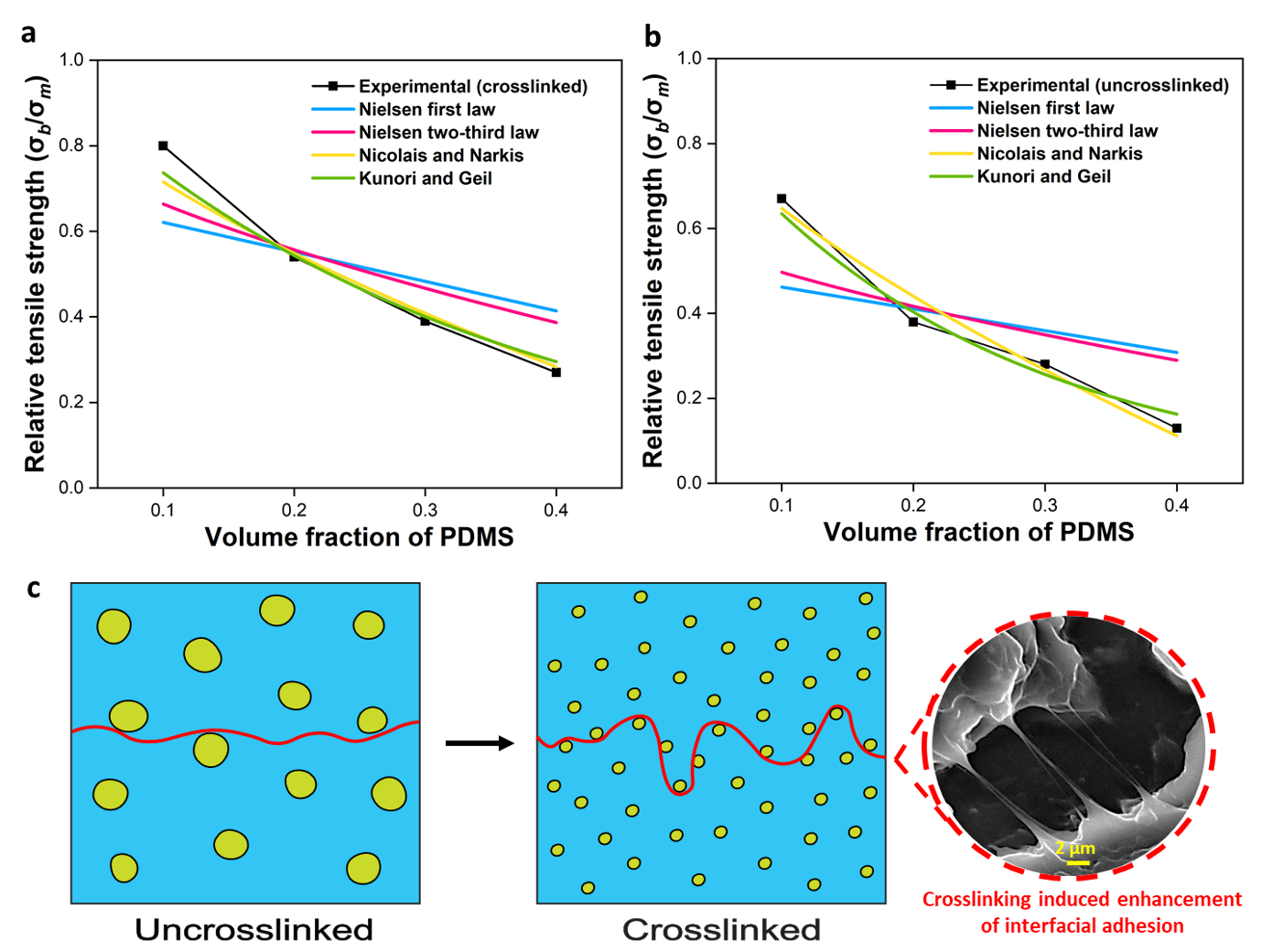
**3.7.3. Influence of crosslinking on the interfacial strength**

Different theoretical models have been described assuming different interfacial behaviour between dissimilar materials to assess the extent of stress transfer between the matrix and dispersed components. These models are based upon the two most common expressions for the composition-dependent mechanical properties of a two-phase system, i.e., the first and two-third power laws.48 The power laws originate from the considerations of the effect of area fraction and the volume fraction of the inclusions in modifying the property (yield stress, tensile strength). The first power relationship of area fraction to volume fraction, in any randomly chosen fracture plane, is derived for a completely random distribution of the dispersed phase. On the other hand, the two-third power law, with an appropriate weightage factor, is derived for the presence of the dispersed phase as spherical inclusions.

