The Dynamic Mechanical Analysis, Impact, and Morphological Studies of EPDM–PVC and MMA-g-EPDM–PVC Blends

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Received 15 September 1997; accepted 25 July 1998

ABSTRACT: The dynamic mechanical studies, impact resistance, and scanning electron microscopic studies of ethylene propylene diene terpolymer–poly(vinyl chloride) (EPDM–PVC) and methyl methacrylate grafted EPDM rubber (MMA-g-EPDM)–PVC (graft contents of 4, 13, 21, and 32%) blends were undertaken. All the regions of viscoelasticity were present in the E' curve, while the E'' curve showed two glass transition temperatures for EPDM–PVC and MMA-g-EPDM–PVC blends, and the T_g increased with increasing graft content, indicating the incompatibility of these blends. The tan δ curve showed three dispersion regions for all blends arising from the α , β , and Γ transitions of the molecules. The sharp α transition peak shifted to higher temperatures with increasing concentration of the graft copolymer in the blends. EPDM showed less improvement while a sixfold increase in impact strength was noticed with the grafted EPDM. The scanning electron microscopy micrographs of EPDM–PVC showed less interaction between the phases in comparison to MMA-g-EPDM–PVC blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1959–1968, 1999

Key words: ethylene propylene diene terpolymer; MMA-*g*-EPDM; dynamic mechanical analysis; incompatibility; impact resistance; scanning electron microscopy

INTRODUCTION

A polymer blend is a mixture of two or more different kinds of polymer chains that are not covalently bonded together. Compatibility of a polymer has to play a crucial role in determining the polymer properties for various end uses. The lack of compatibility between polymers leads to phase separation, thus resulting in poor strength properties. Dynamic mechanical analysis (DMA) is an important tool for determining polymer compatibility. With a view of producing cost effective thermoplastic elastomers, many articles have been published recently on the blends of PVC with various elastomers. They deal either with its compatibility with other polymers or with the improvements of some characteristics.¹ Many recent reports have treated the structure property relationship of impact modified polymers like polypropylene through its melt blending with ethylene propylene copolymers (EPM) or ethylene propylene diene terpolymer (EPDM) rubbers.²⁻⁵ Impact strength as a function of the morphological structure has been discussed,² and the relationship between mechanical properties, such as impact strength or dynamic mechanical behavior, and molecular structure of polymers have also been discussed.⁶ The toughness of a polymer blend is one of the major factors in deciding its practical application. Impact modification of the

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Journal of Applied Polymer Science, Vol. 71, 1959–1968 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/121959-10

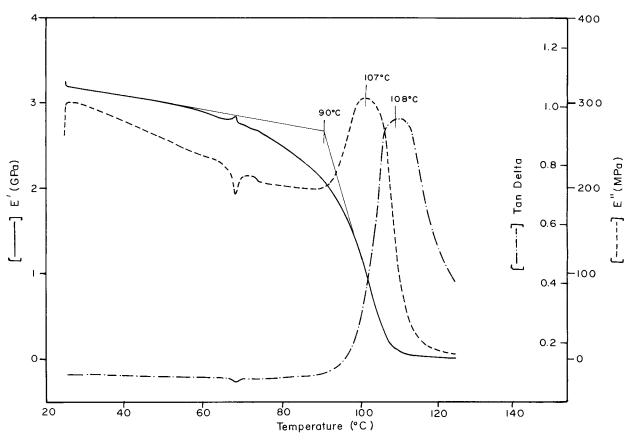


Figure 1 DMA curves for PVC as a function of E'/E'' and tan δ .