Furthermore, these laws have been modified to account for the effects of stress concentrations at the inclusion-matrix interface. For instance, the use of a stress-concentration parameter *S* in first power law (Table 4) was suggested by Nielsen.48 *S* can acquire a maximum value of unity, expressing a continuous stress transfer or no-stress condition. Inversely, the lower the value of *S*, the greater is the stress concentration effect. Similar incorporation of a stress-concentration factor, *S΄*, in the two-third power law was also proposed. As in the case of *S*, *S΄* can also attain a maximum value of 1 that denotes no stress concentration effect, whereas the progressively lower values indicate the increasing presence of stress concentration. Thereby, both these Nielsen's parameters account for the weakness in the structure brought about by the discontinuity in stress transfer. In the third model, Nicolais and Narkis had modified the two-thirds power law to introduce a weightage factor, *Kb*.49 This is an interfacial interaction constant or an adhesion parameter that varies with the blend structure. The value of *Kb*=1.21 suggests spherical inclusion of the minor phase having no adhesion. Interfacial adhesion is assumed to improve at *Kb* < 1.21, and the lower the value, the better the bonding. Finally, the Kunori and Geil or the porosity model account for the weakness in the structure or stress concentration by assuming that the dispersed phase is equivalent to pores or voids in the matrix.50 These pores or voids act as another form to specify the complete debonding or poorest adhesion at the phase boundaries and are described by the parameter, . The more significant the reduction in the mechanical property, the higher will be the value of . In proportion, higher is the extent of stress concentration; poorer is the interfacial adhesion.

In the present work, the variations in ultimate tensile strength data with PDMS volume fraction were analysed using prediction models, and the results are presented in Figure 6(a-b). The calculated values for the stress concentration parameters are listed in Table S4. Irrespective of the chosen model, the analysis indicated an improvement in compatibilisation and interfacial adhesion post dynamic vulcanisation process. Using Nielsen's first power law, the stress-concentration factor, *S*, was determined to be 0.5 for the pristine and 0.8 for the dynamically vulcanised blends. A similar trend was observed for the two-third law, where *S΄* was calculated as 0.6 and 0.9, respectively, before and after crosslinking. Thus, for either of the two Nielsen's parameters, the higher values could be attained for the dynamically vulcanised system. Considering that *S/S΄*=1 represents an ideally adhered interface, it is fair to say that post-crosslinking, the blends comply better with the condition of perfect adhesion and are suggestive of interfacial strengthening. Yet, as the values remained smaller than unity, the existence of a degree of stress-concentration effect cannot be overruled entirely. It is also to be noted that the experimental curves were in deviation from the theoretical fit for most volume fractions of PDMS in both cases. On the other hand, for Nicolais and Narkis and Kunori and Geil, the experimental data points fell closer to the theoretical curves and were well-agreeing with the estimated values across all compositions. Accordingly, these can be considered to establish better suitability and offer acceptable confidence over the first or fractional power-law models for the experimental correlation.

Within the Nicolais and Narkis model, the additionally introduced weightage factor, *Kb*, is directly proportional to the extent of stress-concentration among the spherical inclusions of the minor phase and the continuous matrix. The magnitude of *Kb* was estimated to be 1.6 for the uncrosslinked blend, and a notable reduction to 1.2 was observed for the crosslinked blends. Despite the reduction, it is to be mentioned that a value of *Kb* ≥ 1.21 suggests discontinuity at the interface. The porosity parameter in the Kunori and Geil model is another factor to study the state of stress concentration in the blends quantitatively. A fitted value of = 4.5 for the pristine blends is typically implicative of a complete debonding and no adhesion. This poor interfacial interaction can be attributed to the coalescence and the formation of sequentially larger silicone domains (Figure 6c). In contrast, = 2.9, as obtained for the dynamically vulcanised TPU/PDMS system, indicates considerably improved adhesion at the interface. Altogether, the present analysis leads to identical conclusions and strengthens their validity with reference to the superior mechanical properties of the crosslinked blends.



**Figure 6. Stress-concentration assessment:** Tensile yield stress data as a function PDMS volume fraction for: **(a) crosslinked blends; and (b) uncrosslinked blends.** Different theoretical models based upon Nielsen’s first and two-third power laws, Nicolais and Narkis equation, and Kunori and Geil equation were utilised to investigate the variations arising in interfacial properties upon dynamic vulcanisation. Crosslinked blends are associated with improved interfacial adhesion, confirming the successful *in situ* compatibilisation of TPU/PDMS blends; **(c) Mechanism of interfacial strengthening through dynamic vulcanisation process:** Finely dispersed, crosslinked polydimethylsiloxane (PDMS) within the polyurethane matrix allows stress transfer from the rigid plastic phase to the soft rubber phase. This effectively arrests the crazes initiated at the phase interface from growing into catastrophic failure. In contrast, the coarse and debonded domains of uncured PDMS would rupture at small stresses and decrease the tensile strength and deformability of the uncrosslinked blends

**4. Discussion**

The long-term clinical durability of silicones has been shown to reach up to 32 years post-implantation, and is attributed to their low surface energy, high oxidative, hydrolytic and chemical stability.67–69 Given the excellent biocompatibility and biostability of silicones, the PDMS based modification can improve the properties of TPU in several aspects that are desirable of an implantable biomaterial. Accordingly, there is a growing interest in designing silicone incorporated polyurethanes for different biomedical applications.17,70

Against this backdrop, the processability and structural properties of the newly developed library of TPU/PDMS blends is critically analyzed in this section in reference to the polymer processing principles and various phenomenological models. We have adopted a distinct reactive melt-mixing strategy, inspired by dynamic vulcanisation methodology to develop *in situ* compatibilised TPU/ PDMS blends. Conventionally, PDMS requires a curing (crosslinking) process to attain higher mechanical properties, chemical and thermal stability, and biostability. However, vulcanised rubbers containing covalently crosslinked permanent macromolecular networks are not reprocessable, reshapable or recyclable. The implementation of the dynamic vulcanisation route allows for the selective crosslinking of the PDMS phase during its intimate melt mixing with a non-vulcanising thermoplastic component. This processing strategy results in a binary blend, where a crosslinked elastomeric network is interspersed in a melt-processable plastic matrix. The final microstructure and performance of thus prepared blends are influenced by several factors, including the chemical and physical characteristics of the rubber (R) and thermoplastic (P) phases, the composition ratio of the blend (R/P), the methodology followed for performing dynamic crosslinking, the crosslinking density of the rubber phase, and the processing conditions.25,26 Accordingly, these aspects have also been investigated for the TPU/PDMS system designed herein.

For instance, the R/P ratio significantly affects the size of the dispersed rubber domains. Usually, the size of the rubber domains increases with an increase in R/P. This is because during mixing, the probability of coalescence of rubber droplets that collide with neighbouring ones increases with increasing rubber phase content, and they become less liable to split.71 Although a typical TPV is characterised with a relatively predominant rubber phase (R/P ≥ 1) to obtain high elasticity; the PDMS content is varied from 10-40 weight% for the present blends to retain the mechanical characteristics of TPU while improving its oxidative and hydrolytic stability through the incorporation of silicone. The degree and rate of crosslinking reaction of the rubber phase also play a critical role in the break-up and coalescence of the rubber particles during dynamic vulcanisation. This, in turn, can significantly affect the size of the rubber phase domains, morphology development, and thereby the mechanical properties of the resultant TPVs. 32,52,56 In general, an increase in the content of crosslinking agents is reported to induce a higher crosslinking density and rate and faster development of morphology.25 Although a higher crosslinking density can restrain the rubber domains from coalescence, an overly crosslinked rubber phase will also be averse to break-up and increase the size of the elastomeric domains. As with the concentration, the type of crosslinking agent is also decisive towards the properties of the TPVs by changing the crosslinking rate.

Among the different types of curing agents, dicumyl peroxide (DCP) is frequently associated with blends exhibiting a higher degree of crosslinking and finely dispersed rubber domains.72,73 The smaller particle size of the dispersed rubber in the DCP system is further reported to ascribe higher tensile and impact strength.72 A similar observation is made for the TPU/PDMS blends, crosslinked with progressively increasing loadings of DCP from 0.3 to 0.8 weight %. The increasing crosslink density led to a systematic enhancement of tensile strength and modulus, but % elongation at break deteriorated due to constrained molecular mobility. Thereby optimised concentration of crosslinking agent was used to generate a series of dynamically vulcanised blends with varying contents of PDMS. The assessment of mechanical properties established the superior characteristics of these crosslinked blends over their uncrosslinked counterparts. It is well-known that the compatibility of component polymers plays a fundamental role in enhancing the mechanical properties of the blends, and this is anticipated to be the determinative factor for the better performance of the crosslinked blends as well.