glassy phase is possible if sufficient adhesion between the rubbery phase and the glassy phase is present. But most polymers are incompatible with each other; hence, grafting is necessary to bring out sufficient adhesion between the two phases. Such a modification has been made on polystyrene (so-called high-impact polystyrene, or HIPS),^{7–9} where the grafted chain is compatible with the continuous matrix to impart adhesion between the rubbery phase and the glassy polystyrene phase. Styrene and methylmethacrylate copolymer is grafted on to polybutadiene to prepare high-impact transparent or translucent material.¹⁰ S. Shaw and R. P. Singh prepared EPDM-g-(styrene-co-methylmethacrylate) and blended it with polystyrene for impact modification. Though the literature contains a lot of information about the impact modification of PVC by rubbers, there is scant mention of the dynamic mechanical properties, impact, and morphological properties of EPDM and MMA-g-EPDM-PVC blends. In the present work, an attempt has been made to improve the impact strength of PVC by blending it with MMA-g-EPDM rubber for outdoor applications, as acrylonitrile-butadienestyrene (ABS) impact-modified PVC suffers from poor weather resistance at outdoor applications. EPDM, a weather-resistant rubber, can sacrifice its pendent double bonds with ozone, keeping the backbone intact. The polar chains of MMA on to EPDM backbone will provide better interfacial adhesion with PVC, which will improve the impact strength as well as the weather resistance. Dynamic mechanical and morphological studies have also been carried out.

EXPERIMENTAL

Materials

PVC resin supplied by M/S Shriram Fertilizers and Chemicals, Kota, India, having a viscosity average molecular weight (M_v) of 65,000 was used for the present studies. EPDM was supplied by M/S Herdilia Unimers Ltd., Bombay, having 57% ethylene, 43% propylene, and 7.5% diene contents. Thermal stabilizers, dibasic lead stear-

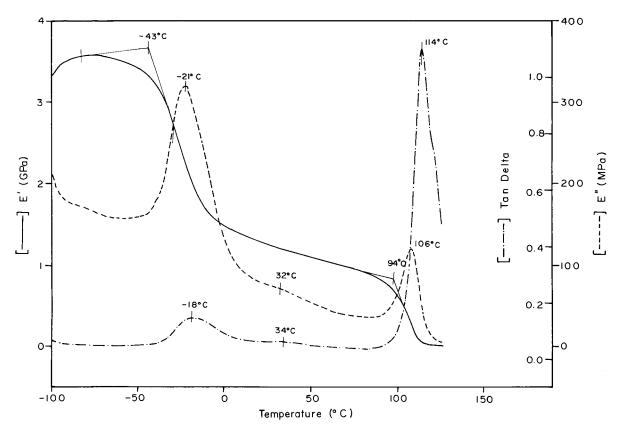


Figure 2 DMA curves for EPDM–PVC as a function of E'/E'' and tan δ .

ate (DBLS), and tribasic lead sulphate (TBLS) used were supplied by M/S Waldies Ltd., Delhi. Zinc stearate and stearic acid were used as processing aids and lubricants. The MMA-g-EPDM used was prepared in the laboratory.

PREPARATION OF BLENDS

EPDM and methyl methacrylate (MMA) grafted EPDM rubber (MMA-g-EPDM) was blended withpoly(vinyl chloride) (PVC). EPDM–PVC and MMA-g-EPDM–PVC blends in a 20 : 80 ratio were prepared by a melt blending technique using 2.5 parts per hundred (pph) tribasic lead sulphate (TBLS), 1.5 pph dibutyl lead stearate (DBLS), 1 pph zinc stearate, and 0.5 pph stearic acid of resin, respectively.

MEASUREMENTS

The measurement of dynamic mechanical properties of the blends was carried out in a Du-Pont 983 dynamic mechanical analyzer (DMA) operated at a fixed frequency of 1.0 Hertz. All the experiments were carried out in a shear mode over the temperature range of -100 to 150° C at a 5°C/min temperature rise, using liquid nitrogen as a cryogenic medium.

The dimensions of the test specimens were 13 \times 11 \times 3 mm. The damping was recorded against temperature, and the plots were processed by computer for determination of components of the complex modulus of elasticity, that is, the storage (E') and loss (E'') moduli and the tan δ values.

The notched samples for impact strength were prepared according to ASTM D-256. Izod impact strength of notched samples was measured on a pendulum-type impact testing machine of Fuel Instruments and Engineers Pvt. Ltd., having an energy range of $0-1.4 \text{ kg/cm}^2$. Breaking energy was calculated from the difference in potential energy of the pendulum striker before and after striking. For determination of impact strength, the breaking energy was expressed per unit breadth of the specimen⁶ without any further correction for kinetic energy. Hence, these values may be emphasized only for their relative magni-