To gain further insights into the mechanical response, the experimental results obtained from the uniaxial tensile and compression tests were evaluated against the theoretical calculations based upon the parallel, series, Halpin Tsai, Coran and Takayanagi models.40–43 Most of these models are applicable within a limited range of compositions since morphological variations with composition are common in polymer blends. In the same manner, the correlation of tensile and compression properties of the crosslinked blends with different models also varies with the composition. At lower PDMS concentration, the experimentally determined strength and modulus for the crosslinked blends (DT9P1 and DT8P2) are in agreement with the upper-bound parallel and Halpin Tsai model predictions. The fine trends between the experimental data and upper-bound calculations indicate the possibility of a near-perfect state of interfacial bonding between the thermoplastic matrix and the dispersed rubber domains. It is also likely that at lower concentrations of PDMS, the agglomeration and structural inhomogeneity of the dispersed domains are insignificant, as also assumed in these models. Another presumption that is made with reference to the morphology of the dispersed phase in the Halpin Tsai model is the spherical form of the rubber domains (l/d=1). Therefore, it can further be conjectured that as the amount of PDMS is increased in the blends, the crosslinked spherical domains of silicone rubber transform into an interlinking elastomeric network. This speculation is in concord with the calculations of the Coran model.42 It is observed that the Coran equation at n=7.5 provides a close fit with the experimental data points of crosslinked blends in most instances. Corresponding to n=7.5, the value of *f* varies from 0.8 in 90/10 to 0.1 in 60/40. The sequentially decreasing magnitude of *f*, a function of phase morphology, suggests the systematic development of continuity in the dispersed PDMS phase from DT9P1 to DT6P4. The predictions of the combinatorial Takayanagi model are also well-suited to the blends DT7P3 and DT6P4 in most instances. The Takayanagi equation estimates the mechanical behavior based upon parallel-series coupling.43 In the present work, the % parallel character was considered as 15% for an improved theoretical fit. Therefore, the capability of this model to predict the mechanical response beyond DT8P2 reflects the gradual diversion of the crosslinked blend properties from the overestimations of the parallel model. Unsurprisingly, the properties of the pristine, uncrosslinked blends were in the closest proximity of the theoretically derived values from the series model, under both tensile and compression loading. In fact, the tensile modulus for the entire range of PDMS variations exhibited a negative deviation from the lower bound values predicted for the TPU/ PDMS system. This is ascribed to the poor mechanical properties of the uncured PDMS, which would rupture at small strains and consequently, decreases the deformability of the blends.

The prediction models can also be applied to study the weakness in the structure brought about by the discontinuity in stress transfer and the generation of stress concentration at the interfaces. Sufficient interfacial adhesion facilitates stress transference from the rigid plastic phase to the soft rubber phase, effectively preventing the crazes and micro-voids from growing into catastrophic defects. In order to understand the extent of interfacial adhesion, Neilsen's first power-law, Neilsen's two-third power-law, Nicolais and Narkis model and Kunori and Geil model have been used previously for the theoretical predictions and analyses of polypropylene/styrene-ethylene butylene-styrene, polycarbonate/high-density polyethylene, polycarbonate/ethylene-methyl acrylate, polyamide 6/ethylene vinyl acetate blends and several other composites.44,50,74,75 These models were, thus, also employed to comparatively assess the tensile strength properties of the uncrosslinked and crosslinked TPU/PDMS blends. With either of the two power laws, the experimentally determined data could not establish a close fit with the theoretical curve. Even so, the values of Nielsen's parameter in the first (*S*) and two-third power-law models (*S′*) for the crosslinked blends were in good agreement with the no stress concentration condition. The adhesion parameters, *Kb* and , also exhibited notably reduced values for the crosslinked blends compared to uncrosslinked counterparts, as desired. Therefore, regardless of the fitted model, the predicted stress-concentration/adhesion parameters were more favourable for the crosslinked blends, recommending a strengthened interface. Further, these observations reinforce the notion of the poor mechanical behaviour of the uncrosslinked blends and their associated characteristics as an immiscible polymer system.