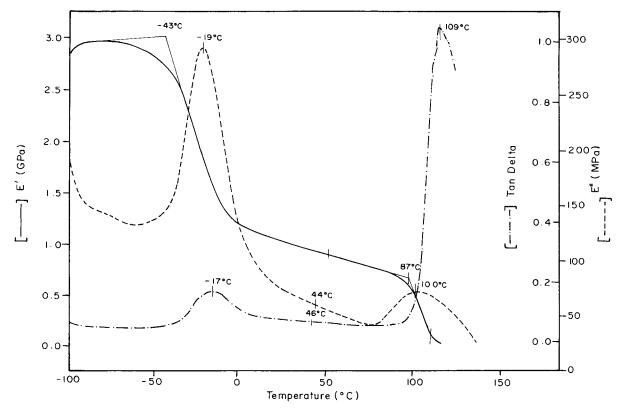


Figure 3 DMA curves for MMA-*g*-EPDM–PVC as a function of E'/E'' and tan δ (4% grafting).

tudes, as done in this work. The minimum number of samples tested for each case was five, and the results were quite consistent, within 4-6%.

Cryogenically impact-fractured surfaces were made for fracture surface analysis and studied by using a stereoscan model S_4 -10 of Cambridge Scientific Instruments Ltd. Surfaces were made conductive by the deposition of a layer of silver and palladium by the vacuum evaporation technique. Scanning electron micrographs were taken at several magnifications up to $6600 \times$.

RESULTS AND DISCUSSION

The results of dynamic mechanical measurements are given in Figures 1–6. Figure 1 represents the DMA curves for PVC, and showed all the five regions of viscoelasticity. Glassy behavior was observed up to 70°C, where the modulus was maximum 3.4 GPa and the storage modulus curve E' was almost a straight line because, at low temperature, the atoms in a polymer chain are restricted to isolated vibrational motions, and the bulk polymer is stiff and glassy in behavior. But at 90°C, the glass-rubber transition region, the inflection of the curve showed a decrease in modulus to 2.5 GPa within a 20°C temperature span. The glass rubber transition region is generally associated with the onset of long range coordinated rotational and translational motions involving from 10-20 carbon atoms, and an amorphous polymer becomes much softer and rubberlike. Above the glass transition lies the rubbery plateau region where the flow of the rubbery region is hindered by physical entanglements of chains. At a still higher temperature, the rubbery flow and the liquid flow regions are encountered. At these higher temperatures, molecular motion is sufficiently rapid so that the molecules behave more nearly independently, and the modulus drops substantially due to the increasing role of viscous flow.

The damping (dissipation factor E''/E' or tan δ) curve goes through a maximum and then a minimum as the temperature is raised. In the region where the dynamic modulus curve (E') has an inflection point, the internal friction (tan δ) curve

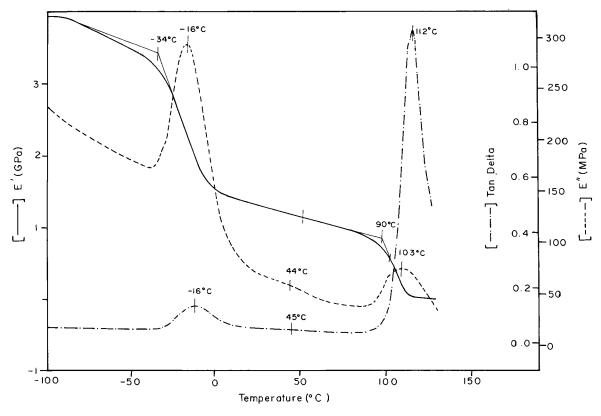


Figure 4 DMA curves for MMA-*g*-EPDM–PVC as a function of E'/E'' and tan δ (13% grafting).

goes through a maximum. This dispersion occurs in the glass transition region.¹¹ The loss modulus E'' goes through a peak at a slightly lower temperature than does the dissipation factor E''/E'.

Figure 2 represents the DMA curves for the EPDM-PVC blends. All the viscoelastic regions were clearly indicated and distinguished fairly to that of PVC in the dynamic modulus curve E'. The peak at -43° C was due to the T_g of EPDM, and the peak at 94°C was due to PVC as the modulus sharply decreases after T_g . There were two clearly separated peaks in the loss modulus (E'') of EPDM–PVC blends, and there was a pronounced valley in between the peaks, which indicates phase separation between EPDM and PVC, and was indicative of incompatibility in these blends. The incompatibility of these blends were also reported by K. Sudhaker and R. P. Singh.¹² Of the two peaks in E'' in the EPDM–PVC blends, the one at 106°C was from the PVC phase, and the other, at -21° C, was due to EPDM. The dissipation factor or tan δ was observed having three dispersion regions labeled as α , β , and Γ . The α peak was observed at 114°C, while the β and Γ peaks were found at 34 and -18° C, respectively.

There was a marked difference in the transition behavior of blends when EPDM was substituted by increasing levels of MMA content in the MMA-g-EPDM–PVC blends. At lower levels of grafting (4 and 13%), the T_g of the blends was reduced (Figs. 3-4); while at a higher graft content (21 and 32%), the T_{g} was observed to be increasing (Figs. 5-6). This fairly indicates at lower grafting levels that there is good interaction between the phases of EPDM and PVC due to the polarity produced in the EPDM segment by the incorporation of MMA. This was indicated by the widening of the peak at T_g and the reduction of the peak height, which indicates that a partial compatibility or semicompatibility has been produced in these blends. The rubbery phase was still well defined, having its own T_g at -19 and -16° C. The increase in T_g and modulus of the blends at a higher graft content may be attributed due to the high molecular weight of poly(methyl methacrylate) (PMMA) formed on the EPDM chains. The inflection or plateau region of the modulus curve was due to chain entanglements. Since high-molecular-weight polymers have more entanglements, the plateau region is more prominent and

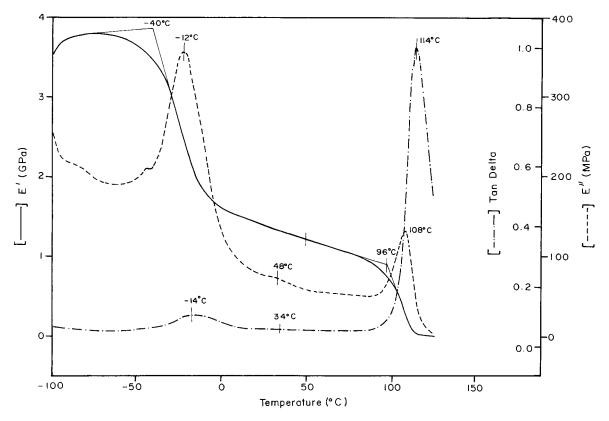


Figure 5 DMA curves for MMA-*g*-EPDM–PVC as a function of E'/E'' and $\tan \delta$ (21% grafting).

covers a wider temperature range with the highermolecular-weight materials. Chain entanglements delay the onset of viscous flow, so the minimum in damping decreases as the molecular weight increases. Although the MMA-g-EPDM-PVC blends do exhibit a two-phase behavior, but at 4 and 13% grafting, the T_g of the blends shifted down and closely approached the T_g of PVC, shown at 100 and 103°C, and a broadening of the peak occurred. The T_{σ} values in partially compatible blends are expected to shift towards each other.13-14 At 21 and 32% grafting, the T_{σ} values shifted to higher temperatures, 108 and 114°C, respectively, and the damping values decreased with a reduction in peak height. The secondary damping peaks or viscoelastic relaxations in the grafted blends with increased graft concentration shifted to higher temperatures with a decrease of peak height. This may be attributed to the increased grafting as there could be an increased number of PMMA chains in the graft, and the entanglement of these chains may have hindered the motion of the -C-O-CH₃ chains of PMMA.¹⁵

The impact strength of the blends is given in Figure 7. Impact strength of PVC was consider-

ably increased when blended with MMA-g-EPDM in comparison to EPDM. The maximum impact strength was found for 20% of EPDM and at 13% of graft content. The impact strength increased, attained a maximum value, and then decreased, with an increase in the graft content in MMA-g-EPDM-PVC blends. According to the studies of Haff et al.,¹⁶ depending on the degree of grafting and the milling conditions, the rubber particles may form necklaces or loose networks, a morphology that strongly affects the properties of the plastics. The reported results are as follows. Particles with incomplete graft shells, obtained at low grafting levels, agglomerate to large clusters, giving poor mechanical properties. At intermediate grafting levels, the rubber particles agglomerate only slightly, and the resulting blends have good impact strength. A high degree of grafting leads to a fine dispersion of the rubber particles and low impact strength.¹⁶ For PVC-ABS blends, they show that the best impact properties occurred at around 25% grafting levels.