The increased adhesion in dynamically vulcanised systems can be explained by fine and uniformly dispersed silicone rubber particles. In contrast, the pristine blends are identified with large dispersed domains of silicone that can further undergo coalescence, ensuing gross phase separation as confirmed by the fractographic examination. Moreover, it has also been suggested in the literature that there is a likelihood of crosslinking induced chemical graft formation or interlinking between the rubber and thermoplastic chains during dynamic vulcanisation. This strengthens the interface through closer interaction. Consequently, the crosslinked blends, stabilised by molecular entanglements, can sustain high stress for long periods and are characterised by superior mechanical properties. A third rationale can be hypothesised with reference to the crystallisation behaviour of the blends. In a dual-phase system consisting of a semi-crystalline thermoplastic matrix and elastomeric dispersed domains, the matrix crystallises in the presence of the rubber droplets. This contraction onto the amorphous rubber phase generates a pseudo-adhesion and promotes the stress transfer at the interface, thereby improving the mechanical properties of the blend. However, unlike a rigid crosslinked phase, an uncured rubber will still be in a deformable state during this process and expected to undergo local deformations with a possibility of micro-voiding due to the high immiscibility of these two blend components. A similar observation was made by Leclair et al. while investigating binary blends of polycarbonate, high-density polyethene and polystyrene.75

Besides the definite potential for implantable biomaterials and biomedical devices, TPU/PDMS blends are an attractive candidate to be explored in soft robotics, wearable electronics and stretchable sensors. On a different front, the prospect of harnessing the *in situ* crosslinking methodology for PDMS in a different thermoplastic matrix than TPU is also intriguing. It has been demonstrated here that dynamic vulcanisation can successfully integrate component polymers with vastly dissimilar physical and chemical characteristics. Therefore, an analogous strategy can be adapted for different silicone enriched blend systems with customised functionalities. For instance, PVDF is an interesting alternative thermoplast, owing to its biocompatibility, remarkable chemical and high-temperature resistance, good barrier and piezoelectric properties. Similarly, the use of polyamide can help realise excellent oil and solvent resistance and good environmental stress cracking resistance at elevated temperatures while retaining properties of PDMS. Another extension of this work can be contemplated in the realm of bio-based TPVs, where the PDMS based modification of a biodegradable thermoplast such as PLA can be carried out to further improve its inherent brittleness.

Taken together, the present study represents a fundamental investigation on the development of TPU/PDMS blends through a TPV inspired strategy. The wide array of characterisations allows the unambiguous detection of the compatibilised behaviour upon dynamic vulcanisation. Thereby, the newly designed series of reprocessable blends, endowed with a broad spectrum of mechanical properties, paves the way to translate silicone modified polyurethanes over the conventionally crosslinked silicone rubber for diverse applications. This is of particular relevance as although TPVs have become the fastest-growing class of elastomers to replace unrecyclable petroleum-based thermoset rubbers, their existing manufacture is primarily limited to a combination of ethylenepropylenediene and styrenebutadiene rubbers with thermoplasts such as polypropylene and polyamide.25

**Conclusions**

In the present study, we have fabricated polydimethylsiloxane modified thermoplastic polyurethane blends through reactive melt-mixing. Dynamic vulcanisation was employed to ensure the *in situ* compatibilisation of the binary blends. From the different sets of physical, morphological, mechanical and theoretical characterisations, the following conclusions can be drawn:

(a) The melt-processability of the TPU/PDMS blends at different peroxide crosslinker concentrations was investigated, based on the torque profile variations. The overall crosslink density as well as the extent of the crosslinkable phase increased with an increasing amount of peroxide crosslinker and the weight % of the PDMS phase. The increase in crosslinker concentration to 0.8% resulted in a progressive improvement in tensile strength and modulus, while an accompanying reduction in percentage elongation at break was also noted.

(b) The incidence of dynamic crosslinking was shown to enhance thermal stability, as indicated by the thermogravimetric and differential thermogravimetric analyses. A significant improvement was observed with respect to the degradation temperature of PDMS as well as the soft and hard segments of TPU.

(c) The morphological analysis of the tensile-fractured blend surface further confirmed the reactive compatibilization and the development of a finer microstructure upon dynamic vulcanization. While the uncrosslinked blends exhibited a gross phase-separation, an improvement in interfacial adhesion and the strengthening of the crosslinked blends were evident through the greater miscibility of the binary phases and microfibril formation.

(d) The experimental data for the crosslinked blends fitted well with the Halpin−Tsai, Coran, and Takayanagi models. On the other hand, the uncrosslinked blends closely resembled the lower-bound values from the series expression for most of the compositions. Moreover, thetheoretical estimation of the stress-concentration parameters also supported the in situ compatibilization and enhanced interfacial interaction upon dynamic vulcanization.

At the closure, it must also be underlined that the fabrication of TPV-based products is often pursued by a somewhat trial and error methodology with an insufficient understanding of the structure−property relationship. The utilization of different phenomenological models, as illustrated for the present library of TPU/PDMS blends, can provide us with critical guidelines for predicting structural properties and gaining insights into the process of dynamic vulcanization for a new and unfamiliar blend system.

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