In the present system, the grafting level is 4-32%, and the proper dispersion of the graft blends in the PVC matrix is established with the

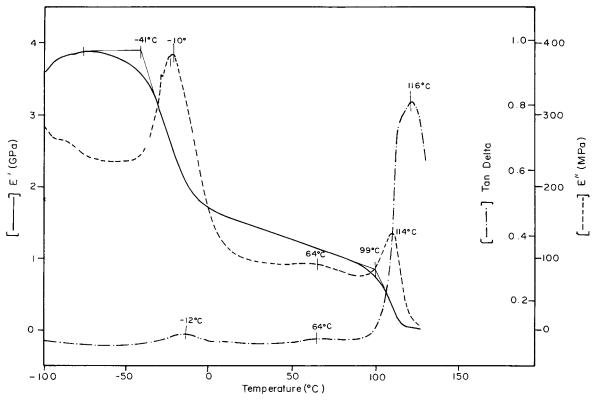


Figure 6 DMA curves for MMA-g-EPDM–PVC as a function of E'/E'' and tan δ (32% grafting).

support of the micrographs obtained by scanning electron microscopy (SEM) analysis. The impact properties may be attributed to the following rea-

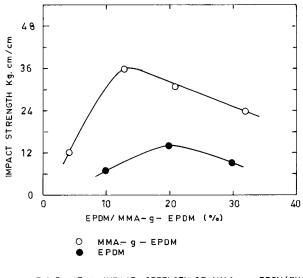


FIG 7 IZOD IMPACT STRENGTH OF MMA-g-EPDM/PVC AND EPDM/PVC BLENDS.

Figure 7 Izod impact strength of MMA-*g*-EPDM–PVC and EPDM–PVC blends.

sons. Here, the PMMA copolymer acts as an interfacial agent. It is well established that interfacial agents such as block and graft copolymers are known to reduce the interfacial tension and, hence, are expected to increase the degree of dispersion in blends.¹² Also, interfacial adhesion is a more important factor in rubber toughening^{17,18} so, here, as the graft percentage was increased in the blend, the impact strength of the PVC–MMAg-EPDM system increased. After a certain percentage of grafting, that is, after 21–32%, the

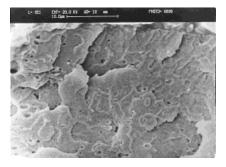


Figure 8 Scanning electron micrograph of impactfractured specimen of PVC.

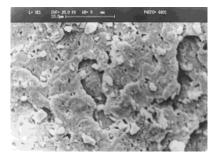


Figure 9 Scanning electron micrograph of impactfractured specimen of EPDM–PVC (10%).

impact strength of the blends started decreasing. This can be understood from the brittle nature of PMMA at higher molecular weight, which reduces the impact strength. The adhesion between the interfacial agent and the polymer matrix should be reasonable, and, also, the dispersion of the minor phase (grafted rubber phase) should be in an intermediate level, that is, not very coarse and not finely dispersed.

S. Shaw and R. P. Singh⁷ showed in the blends of polystyrene (PS)-EPDM-g-styrene-co-methyl methacrylate that there is an increase in the impact strength of polystyrene to 4.5 wt % of rubber and then a decrease of impact strength at high concentrations due to increase in incompatibility of the blends, because of the increase of incompatible methacrylate component. This may lead to decrease in adhesion of graft copolymer to the polystyrene and also to the agglomeration of graft copolymer. They further observed that the incompatible copolymers consisting of incompatible monomers, such as styrene and methyl methacrylate, resulted in an increase of the intermolecular spacing, poorer packing, lower density, and softer properties,¹⁹ which lead to a decrease in the impact strength.

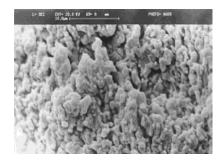


Figure 11 Scanning electron micrograph of impactfractured specimen of EPDM–PVC (30%).

The SEM micrographs of the blends are shown in Figures 8-15. A brittle, scaly, fibrilar surface was observed for PVC with the microcharacteristics typical of a rigid and glassy surface. The EPDM present in blends was identified as discrete droplets (10% EPDM) or as islands (20 and 30% EPDM), and the MMA-g-EPDM present in the PVC matrix was identified as sphaghetti-like, long, elongated structures (4 and 13% grafting) to large domains with pronounced cavities (21 and 32% grafting), and a change in the surface morphology was observed. From the micrographs, it could be observed that EPDM-PVC blends were immiscible; the EPDM droplets were clearly distinguished in the PVC matrix (Fig. 9). With 20% EPDM (Fig. 10), though it appeared that there was better adhesion between two phases, yet the matrix was not continuous; the two phases were separated. The EPDM was evenly distributed in the PVC matrix, and the structure looked like a termite house. The peaks were reflected as white hazy portions, while the pits were shown by the dark areas. For 30% EPDM (Fig. 11), a pronounced cavity formation took place, as shown by the dark shaded areas, which indicate the incompatibility of blends. The introduction of MMA into

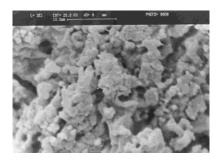


Figure 10 Scanning electron micrograph of impactfractured specimen of EPDM–PVC (20%).



Figure 12 Scanning electron micrograph of impactfractured specimen of MMA-*g*-EPDM–PVC (4% grafting).

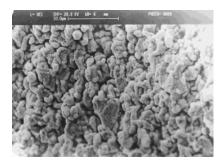


Figure 13 Scanning electron micrograph of impactfractured specimen of MMA-g-EPDM-PVC (13% grafting).

the chain of EPDM made the otherwise round droplets of EPDM elongated like noodles (13% grafting) (Fig. 13) to large domains (21 and 32% grafting) (Figs. 14-15), which resulted in coarseness of the surface and was related to the ductility of the materials.^{20,21} The fracture behavior of EPDM-PVC differs from that of the MMA-g-EPDM-PVC blends. With an increasing concentration of EPDM, fine distribution of EPDM in the PVC matrix occurred, but the regular voids and pits were increased with increased concentration of EPDM, as shown in Figures 9-11. This showed a two-phase morphology with the least interfacial adhesion between the phases of EPDM and PVC. In the case of MMA-g-EPDM, there was an interaction between the phases (4% grafting). The very fine distribution of grafted EPDM in the PVC matrix clearly indicates that MMA has produced polarity in grafted EPDM, which enhanced the interfacial adhesion. At 13% grafting, it was observed that the round droplets of EPDM were absent, and the EPDM particles elongated, due to grafting, which enhanced the interfacial adhesion with PVC. Beyond 13% grafting, however, large domains of MMA-g-EPDM were clearly observed

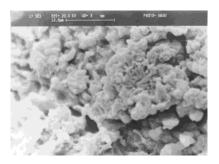


Figure 14 Scanning electron micrograph of impactfractured specimen of MMA-*g*-EPDM–PVC (21% grafting).

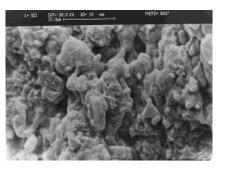


Figure 15 Scanning electron micrograph of impactfractured specimen of MMA-*g*-EPDM–PVC (32% grafting).

where agglomeration of MMA-g-EPDM started due to the incompatibility between the phases, which led to cavity formation. The cavities were well defined with increased grafting to the level of 21–32% and represented a two-phase behavior. All the micrographs also showed tiny round droplets of the ungrafted EPDM sporadically dispersed and embedded in the PVC matrix. The domain size increased significantly with the increased grafting. The limited compatibility was observed with 4 and 13% grafting, where an interaction exists between the PVC and MMA-g-EPDM. In such a blend, the impact strength was maximum.

CONCLUSIONS

The blends of EPDM–PVC and MMA-g-EPDM– PVC were incompatible, and the impact strength of PVC was maximum at 20% EPDM and 13% grafting. The impact strength of PVC was increased by a sixfold margin when blended with MMA-g-EPDM rubber with 13% grafting as compared to EPDM rubber, which improves the impact strength by twofold only.

The authors thank Dr. D. A. Dabholkar, Director, Shriram Institute for Industrial Research, for his constant help and encouragement in carrying out this work.

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